

ION EXCLUSION CHROMATOGRAPHY: MOLASSES PRETREATMENT AND HIGH TEST MOLASSES PRODUCTION

SB DAVIS, SD PEACOCK AND SN WALFORD

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

Abstract

A process for increasing the value of final molasses by converting it to high test molasses (HTM) was investigated at laboratory scale. This involved firstly pretreatment of the molasses to achieve clarification and partial de-ashing. Of the methods tried, acidification and sucrose inversion with sulphuric acid, followed by centrifugation, was the most promising. Ion exclusion chromatography was then used to separate an invert-rich stream resembling HTM. The recovery of invert rather than sucrose enabled a good separation to be achieved without expensive pretreatment processes such as softening, thus possibly leading to an economically viable process.

Keywords: molasses, ion exclusion, clarification

Introduction

In the 1996-97 season, more than 250 000 tons of sucrose left South African sugar mills in the form of low value molasses, along with potentially valuable reducing sugars. Higher revenues could be earned if these sugars could be recovered in a more useful form. Existing cane molasses desugarisation methods aim at isolating sucrose by ion exclusion chromatography, which has been described previously for the recovery of sucrose from refinery jet 4 (Peacock, 1995). While the process is technically feasible, the economics do not seem favourable at present. This results from expensive pretreatment requirements and poor separation efficiency due to the high ash content of final molasses.

Ion-exclusion (IEX) as a process for separating ionic from non-ionic solutes using ion exchange resins was first described by Wheaton and Bauman (1953). IEX chromatography is carried out extensively in the beet sugar industry for desugarisation of molasses (Chertudi, 1991) and is used for isolation of fructose in the high fructose corn syrup industry (Saska, 1996). Two factors mitigate against applying the same technique to cane molasses, *viz.* higher suspended solids and divalent cation concentrations (Rearick and Kearney, 1996). The suspended solids in cane molasses can cause the blockage of the resin column, and thus a low turbidity feed is required. Low divalent cation concentrations are required in both beet and cane molasses to inhibit the ion-exclusion resin from converting to the calcium

form and thereby decreasing the ash/sucrose resolution. Maximum values as low as 400 ppm/Bx calcium have been recommended (Kakihana, 1989).

The production of high test molasses (HTM) from final molasses is a possible route for increasing the value of the latter. The aim of this work was twofold: to evaluate various pretreatment processes for the reduction of both turbidity and divalent cations to produce a feed suitable for ion exclusion, and to study the feasibility of decreasing the ash content of inverted molasses by an ion exclusion method, to produce an 'HTM equivalent' product.

Pretreatment options

Many processes for the molasses pretreatment were considered, and it was not possible to follow a rigorous experimental programme. Thus, in this section, the methods and the results are described together to enable the progress of the work to be followed more clearly.

Pressure filtration

Pressure filtration of final molasses samples from Darnall mill (DL) diluted to 65° brix was attempted at elevated temperatures, with and without filter aids. Filtration was done at 80°C and 7 bar gauge pressure in a 30 cm diameter batch filter. Two different cloths were used, namely a standard refinery carbonation filter cloth and a coarser woven cloth. The filter aids used were a diatomaceous earth type (Dicalite Superaid), and a perlite type (Dicalite 471SP). Filtration rates were extremely poor, and in some cases no filtrate was produced.

Three possible reasons for the poor filtration were proposed: viscosity, macromolecules (such as starches, dextrans and gums) and refractory suspended solids. The effect of viscosity was tested by attempting to filter a low viscosity molasses from Malelane mill, but very poor filtration was again the result. Microscopic examination of the molasses revealed many fine crystals ranging in size from 1 to 20 micrometres. Most of the turbidity in the molasses was of a crystalline nature, with very little or no bagacillo. Samples of these crystals were collected from a filter cloth after an attempt at molasses filtration, and analysed by x-ray fluorescence (XRF) and x-ray diffraction

(XRD) techniques. This material was found to consist mostly of syngenite ($K_2Ca(SO_4)_2 \cdot 2H_2O$) and magnesium syngenite ($K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$) with some co-crystallisation of potassium chloride. Syngenite is very similar to gypsum ($CaSO_4 \cdot 2H_2O$) and has a similar crystal morphology. Thus syngenite could be expected to have the same poor filtration characteristics as gypsum, and could explain some of the difficulties experienced in filtering molasses.

As neither syngenite nor precipitated potassium chloride are found in evaporator scale or in syrup, it was concluded that these crystals must have precipitated either during pan boiling or during storage at the Sugar Milling Research Institute (SMRI), as the samples were allowed to cool before testing. Samples of A-, B- and C-molasses were therefore taken from the centrifugal outlets at Felixton (FX) mill, diluted to 65° brix with hot water and immediately centrifuged in an Alfa Laval laboratory disc-bowl centrifuge. A trace of syngenite was found in the A-molasses, with significant quantities present in B- and C-molasses, indicating that syngenite precipitates during B- and C-pan boiling. The presence of syngenite in B- and C-molasses was first reported early this century, and was discussed during the 1962 and 1965 congresses of the International Society of Sugar Cane Technologists (Proskowetz and Chen, 1963; Chen and Proskowetz, 1967).

It was concluded that the presence of syngenite in molasses is largely responsible for the poor filtration characteristics, and that filtration as a means of lowering turbidity is unlikely to be successful.

Froth flotation

Processes in sugar production that lead to precipitates that are difficult to filter, such as phosphatation, use dissolved air flotation for solids separation. As molasses filtration was not successful, trials with dispersed air froth flotation were performed on diluted (65° Bx) molasses. For these tests, a reactor fitted with an air sparger and a high speed, high shear stirrer was used. Compressed air was used to generate the foam, which was removed by hand from the top of the reactor. Several flocculants commonly used in flotation processes in the sugar industry were tried, but none produced a significant foaming effect in the molasses. Based on the similarities between syngenite and gypsum, research indicated that a fatty acid flotation agent used in the minerals industry, sodium lauryl sulphate, might produce a separation. This produced a very stable foam, but little separation occurred, and the physical and chemical properties of the molasses were unaffected. This, coupled with the low recoveries of molasses achieved, led to no further work being done on this technique.

Centrifugation

Molasses clarification by centrifugation has been studied by several workers (Proskowetz and Chen, 1963; Davis and Clarke, 1963; Chen and Proskowetz, 1967; Thompson, 1993), with good turbidity removal possible under certain conditions. A solids-

retaining disc-bowl centrifuge was borrowed from Alfa-Laval to determine how effectively syngenite could be separated in such a device.

A sample of molasses was diluted to 65° brix, heated to 80°C and centrifuged at a low flow rate to maximise removal of solids. Microscopic examination of the clarified molasses showed that most of the syngenite crystals (typically those larger than 1 µm) had been removed. Analysis of the molasses showed that centrifugation eliminated 45% of the calcium and 15% of the magnesium in the form of syngenite and magnesium syngenite.

Samples of DL molasses were diluted to various brixes and centrifuged at 80°C. The clarified molasses was examined microscopically to obtain a qualitative idea of crystal size and degree of solids removal. Centrifugation at 86° brix (undiluted) removed only the largest syngenite crystals, and subsequent dilution of the clarified molasses to 65° brix still left a large quantity of fine crystals in the molasses. The high viscosity of the undiluted molasses considerably reduced the settling rate of the crystals in the centrifuge, and hence only the largest were separated. Molasses centrifuged at 75° brix and subsequently diluted to 65° brix contained only a few fine crystals, as most were separated in the centrifuge and the remainder dissolved during dilution. A sample of this material was retained for laboratory scale ion exclusion column tests.

The overall effect of brix on separation efficiency is a combination of two opposing effects. At high brixes, the molasses viscosity is high and therefore settling rates are low. However, on dilution to lower brixes, many smaller crystals dissolve and larger ones may be reduced in size, thereby again lowering the overall settling rate, and releasing calcium into solution. Thus the optimum brix for centrifugation depends on the crystal size distribution and crystal content of the molasses, as well as its viscosity.

It must be noted that centrifugation will remove precipitated ash only, and that the soluble components, consisting mainly of sodium and potassium salts, will not be removed. Although calcium and magnesium salts present in molasses are largely removed because of their low solubilities, significant residual concentrations will still remain after centrifugation. Therefore chemical precipitation of dissolved calcium and magnesium before centrifugation will be required to reduce the residual concentrations of these elements in the clarified molasses.

Chemical precipitation methods

The basis for these methods is the addition of an anion that will form low solubility compounds with the calcium and magnesium ions. The precipitated compounds can then be removed by centrifugation. Based on the solubilities of calcium and magnesium salts in water, the carbonate, sulphate, sulphite and phosphate anions were selected for testing. The last three are most conveniently added as the acids, which will produce sucrose inversion, a desirable side effect for the production of HTM. However, if sucrose recovery is required, costly neutralisation with sodium

hydroxide will be necessary. The carbonates of calcium and magnesium have the lowest solubilities of the compounds considered, and thus carbonatation was investigated first.

Carbonatation. Batches of molasses diluted to 75° and 65° brix and heated to 80°C were carbonated at a pH of approximately 7,5 by sparging with CO₂ gas and high speed stirring. Under these conditions, however, CO₂ is not very soluble and only a slight change in pH was noted. As a result, little extra sludge was removed in the centrifuge in the form of CaCO₃ and MgCO₃ and magnesium levels remained unchanged, although calcium levels were slightly lower in the centrifuged molasses.

A further test was performed at a higher pH, with NaOH being used to raise the pH to 10 before CO₂ was bubbled in, reducing the pH to 8,0 before centrifugation. From this pH change it was judged that a considerable quantity of CO₂ had been dissolved. On centrifugation, though, virtually no sludge was removed and no visual change in turbidity was seen. Microscopic examination of the molasses showed considerable quantities of small crystals of micron size, and it is probable that these were too small to be removed in the centrifuge. It would thus appear that the high pH caused dissolution of the existing crystalline syngenite phase, which either did not reform when the pH was reduced, or, more likely, came down too finely divided to be removed by centrifugation.

A further test was performed where the pH of the molasses was adjusted to 7,0 and solid sodium carbonate was added slowly to raise the pH. This method overcame the problem of dissolution of the solid phases, but severe foaming from the release of CO₂ gas was experienced, and the test could not be completed. A similar problem was encountered when solid sodium bicarbonate was used, and the method was judged to be unworkable on this scale.

Sulphitation. Sulphitation was the next method to be tested, as it is a well-established purification technique in the sugar industry and is easy to apply. The stoichiometric quantity of sulphur dioxide required to precipitate all of the soluble calcium and magnesium in a molasses sample was calculated and the amount of sodium hydroxide required to neutralise this quantity was added to the molasses at 80°C and 65° brix. The molasses pH was then adjusted to its original value by sparging with sulphur dioxide. The molasses was stirred for 30 minutes before centrifugation.

Analysis of the clarified molasses revealed that the sulphitation process had not caused any further precipitation of calcium and magnesium salts, and the molasses had the same concentrations of calcium and magnesium as a sample that had been centrifuged only. While it was expected that sulphitation might reduce the molasses viscosity, measurements showed that this was not the case. The viscosity of the untreated molasses was 0,3 Pa.s, the viscosity of the molasses that was centrifuged only was 0,08 Pa.s, and the viscosity of the sulphited and centrifuged molasses was 0,2 Pa.s. The poor result for the sulphited sample was probably caused by the formation of fine crystals of calcium sulphite,

which could not be removed efficiently during centrifugation. Thus, sulphitation did not improve the characteristics of the molasses and this method was abandoned.

Acidification. In this method, sulphuric acid was used to provide additional sulphate ions to cause further calcium and magnesium precipitation. No costly sodium hydroxide was required for neutralisation, and the resulting sucrose inversion is desirable for the manufacture of HTM.

Batches of final molasses from Gledhow mill were diluted to either 75° or 65° brix, and sufficient concentrated sulphuric acid was added with vigorous stirring to reduce the pH₈₅ to the desired value (1, 2, 3 or 4). The samples were heated to 85°C and stirred gently for 18 hours before centrifugation. Two control samples were diluted, heated and stirred at the natural pH₈₅ of the molasses of 5,4 for a similar period before centrifugation. Samples of the clarified molasses and the sludge were submitted for analysis.

As expected, all samples apart from those kept at the natural pH were completely inverted. However, there was some evidence of the breakdown of reducing sugars at pH₈₅ 1 and 2, and small amounts of hydroxy methyl furfural (HMF) were thought to have been produced. Better separation of sludge from molasses was achieved at 65° brix than at 75° brix, with the sludge appearing pale brown, having the characteristics of gypsum (CaSO₄.2H₂O), and containing little molasses. Table 1 shows that significantly higher masses of sludge were recovered at 65° brix than at 75° brix, demonstrating the importance of low viscosities during centrifugation and the better separation achieved with lower density solutions, as both density and viscosity are strong functions of the molasses brix. This confirms the trends predicted by the design equations for the centrifuge, in which Stokesian settling rates are assumed.

Table 1
Sludge recoveries from acidified molasses.

Molasses pH ₈₅	Sludge % centrifuge feed at 75° brix	Sludge % centrifuge feed at 65° brix
1	7,0	29,5
2	9,9	20,2
3	8,5	21,8
4	8,2	21,6
5,4	5,7	8,7

Calcium was substantially removed for the tests at low pH values and at 65° brix, as shown in Figure 1. The trend was not as marked for the tests run at 75° brix, but the result for the pH 1 test at this brix may have been affected by evaporation of water overnight from the sample. Magnesium was not significantly removed under any conditions, with 3 500 to 4 000 ppm on sample remaining in all samples. The sulphated ash levels were reduced for the low pH tests at 65° brix (see Figure 2), with a minimum of 8,4% being achieved at pH 2 or 3, compared with 11,4% in the non-acidified centrifuged sample. This is more

than is permitted for HTM (<3,5% ash on sample) but is still a significant reduction, and this method gave the best result of all the methods tried.

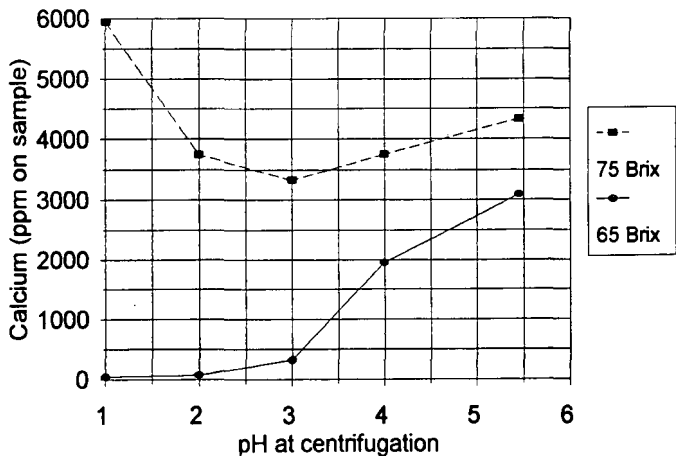


Figure 1. Calcium levels in clarified molasses as a function of pH.

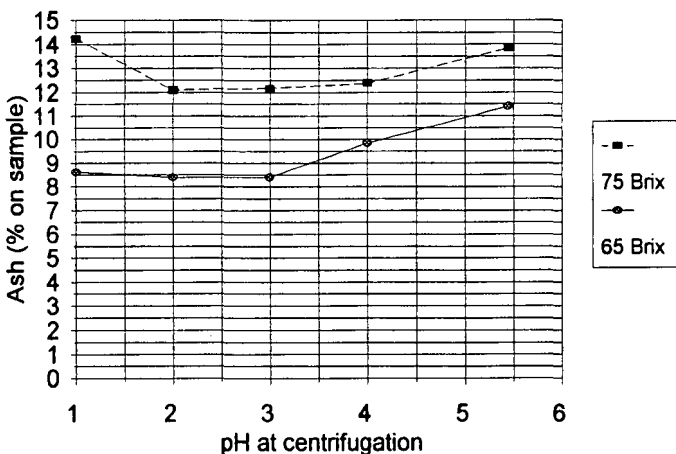


Figure 2. Ash removal from molasses as a function of pH.

Softening

A further method of lowering divalent cation concentrations is by ion exchange softening. This is best done at the clear juice stage, as described by Davis *et al.* (1997). Softening will reduce the divalent cation concentrations to very low levels, but it will, however, increase the monovalent cation (Na and K) concentrations correspondingly, and the ash content of the molasses will not be substantially affected.

Some workers in this field hold the view that membrane filtration is necessary before ion exchange softening, to remove all turbidity from the juice to prevent resin column fouling and to provide a turbidity free feed for the ion exclusion process downstream. Results of ion exchange softening trials performed at FX (Davis *et al.*, 1997), at Sezela (Thompson, 1994) and at the SMRI (personal communication, 1994) have shown that thorough filtration before softening is not required, and that

coarse screening is sufficient for the protection of the columns from particulate matter. Furthermore, this work has shown that nearly all of the turbidity present in B- and C-molasses is syngenite. Due to the very low levels of calcium present in softened molasses, syngenite would not be present and it is thought that no turbidity removal step would be required for ion exclusion. Thus, ion exchange softening of clear juice would remove the need for membrane filtration of the juice, and produce a sufficiently clear molasses feed for ion exclusion.

Ion exclusion chromatography

Ion exclusion separation is dependent on the physical and chemical properties of the resin and no net ion exchange takes place. Variables that affect the separation include resin particle size, elution flow rate, resin cross-linkage and feed injection volume, and have been well documented (Simpson and Wheaton, 1954). Factors affecting beet molasses desugarisation are understood. However, no reference has been made to the effect of divalent cations on the isolation of *invert* made from cane molasses using a pretreatment method as described above.

Experimental

Ion exclusion column. The ion exclusion column consisted of a jacketed glass column (430 x 25 mm inner column contained in a 430 x 50 mm outer column) with adjustable end fittings, slurry packed with Purolite PCR 642 Na²⁺ resin (172 mL). Resin and eluent temperatures were maintained at 60°C by an external water bath and pump. The eluent (water) was stored in a 2 L Pyrex bottle in the water bath to ensure temperature equilibration. A Technicon Auto Analyser Pump (Pump III) was used with appropriate silicon tubing to deliver a flow of 2 to 2,5 mL/min at the outlet of the column. Fractions from the column (4 to 4,5 mL) were collected using a LKB Fraction Collector (17000 Minirac). The resin was converted to the sodium form by pumping a solution of 10% sodium chloride (250 mL) through the column and then washing with water (1 000 mL).

Analysis. Collected fractions and standards were diluted with water (1:10 and 1:50 respectively) and analysed for ash, glucose and fructose by HPLC (Day-Lewis, 1993). The concentrations found in the starting material prior to separation were used for recovery calculations. Concentrations of glucose and fructose in the starting molasses, for calculations of yields, were determined by HPIC (Day-Lewis and Schäffler, 1992) while ash was determined as sulphated ash. A relative colour value for individual fractions and starting molasses solutions was measured by reading the absorbance at 420 nm (against water) on a Philips PU8620 spectrophotometer using a 10 mm cuvette.

Results and discussion

Ash concentration. Previous work had shown that a feed volume of 5% of column volume was an optimum sample volume (Walford, 1997). The effect of ash concentration on the ash/glucose separation was studied by preparing synthetic ash/glucose

¹MC Thompson, Sugar Milling Research Institute (1994)

solutions using sodium sulphate (1 to 15%) and glucose (15% fixed). Sodium sulphate was used as a model ash compound to minimise the effects of ion exchange with ions present on the resin. Ionised sodium sulphate is excluded from the resin, resulting in the fronted peak. The glucose is distributed between the resin phase and the eluent phase (water), hence moving at a slower rate through the column and generating an essentially Gaussian peak shape (Figure 3). As the ash concentration increases, the initial elution point of the ash peak remains constant, but the apparent apex of the sulphate peak and tail move downstream into the area of glucose elution. It encroaches into the glucose peak and thereby reduces the purity and yield of any collected glucose fraction.

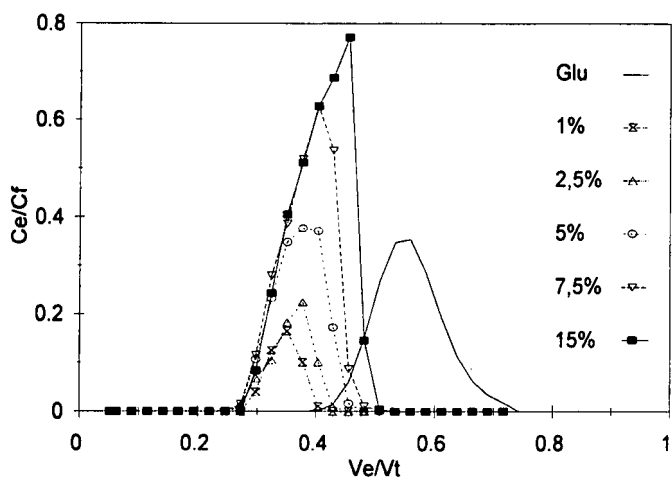


Figure 3. Effect of ash concentration on the ash/glucose separation. (V_e/V_T ratio of effluent volume to resin bed volume and C_e/C_f = ratio of effluent concentration to original concentration.)

Resolution (R) is a convenient chromatographic parameter expressing the efficiency of separation of adjacent peaks. It is defined (Ettre, 1993) as:

$$R_s = \frac{(t_{R2} - t_{R1})}{(W_{b1} + W_{b2})/2}$$

where: t_R = retention time of peak of interest

W_b = peak width at base.

Resolution accounts for both the narrowness of the peaks and the separation between the peak maxima. Analytical analyses require baseline separation ($R \geq 1.5$). For preparative separations values as low as $R = 0.4-0.6$ are considered acceptable (McDonald and Bidlingmeyer, 1987). Figure 4 shows that, as the quantity of ash increases, resolution decreases approximately three fold, as would be expected for a less efficient separation.

Divalent cation effect. A synthetic molasses was made up using calcium, magnesium and potassium salts and glucose. Based on previous data for South African molasses, these are the most important cations present (MacGillvray and Matic, 1970; Soffiantini *et al.*, 1971). The relative ratios and masses of individual salts used are shown in Table 2. These were added to

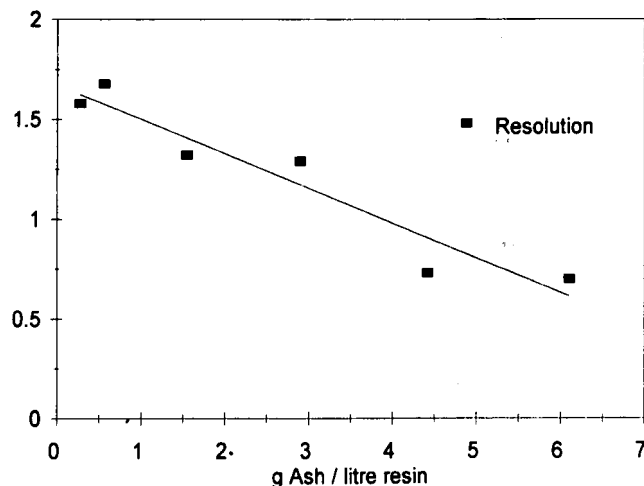


Figure 4. Effect of ash concentration on the ash/glucose resolution.

15 g of glucose and made up to 100 mL with water to produce a 5% ash/15% glucose solution. Five repetitive separations with this solution were made with no significant change in the ash/glucose resolution being detected (Table 3). It is believed that an equilibrium between the di- and monovalent cations is achieved which does not affect the ash/glucose separation to the same degree as the ash/sucrose separation. Monosaccharide separation is enhanced in the presence of divalent cations while sucrose separations are adversely affected (Goulding, 1975). Reduction of calcium levels *per se* as proposed for desugaring plants is thus not a requirement for invert separation, but ash levels may need to be reduced for economic throughput and product specification.

Table 2
Ratio of cations added to synthetic molasses.

Cation	Ratio	Salt	g/100 mL
Potassium (K)	4,0	KCl	2,68
Calcium (Ca)	1,2	CaCl ₂ ·2H ₂ O	1,50
Magnesium (Mg)	1,0	MgCl ₂	0,81

Table 3
Effect of divalent cations on resolution.

Replicate run	1	2	3	4	5
Resolution	0,45	0,46	0,45	0,46	0,48

Separation of treated molasses. Two forms of treated molasses were used as feed material. Portions of 65° brix, centrifuged molasses were diluted to 20° and 40° brix and all three samples (20°, 40° and 65° brix) inverted using invertase. Completion of inversion was checked by HPLC. Acid treated molasses (65° brix inverted at pH 3 using sulphuric acid, then centrifuged to

remove precipitated calcium sulphate) was diluted to 50° brix. The ash and calcium level of these samples is shown in Table 4. Each of these samples (in duplicate) was used as a feed material to the ion exclusion column. Ash, glucose, fructose and colour were analysed for each fraction. The resultant profile of each separation is shown in Figure 5. As shown with the sodium sulphate, as the quantity of ash increases, the separation efficiency of the column decreases. It can be seen that when using normal, centrifuged, invertase inverted molasses, the recovery of ash-free invert drops considerably above the 40° to 50° brix range. This is due to the quantity of ash present in the starting molasses tailing into the invert peak. By combining fractions of glucose and fructose as invert with little or no ash, a recovery and ash/invert ratio can be calculated for each separation. The values obtained are given in Table 5. It is clear that invert recovery and final concentration of ash in the invert solution is dependent on the initial quantity of ash in the starting material; the lower the initial ash concentration, the higher the invert recovery for any given ash/invert ratio.

Table 4

Comparison of molasses used for ion exclusion separation.

Molasses treatment @ 65° brix	Ash on sample (%)	Calcium (ppm)
Centrifugation	11,4	3 500
pH 3 inversion + centrifugation	8,4	400

Table 5

Inverted fraction recovery from inverted molasses.

Starting molasses		Invert fraction		
Treatment	°Brix	Recovery (%)	Ash (%)*	°Brix
Centrifuged, enzyme inverted	20	98	1,5	1,0
	40	94	1,9	3,0
	65	50	4,4	3,5
Centrifuged, acid inverted	50	85	4,0	3,1

*On dry substance

All the separations described were batch based which results in restricted column utilisation, limited throughput and low concentration of the output stream due to dilution by the eluants while on the column. Simpson and Bauman (1954) recognised this problem and described a recycling technique to produce a product stream having a concentration at least equal to the initial concentration. Although the work describes the separation of sodium chloride and ethylene glycol, more recent authors have used sodium chloride and glucose (Nigam *et al.*, 1981) and glucose and fructose (Barker and Thawait, 1986). Using the principles described in these papers and the data from the acid

inverted molasses it would appear that a recycle batch method should give at least a 10-15° brix invert solution with less than 3,5% ash. The major drawback with the recycle batch method is a discontinuous product stream. Simulated moving bed (SMB) processes have been developed which overcome this problem (Saska and Lancrenon, 1994; Rearick and Kearney, 1996; Saska *et al.*, 1992). The resulting continuous output stream would have a composition similar to the batch recycle output.

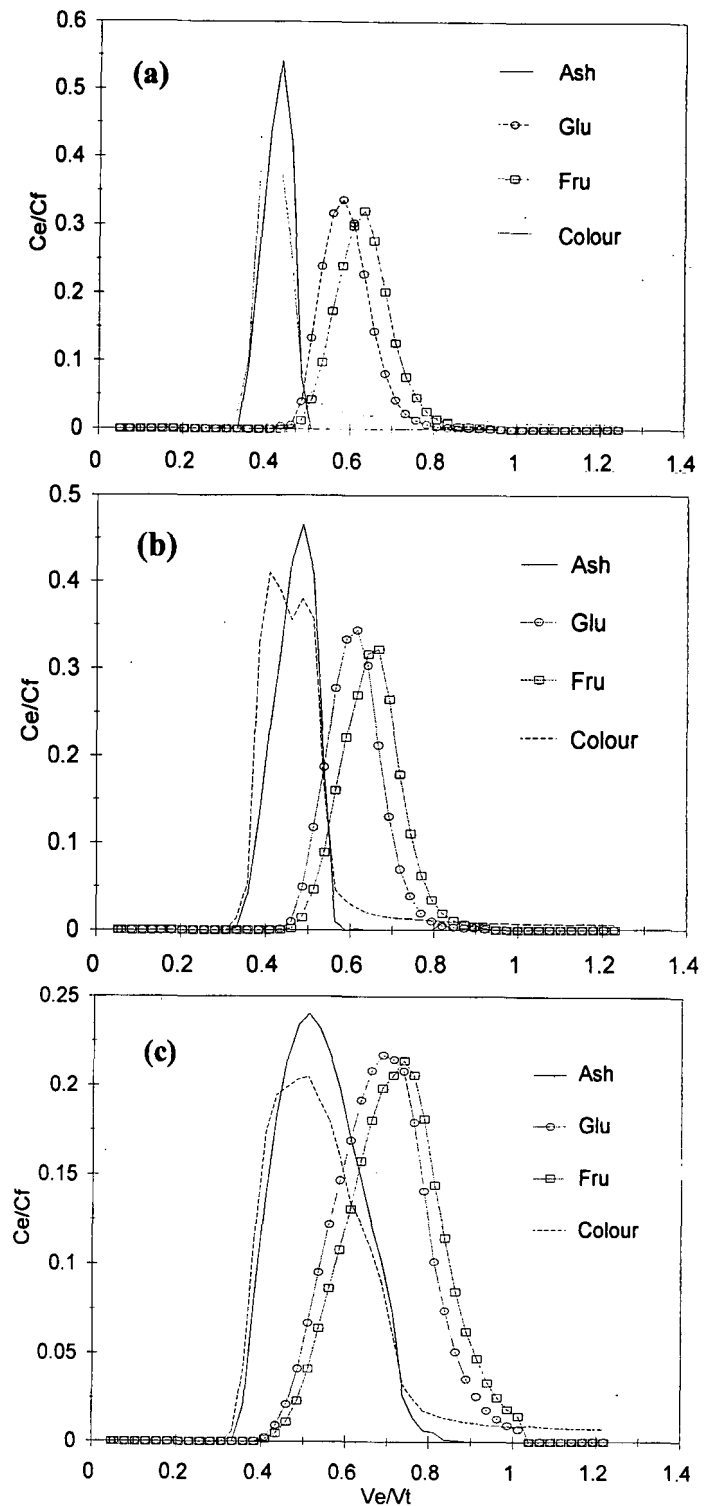


Figure 5. Separation of ash, glucose, fructose and colour of (a) 20° Bx, (b) 40° Bx and (c) 65° Bx centrifuged, enzyme inverted molasses. (V_e/V_T = ratio of effluent volume to resin bed volume and C_e/C_f = ratio of effluent concentration to original concentration.)

Conclusions

For the recovery of an invert sugar stream from C-molasses by ion exclusion chromatography, turbidity removal and the lowering of ash levels are required. The pretreatment method evaluated here that best meets these objectives is acidification with sulphuric acid to a pH of 3, followed by centrifugation. Good turbidity removal is achieved and ash levels are decreased by around 50%.

Further work on pretreatment may be needed to improve the ash removal from molasses if lower levels than can be presently achieved are needed for optimum separations. Theoretically, carbonatation appears to be the best method, as the very low solubilities of calcium and magnesium carbonates would enable virtually complete removal of calcium and magnesium, and a reduction in ash levels. However, technical problems with carbonatation need to be overcome before the process would be viable.

A batch ion exclusion system has been described to determine the effects of molasses non-sugars on an ash-invert separation. It was determined that optimum conditions were achieved at a feed volume of 5% of column volume with a starting material at approximately 50° brix. The system was used to demonstrate the feasibility of using molasses as starting material and isolating invert from other components present to produce an HTM equivalent material. The most promising starting material was acid inverted molasses due to the removal of ash before separation. It was found that calcium had no discernable effect on this separation.

A preliminary economic analysis of a proposed process based on this investigation (Bernhardt, 1997) suggests that it could be economically viable, with some potential for improvement. The process needs to be tested and optimised in a pilot plant before a full feasibility study can be done.

REFERENCES

- Barker, PE and Thawait, S (1986). Separation of fructose from carbohydrate mixtures by batch and semi-continuous chromatographic operation. *Chem Eng Res Des* 64: 302-307.
- Berhardt, HW (1997). An economic analysis of the production of high test molasses (HTM) from final molasses. Sugar Milling Research Institute Technical Report No. 1752, 10 pp.
- Chen, JCP and Proskowetz, F (1967). Further investigations of the centrifugation of B-molasses. Proceedings of the XII Congress of the International Society of Sugar Cane Technologists, held 28 March to 10 April 1965 in San Juan, Puerto Rico. pp 1677-1683.
- Chertudi, KP (1991). The Tasco chromatographic separator at Twin Falls factory. *Int Sug J* 93 : 28-32.
- Davis, CW and Clarke, WB (1963). Removal of sludge from B-molasses by centrifugal separation. Proceedings of the XI Congress of the International Society of Sugar Cane Technologists, held in Reduit, Mauritius. pp 856-865.
- Davis, SB, Peacock, SD and Walthew, DC (1997). Pilot plant investigation of clear juice softening. *Proc S Afr Sug Technol Ass* 71 (in press).
- Day-Lewis, CMJ (1993). Progress report on a rapid screening test for cane quality. Sugar Milling Research Institute Internal Report 1/93, 4pp.
- Day-Lewis, CMJ and Schäffler, KJ (1992). Analysis of sugars in final molasses by ion-chromatography. *Proc S Afr Sug Technol Ass* 66: 131-135.
- Ettre, LS (1993). Nomenclature for chromatography. IUPAC Recommendations 1993. *Pure and Appl Chem* 65: 819-872.
- Goulding, RW (1975). Liquid chromatography of sugars and related polyhydric alcohols on cation exchangers. The effect of cation variation. *J Chrom* 103: 229-239.
- Kakihana, I (1989). Sugar recovery from cane molasses by continuous chromatographic separation system. *Proc Jap Sug Ref Technol* 37: 11-15.
- MacGillvray, AW and Matic, M (1970). Composition of South African final molasses. *Proc S Afr Sug Technol Ass* 44: 81-87.
- McDonald, PD and Bidlingmeyer, BA (1987). Preparative liquid chromatography. *J Chromatography Library*, Vol 38. Elsevier, 341 pp.
- Nigam, PC, Singh, D and Sharma, RN (1981). Studies on ion exclusion phenomena. *Ind Eng Chem Proc Des Dev* 20: 182-188.
- Peacock, SD (1995). Ion exclusion desugarisation of refinery jet 4. Part 1: technical feasibility. Sugar Milling Research Institute Technical Report No. 1725, 12 pp.
- Proskowetz, F and Chen, JCP (1963). Centrifugation of B-molasses and its clarification effect. Proceedings of the XI Congress of the International Society of Sugar Cane Technologists, held 24 September to 5 October 1962 in Reduit, Mauritius. pp 866-869.
- Rearick, DE and Kearney, M (1996). Removal of nonsugars from cane molasses by ion exclusion chromatography. Proceedings of the XXII Congress of the International Society of Sugar Cane Technologists, held 7-15 September 1995 in Cartagena, Colombia. pp 167-171.
- Saska, M (1996). Membrane based separations and countercurrent multicolumn systems for decolourisation, ion-exchange and ion exclusion: emerging technologies for the sugar industry. Proceedings of the XXII Congress of the International Society of Sugar Cane Technologists, held 7-15 September 1995 in Cartagena, Colombia. pp 147-160.
- Saska, M and Lancrenon, X (1994). Applications of continuous chromatographic separation in the sugar industry. III. Desugarisation of cane molasses. *Int Sugar J* 96: 403-410.
- Saska, M, Wu, MD, Clarke, SJ and Iqbal, K (1992). Continuous separation of sugarcane molasses with a simulated moving-bed adsorber. Adsorption equilibria, kinetics and application. *Separation Science and Technology* 27: 1711-1732.
- Simpson, DW and Bauman, WC (1954). Concentration effects of recycling in ion exclusion. *Ind Eng Chem* 46: 1958-1962.
- Simpson, DW and Wheaton, RM (1954). Ion exclusion column analysis. *Chem Eng Prog* 50: 45-49.
- Soffiantini, VA, Jennings, RP and Wilkes, R (1971). Seasonal variations in molasses composition. *Proc S Afr Sug Technol Ass* 45: 99-106.
- Thompson, MC (1993). Progress report on the centrifugal clarification of molasses. Sugar Milling Research Institute Technical Report No. 1653, 27 pp.
- Thompson, MC (1994). Softening of clear juice. *Proc S Afr Sug Technol Ass* 68: 115-120.
- Walford, SN (1997). Production of invert from final molasses using ion-exclusion chromatography. Sugar Milling Research Institute Technical Report No. 1751, 12 pp.
- Wheaton, RM and Bauman, WC (1953). Ion exclusion: A unit operation utilising ion exchange materials. *Ind Eng Chem* 45: 228-233.