

REVIEW OF THE PROCESS DEVELOPED AT THE SMRI TO MAKE INVERT SUGAR FROM CANE MOLASSES BY CHROMATOGRAPHIC SEPARATION

HW BERNHARDT, SB DAVIS, SD PEACOCK AND SN WALFORD

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

Abstract

The separation of invert sugars from cane molasses involves pretreatment of the final molasses to remove suspended solids and calcium salts, inversion of the sucrose in the molasses and chromatographic separation of the inverted sugars from the various dissolved constituents that are normally present in the molasses. Details of these processes, which were carried out on a laboratory and a small pilot plant scale, are presented. The main economic factors affecting the profitability of the operation, including a sensitivity analysis, are also described.

Introduction

The current domestic selling price for final molasses (ex factory) is R164/ton. South Africa produces a surplus of molasses, and this is sometimes exported at a loss. The average sucrose content of South African molasses during the 1998-99 season was 31.0%, while the corresponding fructose and glucose contents were 7.9 and 5.8% respectively. The domestic selling price of raw sugar is R2 342/ton. Assuming the sucrose equivalent of the invert sugars, fructose and glucose, then the sugar content in one ton of molasses would have a value of R1 047 (44% of R2 342). Another constituent of molasses that has considerable commercial value is potassium (K). The average potassium content of South African molasses is approximately 4%. South Africa imports all its K fertiliser needs, since there are no local sources. At local fertiliser prices the K in molasses has a value of R113/ton. It is clear therefore that, if the sugars and the K could be extracted cost-effectively from the molasses as two separate products, their combined value would greatly exceed the current selling price of molasses.

Ion exclusion chromatography has the potential to achieve this dual separation. However, it is a relatively new technology, particularly as far as its application in the cane sugar industry is concerned. The technology has been applied with success in the beet industry (Chertudi, 1991). The obstacle to its successful introduction in the cane sugar industry is the relatively high turbidity and concentration of divalent ions (Ca and Mg) in comparison with beet molasses (Rearick and Kearney, 1996). Attempts were made by a multidisciplinary team at the Sugar Milling Research Institute (SMRI) to apply appropriate pretreatment techniques to molasses that would

eliminate these drawbacks and enable the use of ion exclusion technology to produce a product of significantly higher value than final molasses.

This paper gives an overview of the work that was done on that project. A detailed technical report of the experimental results is available (Bernhardt *et al.*, 2000). The current paper focuses on the production of a relatively pure form of liquid invert sugar as the main product. Such a product is a potential carbohydrate source for high value fermentations and it could have numerous uses in the food processing industry. A second commercially attractive product, namely a potassium-based fertiliser, is only briefly mentioned as this aspect requires further development and may form the subject of a further paper.

A simplified flow diagram of the process of making liquid invert sugar is shown in Figure 1. The main elements of the pretreatment involve dilution, acidification and centrifugation. More details on these are given in the subsequent sections.

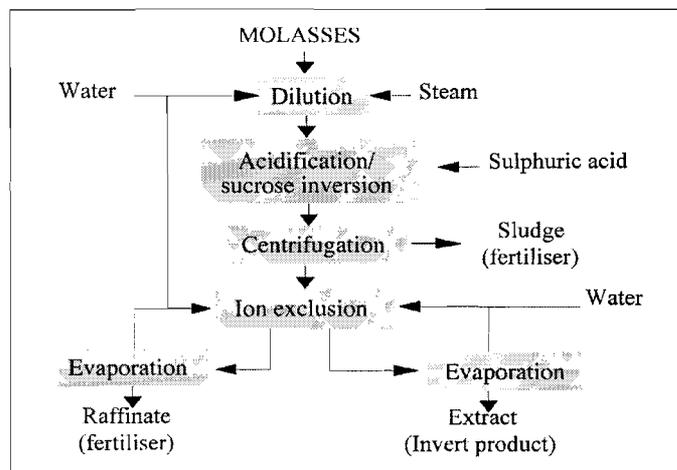


Figure 1. Process flow diagram

Molasses pretreatment methods investigated

The preliminary investigation of the pretreatment of molasses to remove turbidity and divalent cations has been reported previously by Davis *et al.* (1997), and will only be summarised. Filtration, froth flotation and centrifugation in a disc-bowl centrifuge were investigated and, of these, only centrifugation proved to be capable of remov-

ing suspended solids, which consisted largely of syngenite ($\text{CaK}_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$).

Carbonation and sulphitation were also investigated as means of lowering the divalent cation levels (particularly of calcium), but these had no significant effect. Acidification with sulphuric acid to pH 3 was found to reduce residual calcium levels considerably on centrifugation and lowered ash levels from 14 to 8%, although magnesium concentrations were unchanged. Molasses brix and temperature of centrifugation were also found to have significant effects on the separation, and further work was carried out to determine the optimum conditions.

Optimal removal of turbidity and ash

Removal of the syngenite precipitate from final molasses will achieve the dual objective of minimising the turbidity and the ash content, both of which affect the efficiency of ion exclusion. Removal of syngenite does not, however, produce any significant reduction of Mg. Although a high Ca and Mg content does make ion exclusion desugarisation of molasses inefficient when the sugar is mainly in the sucrose form, it was found that if most of the sugar is in the form of invert, the high residual Ca and Mg content does not have a negative effect on separation. The most successful method of removing syngenite was shown to be centrifugation.

A systematic study of the centrifugal clarification of molasses was undertaken as part of this project and the results of the study are fully reported by Bernhardt (1998). Only the main aspects of this study will be highlighted here.

One of the main problems concerning the successful pretreatment of cane molasses for ion exclusion is the considerable range of composition. Not only does molasses sourced from different mills differ with respect to sugar content, but also the amount of ash, the composition of that ash, as well as organic constituents such as colour, polysaccharides and organic acids show a considerable range. An indication of the variability of molasses composition is shown in Table 1. This variability implies that the pretreatment must be adapted accordingly.

Table 1. Analysis of final molasses from South African mills over a season (Thompson, previously unpublished data).

Analyte	Average	Low	High	Standard Deviation
Brix °	82,7	78,2	88,3	2,2
Ca (ppm)	6 170	2 020	12 600	2 290
Mg (ppm)	4 560	3 280	6 020	680
K (ppm)	41 350	31 840	53 690	5 240
Na (ppm)	880	50	3 910	950

The degree of precipitation of syngenite depends on its solubility, which is influenced by the relative concentrations of the component chemical species (Ca^{2+} , K^+ and SO_4^{2-}), as well as the temperature. Precipitation can be promoted by increasing the concentration of one species relative to the others. Rates of precipitation are generally affected by mass transfer considerations – how quickly the components making up an insoluble solid can be brought together. The latter depends on the degree of agitation.

Of all the pretreatment methods tested, dilution of molasses with water and addition of sulphuric acid were the most effective in promoting the precipitation of syngenite and removal of its precipitate by centrifugation. A simple rapid test (Bernhardt, 1998) can be used to determine the optimal dilution and acid addition. Provided that sufficient agitation is applied during dilution and acid addition, the rate of precipitation is very rapid, and no benefit could be found by additional prolonged stirring. The degree of beneficial effect obtained by heating to promote precipitation was found to be variable, depending on molasses origin.

Sucrose Inversion

Not only does sulphuric acid enhance the pretreatment effectiveness, but it also inverts sucrose to invert sugars glucose and fructose. Of importance, from a process economics point of view, is the rate at which this inversion takes place.

A sample of diluted molasses from the Seszela (SZ) mill was acidified with the optimum amount of sulphuric acid determined by the laboratory optimisation test. After centrifugation, the pH of the supernatant was found to be 0,1. It was allowed to stand at room temperature (*ca.* 25°C) for 30 hours during which sub-samples were taken for analysis of sucrose, glucose and fructose. The results are shown in Figure 2.

This figure shows that inversion, at room temperature under the acidic conditions required for adequate pretreatment, is complete in approximately 15 hours. As inversion rate increases with temperature and separation must be done at high temperature (approximately 80°C), a much lower residence time than 15 hours for complete inversion will be necessary. It is desirable to use the shortest residence time pos-

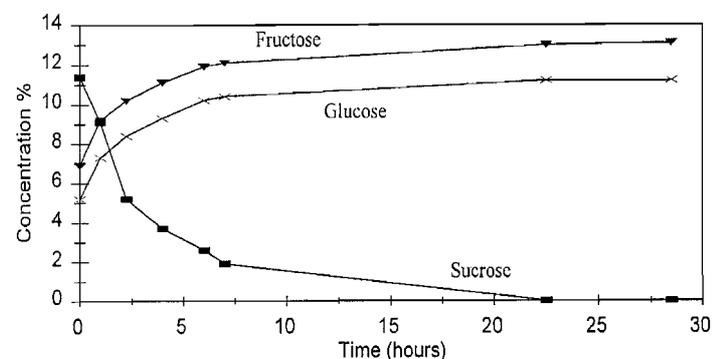


Figure 2. Inversion study at ambient temperature.

sible so as to minimise the degree of degradation of invert sugars to hydroxymethyl furfural and other breakdown products.

Ion exclusion chromatography

Ion exclusion chromatography (IEX) as a process for separating ionic from non-ionic solutes using ion exchange resins was first described by Wheaton and Bauman (1953). IEX is carried out extensively in the beet sugar industry for desugaring of molasses (Chertudi, 1991) and is used for isolation of fructose in the high fructose corn syrup industry (Saska, 1996). Apart from the fact that the sucrose content in beet molasses is almost double that in cane molasses, two additional factors militate against sucrose recovery in 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, thereby decreasing the ash/sucrose resolution. Maximum values as low as 400 ppm/Bx calcium have been recommended (Kakihana, 1989).

Variables affecting the separation include resin particle size, elution flow rate, resin cross-linkage and feed injection volume. These have been well documented for certain organic systems (Simpson and Wheaton, 1954). Factors affecting beet molasses desugaring are understood. Reference has previously been made to the effect of divalent cations on the isolation of *invert sugars* made from cane molasses. The effects of ash concentration, column loading and divalent cations on the isolation of the invert in a batch process have been reported (Davis *et al.*, 1997). It was determined that optimum separation conditions for acid inverted molasses at approximately 50° brix were achieved at a feed volume of 5% of column volume. Recoveries of greater than 85% were recorded with ash contents between 2 and 4%. Calcium was found to have no discernable effect on this separation. The optima were used to produce a high test molasses (HTM) equivalent material which was used for small scale coating trials, as described below.

Pilot plant chromatographic separations

The SMRI pilot plant chromatographic separator and its method of operation have previously been described in detail (Peacock, 1996). However, some minor modifications to the original design have been carried out since that publication, namely the addition of a spray nozzle distributor in the top of the column, and a compressed air supply in the top of the column to assist with achieving a low liquid level above the resin bed. This pilot plant separator was used to carry out some preliminary investigations into the pilot scale separation of invert sugar from pretreated (acidified, inverted and centrifugally clarified) final molasses.

While ion exclusion chromatography makes use of ion

exchange resin to carry out a separation of components based on size and charge, no actual ion exchange takes place between ions in the material to be separated and the resin beads in the ion exclusion column (under normal circumstances). However, if a freshly regenerated resin is used in the column for the first time, some ion exchange will take place, until an equilibrium ion distribution is reached between the resin and the material to be separated. In other words, when pretreated final molasses (rich in calcium, magnesium and potassium) is passed through a bed of freshly regenerated resin in the sodium form, ion exchange will take place until an equilibrium is reached between the cations in the feed and the cations on the resin. Thus, the first batches of product received from a bed of freshly regenerated resin will have a very different cation composition (rich in sodium ions) to subsequent batches, and for this reason, a cation equilibration was carried out before the start of the pilot plant trials.

To carry out the equilibration, a 10% acidified salt solution was made up, with a similar cation composition to that found in the pretreated final molasses. Four hundred litres of this acidified brine were passed through the column in batches of 10 litres, at a flow rate of two litres per minute, thus duplicating the molasses separation process as closely as possible. Following this, the column equilibrium was fine-tuned by passing five 10 litre batches of pretreated molasses through the column.

Once the resin equilibrium had been attained, the column could be put into service. One batch of molasses was separated, and samples of the column effluent sent for analysis. The separation profile thus obtained was found to resemble closely that obtained in the laboratory scale trials. Two 10 litre samples of invert-rich product were then manufactured using the ion exclusion pilot plant. The operating conditions used during the trial are shown in Table 2, and the approximate composition of the samples obtained is shown in Table 3.

In the pilot plant trials, it was found that the total sugar content of the product was lower than had been expected from the laboratory scale trials, and that the colour of the product was much higher than had been expected. The latter could have resulted from the evaporation of the samples in the SMRI laboratory evaporator, as the evaporator capacity is small and a long residence time was required for concentration of the low pH product in this system. Low pH sugar solutions tend to increase in colour during prolonged high temperature exposure.

Table 2. Operating conditions for the pilot plant trials.

Feed brix	65°
Bed volume	200 litres
Bed depth	4 metres
Feed batch size	5% of column volume
Elution water flow rate	0.6 bed volumes per hour
Temperature	80°C

Table 3. Composition of the samples produced.

Dry solids (%)	3
Total sugars as invert (% of dry solids)	62
Ash (% of dry solids)	4,9
Colour (ICUMSA units)	128 000
pH	2,4

As a test of the suitability of the ion exclusion product for use in fermentations, a sample of the product was subjected to a fermentability test. The fermentation proceeded extremely rapidly and a higher than predicted yield based on the sucrose, glucose and fructose present was obtained. The product is thus highly suited to this application.

Coating of VHP sugar with ion exclusion product material

The pol of some VHP sugars exported by the South African Sugar Terminals is lowered by coating these sugars with high test molasses (HTM) to meet certain customer requirements. The HTM used for coating has a pol of about 10°Z, being made up of approximately equal proportions of sucrose, glucose and fructose, and is applied at a dosage of up to 2% (depending on the target sugar pol required). One of the possible uses of an invert-rich material produced from final molasses by ion exclusion is as a cheaper coating material for export sugars, to replace the HTM currently used.

Some concern existed regarding the use of an invert-rich ion exclusion material (referred to as *extract*) for sugar coating. These included the high colour of the extract samples which had been produced at the SMRI in the past, as well as the possible hygroscopicity of the extract-coated sugars due to its almost pure invert nature. In order to determine the technical feasibility of using this material for the coating of VHP export sugars, a series of coating and storage tests was carried out.

A special low-colour, low ash extract was produced on a laboratory scale at the SMRI for use in the coating and storage trials. The ash level of the extract produced was very similar to that of standard HTM, while the colour was approximately double that of standard HTM. However, due to the almost-pure invert nature of the extract, less of this product is required to reduce the coated VHP pol to the export target than would be required when using standard HTM, resulting in similar coated sugar colours for both products.

Storage tests

A sample of VHP sugar was obtained from the sugar terminals and analysed fully. The sugar was sub-sampled into two large portions for storage testing, to determine the keeping characteristics of the sugars, and two small portions, for testing of the hygroscopicity of the coated sugars. The first of the two larger sub-portions of VHP was coated with standard

HTM to a pol of 97,8°Z (requiring the application of 1,6% coating material). The second sub-portion was coated with SMRI-produced extract, also to a pol of 97,8°Z (requiring the application of 1,1% coating material). This target sugar pol was chosen as it represents the worst-case coating scenario, being a very low sugar pol, requiring a large quantity of coating material to be applied.

The coated sugars were then each subdivided into three portions, one for immediate analysis, one for analysis following three weeks' storage and one for analysis following six weeks' storage. The average shipping time for coated export sugar is approximately four weeks. The samples of sugar were stored in sealed plastic sachets under ambient conditions within the SMRI building. It was anticipated that the following effects might be noticed following storage due to the low pH of the coating material:

- Sucrose inversion, which would be evidenced by a drop in the pol of the sugar coated with the extract material
- Colour formation in the coated sugar.

The results of the coated sugar storage trials are shown in Table 4. No drop in pol was noticed in either coated sugar over the six week storage period. The sugar coated with the extract material was found to have a lower moisture content, and a lower reducing sugar content, than that coated with the standard HTM. This is due to the fact that less extract material was required to lower the sugar pol to the target of 97,8°Z, when compared with standard HTM. The coated sugar colours, sulphated ash levels, turbidities and gum levels were found to be similar, as were the coated sugar safety factors. The safety factors were found to be well below the upper limit of 0,25. The pH of the sugar coated with the extract material was lower than that of the sugar coated with the standard HTM.

Table 4: Analyses of the coated sugars used in the storage trials

	VHP sugar before coating	Coated with standard HTM			Coated with extract material		
		Initial	3 wks	6 wks	Initial	3 wks	6 wks
Pol (°Z)	99,26	97,71	97,65	97,69	97,90	97,85	97,86
Moisture (%)	0,09	0,42	0,42	0,40	0,39	0,37	0,39
Reducing sugars (%)	0,18	1,30	1,31	1,16	1,09	0,93	0,94
Sulphated ash (%)	0,11	0,17	0,18	0,19	0,14	0,17	0,17
Safety factor	0,12	0,18	0,18	0,17	0,19	0,17	0,18
Colour (IU)	1 730	2 020	2 170	2 200	2 000	2130	2 170
Turbidity	1 170	1 300	1 310	1 240	1 200	1 330	1 260
Gums	928	1 013	939	1 040	936	978	900
pH (of a 50° brix solution)	6,47	6,34	6,32	6,42	4,53	4,51	4,65

Coated sugar hygroscopicity

The use of extract material for sugar coating may increase the possible hygroscopic nature of the coated sugar due to the almost pure invert nature of the coating material. A test was thus carried out to determine the moisture uptake characteristics of sugar coated with this material, as compared to the characteristics of sugar coated with standard HTM.

The controlled atmosphere used for this test was the SMRI's constant temperature room. This room is maintained at exactly 20°C, and typically has a relative humidity of 50 to 60%. The two remaining small portions of VHP sugar were coated with standard HTM and extract, respectively, to a pol of 97,8°Z and stored in paper envelopes in the SMRI constant temperature room for a period of one week. It was felt that this should allow sufficient time for equilibration of the sugar samples with the controlled atmosphere. The moisture of the coated sugars was determined both before and after the exposure to the atmosphere, as shown in Table 5.

Table 5: Results of the hygroscopicity trial

Sugar coated with:	Standard HTM	Extract material
Initial moisture (%)	0,43	0,46
Moisture after one week (%)	0,25	0,28

It was found that both sugars lost similar amounts of moisture to the atmosphere over the storage period. From this, it can be concluded that the extract material shows no evidence of hygroscopicity when used for sugar coating with subsequent storage at a relative humidity of 50-60%.

The results of the coating and storage trials are very promising. It would appear that invert-rich ion exclusion extract material is a technically viable alternative to standard HTM as a coating material for export sugars, provided that the lower pH of the extract-coated sugar is acceptable to the end-user of the product.

Economic factors

An economic analysis of the process of invert recovery by ion exclusion was undertaken by Bernhardt (1997). The data used for that analysis have been updated and the figures presented here are based on this revision.

The analysis is based on a plant producing 100 000 tons of invert syrup of 78° Bx (containing 75% invert sugar) per annum situated at a raw sugar factory. The current capital cost of this plant (R105 million) is estimated from data published by Pynnonen (1996). The analysis has made provision for the installation of a 40 ton per hour steam boiler but assumes that the increased demand on other utilities (water and electricity) due to the operation of the ion exclusion plant can be met by the existing infrastructure of the sugar factory. For an annual production capacity of 100 000 ton product approximately 200 000 ton final molasses would be

required. A significant proportion of this would have to be transported to the facility from other mills. A transport cost of R40/ton has been applied in the analysis. The average transport cost during the 1998-99 season for transporting molasses from all South African mills to Durban was R56/ton. A significant quantity of the molasses fed to the process will come from the sugar mill where the separation plant is situated, so no transport costs will be incurred for this molasses. For this reason a lower figure than the average transport cost was used. Furthermore, the analysis assumes that the raffinate at 60° Bx, to which the molasses sludge is added, will be used as liquid fertiliser in surrounding cane fields. A corresponding saving of fertiliser costs has been included. The discounted cash flow has been calculated over a project life of ten years and no credit for the residual value of the plant has been given.

The hourly production and consumption figures are shown in Table 6 and the relative variable costs are shown in Table 7.

Table 6: Quantities produced and used per hour

Item	Ton/h
Invert syrup product	13
Molasses used	26
Steam used	40
Water used	15
Raffinate produced	17
Sulphuric acid used	1
Centrifuge sludge produced	2

Table 7: Variable costs per cent for the process

Item	%
Molasses	66,3
Transport	16,2
Steam	8,8
Sulphuric acid	8,1
Power	0,4
Water	0,2

It is clear that the significant cost factors are the raw material (molasses), transport of molasses, steam and sulphuric acid. At the current domestic molasses price (ex mill gate) of R164/ton, and using a selling price of the invert syrup prod-

uct of R850/ton (which is the current selling price for high test molasses) the internal rate of return (using a zero inflation base) was 23,1%. The analysis used the present company tax rate of 30%. At this stage it is uncertain what the market value of the invert syrup will be, but the analysis shown in Table 8 indicates the sensitivity of the internal rate of return to the selling price of the product.

The discounted cash flow model was used for a sensitivity analysis, the results of which are shown in Table 8. As expected, the project profitability is sensitive to all the factors listed, namely capital, product selling price, molasses price and tax rate, with the product selling price having the most significant impact.

Table 8. Sensitivity analysis of the internal rate of return (IRR)

Item	Low	Base case	High
Capital (R million)	95	105	115
IRR %	26,8	23,1	20,0
Product Selling price (R/ton)	700	850	1 000
IRR %	13,4	23,1	32,3
Molasses price (R/ton)	140	164	188
IRR %	26,3	23,1	19,9
Company tax rate %	20	30	40
IRR %	27,0	23,1	19,1

Conclusions

It was shown that, despite the variability of the composition of cane molasses, appropriate dilution with water, acidification with sulphuric acid and centrifugation can reduce the turbidity and ash content of the molasses sufficiently for the successful application of ion exclusion to separate sugars from non-sugars. The acidification will contribute to inversion of sucrose. The pretreated molasses must be preheated to 80°C for ion exclusion. This should yield an acceptable rate of inversion of sucrose to invert sugars. The heating process needs to be well controlled to minimise the formation of breakdown products such as hydroxymethyl furfural. Separation of invert sugars by ion exclusion is more efficient

than separation of sucrose only. Pilot plant ion exclusion studies showed a separation effectiveness comparable with that achieved on laboratory scale. The process was used to make a small quantity of material similar to high test molasses (HTM), which was successfully used to coat VHP sugar. Storage trials of this coated sugar showed no difference in keeping qualities compared with sugar coated with standard HTM. The economics of producing an invert syrup from cane final molasses look promising, provided the product finds market acceptance.

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