ENHANCEMENT OF SUGAR PRODUCTION PART 2: CHROMATOGRAPHIC SEPARATION OF SUGARCANE MOLASSES

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Abstract

The chromatographic separation of beet sugar molasses is a well known and well described process. In contrast, the chromatographic separation of cane molasses is not well established. The paper describes the separation efficiencies of a simulated moving bed (SMB) chromatography pilot plant utilising cane molasses obtained from the Komati Mill. Before separation, the molasses was prepared with the unique TSB Process. The recovery of sugars through the system was 98.4% at a product purity of 99.7%. Experiences and observations related to the chromatography pilot plant are discussed. The SMB system's performance is compared to the reported performance of batch systems.

Keywords: chromatography, ion exclusion, inverted cane molasses, simulated moving bed

Introduction

The simulated moving bed technology (SMB) was introduced in the late 1950s (Broughton, 1961). The introduction of large-scale chromatography in the sugar industry came in 1974 with a process developed by Finnsugar (now Cultor) to recover sugar from beet molasses by ion exclusion.

It is reported that more than 250 000 tonnes of sucrose remain in South African molasses annually (Davis *et al* 1997). The recovery of this and the valuable invert sugars in the molasses could lead to increased profitability of the cane sugar mill.

The chromatographic separation of fructose and glucose is standard practise in the production of high fructose corn syrup (HFCS) (Schenck, 2000). The separation of cane molasses holds significant challenges if compared to that of beet molasses. Cane molasses has a high suspended-solids content that has to be removed before the molasses can be separated on an ion exclusion system. Failure to produce a clean feed for the SMB will result in plugging interspatial and interstatial pathways of the resin. This fouling of the resin causes excessive pressure drop over the system, loss of productivity of the system and general failure of the separation characteristics of the resin.

The separation of molasses from the Komati Mill was tested on a SMB pilot plant supplied by Applexion. The first trials were done during July 1998, followed by trials in 1999, 2000 and 2001. The extent of the trials in 2001 is beyond the scope of this report.

Two objectives were pursued: optimising the sugars recovery and achieving a high purity extract. The performance of a continuous process was also evaluated against that of batch processes reported in literature (Davis *et al*., 1997; Bernhard *et al.,* 1999).

The SMB process

The current systems are all derived from the original UOP Sorbex process (Broughton, 1961). Advances in process control and fluid distribution has led to variations of the rotary valve assembly that was used in the Sorbex process.

Periodic switching of the inlet and outlet ports on one column in the direction of the liquid flow approximates the movement of the resin bed against the direction of the liquid flow. The system is subdivided by the position of the ports into four zones: zone 1, is where the fresh resin contacts the solution enriched with the fast component, resulting in a nearly solute free liquid at the zone outlet that is recirculated to zone 4; in zones 2 and 3 the feed is fractionated in its components and in zone 4 the retained or slower components are washed off the resin before it recycles into zone 1.

Successful operation of a chromatography plant relies on the 'critical value of separation' (Cv). This is the volume of eluent needed for elution of the component from the resin. Critical values are related to the affinity coefficient and can be calculated for the various components by the following relationship:

$$Cv = \varepsilon + (1 - \varepsilon) K$$

Where

ε = Void volume of the resin (approx. 0.38)

K = Affinity Coefficient of the resin or equilibrium coefficient

= (Concentration in resin) / (Concentration in solution)

The operating conditions for a plant is based on setting the various zone flows in relation to the critical value.

In a typical separation system, to achieve a sugar/non sugar split, the components and separation conditions can be summarised as in Table 1.

The resin used in the separation of molasses is a strong cation resin in the monovalent (K^+ or Na^+) form. The resin used in the HFCS industry to separate glucose and fructose is a resin in the Ca^{2+}-form. The design of a SMB requires that the flow rates and switch times be determined so that the desired component flows and purities are obtained at the various product ports.

Table 1. Performance of the various zones to achieve proper separation in a SMB.

	Zone 1	Zone 2	Zone 3	Zone 4
Sugars	Adsorbed	Adsorbed	Adsorbed	Eluted
Non Sugars	Adsorbed	Eluted	Eluted	Eluted
Separation Condition	$< Cv)_{Non\ Sugars}$	$< Cv)_{Sugars}$	$> Cv)_{Non\ Sugars}$	$> Cv)_{Sugars}$

This is an established economically viable process used extensively in the beet sugar industry (Sugar y Azucar, 1994).

There is little information available in literature on the separation characteristics of the resins and systems for the components in cane molasses. Peacock (1996) report on the separation of refinery molasses in a batch column. Davis *et al* (1997) reports on the ion exclusion of inverted molasses obtained using a batch column holding 172 ml of resin at the SMRI. Bernhardt *et al* (1999) described the use of the SMRI batch column in the production of an invert syrup from molasses.

Schneider (1978) mentions the differences in the composition of cane and beet molasses.

He mentions three reasons for the difficulty of handling cane molasses. The first is the high amount of calcium and magnesium in cane molasses. These have to be reduced to about 0.2% CaO on dry substance. The second is the high amount of colloids and suspended matter present in cane molasses. The third difficulty is the high concentration of reducing sugars and colour present in the molasses.

Thompson (1994) described a process to prepare molasses to use in an ion exclusion process. Davis *et al* (1997) also describe methods investigated at the SMRI to prepare molasses for separation in a chromatography unit.

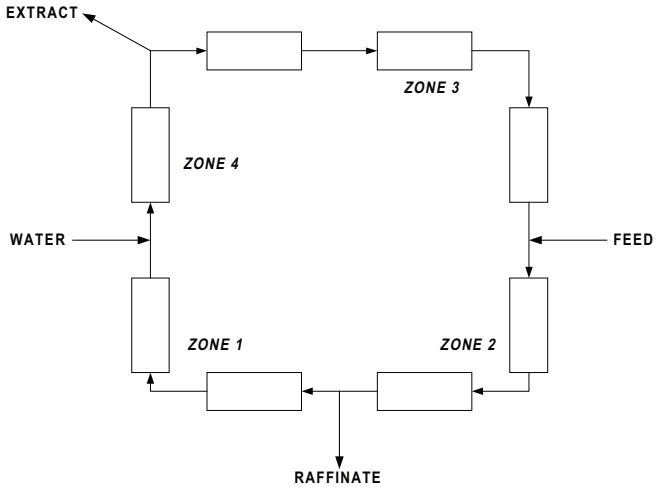

Figure 1. A schematic representation of an eight-column SMB system. Arrows indicates the direction of flow. Column arrangements may vary from process to process and are shown for illustration purposes only (adapted from Charton and Nicoud, 1995).

The pilot plant

Description

Applexion has extensive experience in the food and sweetener industry, which includes experience in the utilisation of SMB chromatography for the industrial separation of a variety of products, amongst others beet molasses.

The pilot plant supplied by Applexion has eight columns, holding 70 litres of resin each. The system is equipped with a control panel. By adjusting the programming of the PLC, the set-up and configuration of the columns in the various zones, as discussed above, can be controlled. The unit operates fully automatically and only needs operator input when a setpoint adjustment is required. A photograph of the plant is presented in Figure 2.

The unit is designed to separate 300 kg dry solids per day when operating at full capacity. The process streams entering the unit are the molasses feed and process water. Flow control loops are connected to both these streams. The flow control is regulated by adjusting the speed of a progressive cavity pump. The raffinate and extract streams leaving the unit are equipped with mass flow meters.

The flowrate, in the case of the extract line, is controlled by a globe valve. The raffinate line is used to control the backpressure over the unit. An electronic pressure transmitter sends the process variable to the controller. The raffinate line is also equipped with a Micro Motion mass flow meter. The unit also has a mass flow meter on the internal recycle loop.

Figure 2. A view of the Chromatography Pilot Plant as installed.

Table 2. The inorganic constituents of beet and cane molasses (Schneider, 1978).

	Beet	Equiv./kg	Cane	Equiv./kg
K /100 Bx	3.8	0.974	2.7	0.692
Na/100 Bx	0.7	0.304	0.3	0.130
Ca/100 Bx	0.15	0.054	1.1	0.393
Mg/100 Bx	0.05	0.041	0.4	0.333
Ca+Mg % Total Equiv.		6.9		46.8

The flowrate of the loop is controlled by a variable speed pump, similar to the water pump. The ability to monitor the density of the loop flow is very desirable because any leakage of sugar or salt will produce a rise in the density of the loop liquid. This serves as an early warning that the separation profile is changing in the system.

The separation parameters are set and are controlled by variations in the flowrates of the five process streams and the retention time of molasses in the columns. Figure 2 shows a view of the pilot plant, with the control panel in the foreground.

Ion exclusion resin

The resin used in the process is supplied by Applexion. Any of the major resin manufacturers like Rohm and Haas, Purolite or Bayer could provide a suitable resin. The resin is an ion exchange resin in the monovalent (Na^+/K^+) form. The functionality of the resin is important. If the same resin is used in the bivalent (Ca^{++}) form, a completely different separation is achieved because of the change in the resin beads. The pilot plant resin is similar to that used in the beet sugar industry to desugarise molasses. One of the most important characteristics of the bulk resin, setting it apart from other ion exchange resins, is the meticulous uniformity of the resin bead size. This is a very important parameter because it allows for equal pathlengths through the width and length of each column, thereby reducing short-circuiting that could negatively influence the separation efficiency.

Table 3. Characteristics of a typical chromatography resin.

Polymer Matrix Structure	Styrene-divinylbenzene
Functional Groups	Sulphonates
Physical Appearance	Spheres
Whole bead count	>98%
Max Operating Temperature	120°C
Bulk Density	Approx. 870 g/L
Mean size	300 – 340 µm
Uniformity Coefficient	<1.15

Part of the product specification for a typical chromatography resin is listed in Table 3 below.

During operation, the resin columns are kept warm by circulating hot process water through the jackets on the outside of the columns. The water temperature is maintained between 85°C and 95°C. Temperature affects the viscosity of the sugar solution and therefore the separation characteristics of the system. The molasses solution is kept hot in a tank with an internal coil. A small heat exchanger was later installed in the molasses feed line to ensure that the molasses entering the system is at the required temperature.

Analysis of feedstock and products

Component analysis of products and feedstock was done using an HPLC fitted with a Sarasep CAR-Ca column and a refractive index detector. The samples, sufficiently diluted, were pumped through the column at 0.5 ml/min and an oven temperature of 80°C was maintained. Brix was determined using an Atago HSR 500 refractometer. Absorbance, from which colour was calculated, was measured at 420 nm using a Helios Gamma UV/Visible Spectrophotometer. A Merck Turbidiquant 1500T was used in the determination of turbidity. For both absorbance and turbidity analysis, a solution of five Brix was prepared.

Preparation of feed molasses

Extensive research has been done in the recent past to develop a process suitable for producing a molasses meeting the requirements for use in an ion exclusion system. Thompson (1994), Davis *et. al.* (1997) and Bernhard *et al* (1999) are local researchers that published work describing this endeavour. The advantage of batch systems is the ease of backwashing the resin, should fouling occur. In an SMB, such luxury does not exist and the feed material consistently has to be of acceptable quality. Saska and Lancrenon (1994) determined that the pre-treatment process must produce a liquid with a turbidity of 10 NTU/Brix or less for use in a prolonged uninterrupted operation. TSB has been working on a process to produce a molasses capable of meeting this stringent requirement for a number of years. During the course of this project attention was given to a variety of potential treatment processes namely: filtration (Saska and Lancrenon, 1994), flotation, centrifugation, carbonitation, sulphitation and acidification (Davis *et al*., 1997 and Bernhard *et al.,* 1999 provide good references to these

methods in their articles). None of the methods reported in literature and investigated on the pilot plant in Komati could yield a product meeting the above requirement. The Product Development team at TSB had to develop a process to treat molasses to meet the requirement. The molasses used in the pilot SMB was prepared with the unique process developed by the Product Development Department of TSB (patent pending). This process involved the removal of the suspended solids and sludge in the molasses to make it suitable for use in packed beds and the inversion of all the residual sucrose in the molasses to glucose and fructose (invert sugars). The process has been tested during more than one crushing season, providing consistent results.

Results and discussion

Trials during 1998

Initial start-up of the separator was done using B-molasses. The molasses used was prepared with a process used in the early stages of the development of the TSB Process. These first trails were done to familiarise the operating crew with the pilot plant. The original setpoint was based on pulse tests and trials conducted in collaboration with Applexion on a laboratory scale separator.

Trials were then conducted on a C-molasses batch prepared with the same process as the B-molasses. The results are reported in Table 4.

The sucrose traces in the feed material also left the separator with the raffinate.

In order to optimise the separation of the unit, a setpoint adjustment was made to move the separation profile across the columns. This change increased the concentration of the extract and raffinate. The results follow in Table 5.

Table 4. TSB Pilot Plant Results – 1998.

	Original Setpoint
Component Recovery	
% Salt to Extract	0.05
% Salt to Raffinate	99.95
% Invert to Extract	89.12
% Invert to Raffinate	10.88
Extract Composition	
Brix	16.2
Invert fraction of Brix (%)	98.85
Salt fraction of Brix (%)	1.15
Raffinate Composition	
Brix	6.9
Salt fraction of Brix (%)	72.11
Invert fraction of Brix (%)	25.11
Feed (DS composition)	
Invert %	72.77
Salt %	21.25

Table 5. TSB Pilot Plant Results – 1998, attempting to optimise the separation.

Component Recovery	**Moving the Separation Profile**
% Salt to Extract	0.03
% Salt to Raffinate	99.97
% Invert to Extract	85.87
% Invert to Raffinate	19.33
Extract Composition	
Brix	19.5
Invert fraction of Brix (%)	99.11
Salt fraction of Brix (%)	0.53
Raffinate Composition	
Brix	10.00
Salt fraction of Brix (%)	52.58
Invert fraction of Brix (%)	33.22
Feed (DS composition)	
Invert %	72.27
Salt %	21.25

The sucrose traces in the feed molasses left the separator in the raffinate.

The data reported above was for a cycle where the unit had not reached equilibrium yet. The unit was run at half the rated productivity for this trial so that additional feed stock could be prepared.

Due to the low production rate, there was a severe loss in temperature in the interconnecting pipes. This increased the viscosity of the solution, resulting in high operating pressures in the system. Due to the installation of a downstream processing plant, the unit was stopped before the onset of equilibrium and no further work was done during 1998. High operating pressures caused a drop in productivity due to a loss in flow rate.

Investigation into the system also showed a thin layer of sludge deposited on top of the resin in the columns. This was a result of the inadequate pre-treatment method used at that time. The resin was removed from the columns to prevent the fouled resin from affecting the results of further trials.

Despite these problems, it is clear that the salt content in the extract also dropped, yielding a higher quality product. The invert sugar loss in the raffinate also increased as a trade-off. Economic analysis of the process would determine the feasibility of such a separation.

Table 6. Condensed Analysis of Molasses for Separations – 1999.

Salts	%DS	23.65
Total invert	%DS	73.79
Colour	ICUMSA	181,866
Turbidity	NTU/Brix	12.07

Trials during 1999

The pilot plant feed for the trials during 1999 was C-molasses prepared with an improved process. The average of the analyses on the feed product is reflected in Table 6 and the results are reported in Table 7.

Typical operating conditions on the pilot plant were:

Inlet temperature of water: 65 °C to 70 °C

Inlet temperature of molasses: 55 °C to 60 °C

Inlet pressure of water: 3.2 bar to 3.6 bar

Inlet pressure of molasses: 1.5 bar to 1.7 bar

Extract temperature: 50 °C to 60 °C

Raffinate temperature: 55 °C to 65 °C

The trials conducted in 1999 disproved the assumption made in 1998 that an adjustment is necessary to improve recovery and the sugar yield. The performance of the pilot plant matched that of the small test unit used in 1997 on C-molasses in Epone, France. The trials in 1999 were conducted at full production capacity of the pilot plant. No problems related to pressure drop were encountered. There also was no sludge layer on the resin, proving that the molasses clarification process was successful.

The effect of temperature was clearly demonstrated at one stage when the feed tank was drained to below the heating coils. The low temperature of the molasses led to a significant increase on the inlet pressure of both the water and the molasses. When hot molasses reached the resin after the level was restored the pressure of both pumps decreased to normal operating pressures. A similar effect was witnessed if the water temperature decreased.

The objectives, namely optimum sugars recovery and high purity were met during these trials. A recovery of 93.9% sugars at 99.7 % purity was reached. The water consumption ratio for the system was 6.084 kg water/kg Brix.

Trials during 2000

During 2000, the SMB was operated to produce extract for evaluation in other studies.

A few changes were made to trace the separation profile over the system. A column profile, for one cycle, was drawn to determine the separation profile and to investigate the trade-off between recovery, purity and water consumption.

A typical profile is presented in Figure 3. The profile in a SMB varies considerably from that obtained in a batch column as reported by Davis *et al.* (1997). This profile provides a snapshot of the separation occurring in the system at a given time. It provides information about the relative position of each component in the system. Analysis of the column data in relation to the various positions of feed inlets and product outlets provides an indication of the separation efficiency of the system. Adjustments to the setpoint of the system would alter the profile.

The results from the trials conducted in 2000 are presented in Table 8.

Table 7. TSB Pilot Plant Results during 1999. Investigation into the effect of modifying the separation profile across the system.

	Average values of the results obtained by adjusting setpoint the same as late 1998	Average values of the results obtained by maintaining the original specification
Component Recovery		
% Salt to Extract	3.2	1.0
% Salt to Raffinate	96.8	99.0
% Invert to Extract	91.5	93.9
% Invert to Raffinate	8.5	6.1
Extract Composition		
Brix	24.7	28.7
Invert fraction of Brix (%)	97.8	99.7
Salt fraction of Brix (%)	0.7	0.2
Raffinate Composition		
Brix	10.7	10.0
Salt fraction of Brix (%)	68.9	71.0
Invert fraction of Brix (%)	19.0	17.6

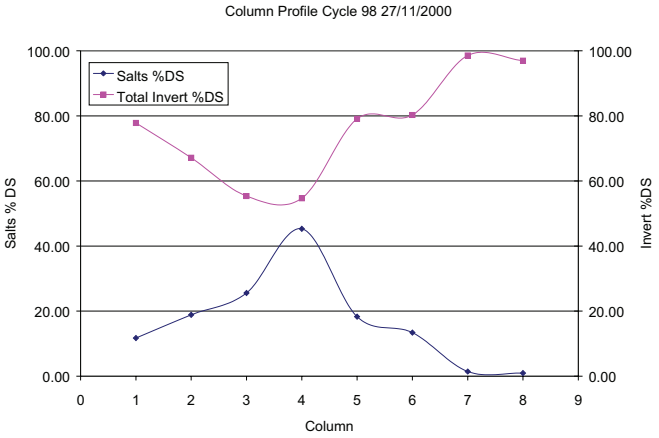

Figure 3. The composition profile during a single step through the eight-column SMB system used for the trials.

The water consumption during these trials was 6.799-kg water/kg Brix. Recovery of invert was 98.37% at a purity of 99.7%. This was a better recovery than that of 1999, at the expense of an increase in water consumption. The economic trade-off of the higher water consumption should be balanced against the higher yield of sugars for a commercial plant.

The molasses used during these trials was prepared using an optimised pre-treatment process. Lagging was installed on the interconnecting piping to prevent unnecessary temperature loss and the feed molasses was piped through a coiled heat exchanger prior to entering the unit. No pressure effects were witnessed at any productivity level of the unit.

Table 8. TSB Pilot Plant Results – 2000 with optimised setpoints.

	Condensed Results 2000
Component Recovery	
% Salt to Extract	0.73
% Salt to Raffinate	99.27
% Invert to Extract	98.37
% Invert to Raffinate	1.63
Extract Composition	
Brix	24.8
Invert fraction of Brix (%)	99.76
Salt fraction of Brix (%)	0.16
Raffinate Composition	
Brix	9.80
Salt fraction of Brix (%)	62.42
Invert fraction of Brix (%)	4.06
Feed (DS composition)	
Invert %	72.21
Salt %	16.24

SMB vs. Batch - Comparative Results

Table 9 lists the results obtained on the Komati SMB with that reported by Davis *et al.* (1997) for their laboratory column holding 172 ml of Purolite PCR642 resin. The batch column was operated at 60°C, similar to the Komati SMB.

Comparing SMB data with that obtained by Bernhard *et al.* (1999) on the 200 litre SMRI batch pilot plant column, in Table 10, provides a similar result.

From these results, it is obvious that the SMB method provides a significant advantage over the batch separation columns. Batch columns could provide the resolution and affinity coefficients necessary to determine the operating parameters for a SMB system.

The energy requirement, should the extract be concentrated, is much less for a SMB system than for a batch column. The potential of colour formation in the evaporator is also reduced due to less residence time required to achieve the target concentration.

Conclusion

Inverted cane molasses can successfully be desugarised on a SMB ion exclusion plant with a sugars recovery of 98.37% and an extract purity of 99.7%. Lower water consumption resulted in a 93.9% recovery for the same purity.

Care must be taken not to foul the resin with suspended solids or foreign materials, emphasising the need for a suitable pre-treatment process. The determination of the column profile should occasionally be done to evaluate the separation performance of the system.

The separation obtained using a continuous process is better than that obtained at the SMRI on a batch column and provides the designer with typical operating data that could be obtained from a commercial installation. Using these results in a feasibility study could significantly alter the economic viability of the project.

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Table 9. Comparison between SMRI Laboratory and TSB Pilot Plant Results.

Starting Molasses		Invert Fraction / Extract		
Treatment	Brix	Recovery (%)	Ash (% on Dry Substance)	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
TSB Process	70	98.37	0.16	24.8

Data obtained from page 151, Table 5. Inverted fraction recovery from inverted molasses.

Table 10. Comparison between Batch and SMB Extract Samples.

	Batch	**SMB**
Dry Solids (%)	3	24.8
Total sugars as invert (% of dry solids)	52	99.76
Ash (% of Dry Solids)	4.9	0.16
Colour (ICUMSA)	128000	32103
pH	2.4	4.76

Data obtained from page 238, Table 3. Composition of the samples produced.

REFERENCES

Bernhardt, HW, Davis, SB, Peacock, SD and Walford, SN (1999). Review of the Process Developed at the SMRI to make Invert Sugar from Cane Molasses by Chromatographic Separation. *Proc S Afr Sugar Technol Ass* 73: 235-240.

Broughton, DB (1961). *US Patent 2,985,589*

Charton, F and Nicoud, RM (1995). Complete Design of a Simulated Moving Bed, *Jnl of Chromatogr A*, 702: 97-112.

Davis, SB, Peacock, SD and Walford, SN (1997). Ion Exclusion Chromatography: Molasses Pretreatment and High Test Molasses Production, *Proc S Afr Sugar Technol Ass* 71: 146-152.

Peacock, SD (1996). Ion Exclusion Desugarisation of Refinery Jet 4, *Proc S Afr Sugar Technol Ass* 70: 171-176.

Saska, M and Lancrenon, X (1994). Applications of Continuous Chromatographic Separation in the Sugar Industry. III. Desugarization of Cane Molasses, *Int Sugar J* 96: 403-410.

Schenck, FW (2000). High Fructose Syrups – a review, *Int Sugar J* 102: 285-288.

Schneider, HG (1978). Ion Exclusion in Cane Sugar Refining, *SIT Paper 415*, Thirty Seventh Annual Meeting.

Sugar y Azucar Special Report (1994). Ion Exclusion Technology and Beet Molasses Desugaring in the United States, *Sugar y Azucar*, February: 16-38.

Thompson, MC (1994). The potential applications of ion exclusion chromatography for the additional sucrose recovery from molasses, *Proc S Afr Sugar Technol Ass* 68: 105-108