ION EXCLUSION DESUGARISATION OF REFINERY JET 4

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Abstract

Ion exclusion is a chromatographic process which separates components from an impure feedstock on the basis of molecular size and charge. A pilot plant ion exclusion separator was constructed to determine the technical and economic feasibility of recovering sugar from refinery jet 4 (the feedstock identified as most promising in terms of ease of treatment). Extensive tests on jet 4 from the Malelane refinery (a carbonatation-sulphitation refinery) have demonstrated the technical feasibility of the process. Sugar boiling trials on the sucrose fraction recovered from the ion exclusion pilot plant have shown considerable improvements in crystal morphology, recoverable sucrose and crystal colour. The effects of the pilot plant operating conditions on the quantity and quality of sugar recovered are discussed.

Keywords: Ion exclusion, chromatography, desugarisation, pilot plant, jet 4

Introduction

Ion exclusion chromatography is a process which separates components from an impure feedstock on the basis of molecular size and charge. The ion exclusion process has been applied to the recovery of sucrose from final beet molasses for more than twenty years (Hongisto, 1977; Schneider, 1978), and has more recently been applied to cane molasses. A pilot plant ion exclusion separator was constructed in order to determine the feasibility of recovering sucrose from South African molasses and other low-purity feedstocks. Refinery jet 4 was identified as the most promising feedstock for study, in terms of ease of treatment, and extensive tests were conducted in order to demonstrate the technical feasibility of the process and to determine the effect of the pilot plant operating conditions on the quantity and quality of sugar recovered.

Ion exclusion pilot plant

The pilot plant chromatographic separator consists of a jacketed stainless steel column of inner diameter 250 mm and height 4 m. Within the column is a packing of 200 litres of strong cation ion exchange resin in the sodium form (Purolite PCR 642). While this resin is similar to ion exchange resins used for water softening, no significant ion exchange actually occurs during ion exclusion. The top of the resin column is equipped with a sight-glass to facilitate inspection of the height of the resin bed. The piping to the column is arranged to allow alternate feeding of either jet 4 feedstock, recycled fractions from the column or elution water (see Figure 1). Provision has also been made for backwash flow through the column, to remove trapped air from the top of the column during startings. During operation, a side-stream of column effluent is withdrawn and passed through a conductivity cell and refractive index (RI) detector. This facilitates peak detection and provides the input signal for automatic control of the column. Elution water to the separator is automatically maintained at the column operating temperature in a steam-heated drum.

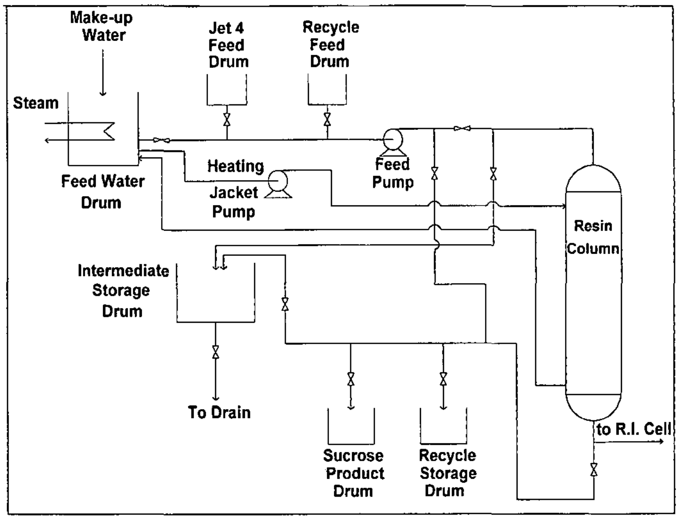

FIGURE 1: The pilot plant chromatographic separator.

The pilot plant column operates as a batch separator. Before injection of the feed sample to be separated, the resin column is fed with hot elution water at a fixed rate. To start the separation, an amount of feed jet is injected onto the top of the column. This is performed by switching valves to feed the column from the jet 4 feed drum as opposed to the elution water drum. When the required quantity of jet has been introduced, hot elution water is once more fed to the top of the column in order to push the feed sample through the resin bed. During their passage through the resin bed, the various chemical components of the jet diffuse into the many microscopic passages within the resin beads. Smaller component molecules in the jet can penetrate more deeply into the beads, and into a larger number of passages, than larger molecules. As time spent within the resin beads is not utilised in moving with the bulk fluid, components are held back in their movement through the column by their diffusion into (and out of) the beads. The degree of retardation of the molecules is dependent on their size, the smaller molecules spending a greater length of time within the beads, and thus suffering greater retardation than the larger molecules. Some molecules within the jet are too large to penetrate the pores of the resin beads, and do not suffer any retardation. These molecules elute from the column with the bulk fluid. Charged molecules (such as the inorganic ash constituents of the jet) are excluded from the resin beads by electrostatic forces, and consequently also elute from the column with the bulk fluid. Thus, separation of components in the jet 4 takes place within the column based on the "affinity" of each component for the resin packing within the bed.

At the column outlet, the elution of the components of the feed jet can be detected by the conductivity cell and RI detector. A typical elution profile (as measured by the RI detector) for jet 4 from the Malelane refinery is shown in Figure 2. Three distinct peaks may be observed. The first contains the components which are least retained (retarded) by the resin beads. These include the high molecular weight components and those which are excluded from the resin on the basis of size (such as the highly coloured compounds and the polysaccharides) or charge (such as the ash components). The second peak is the sucrose fraction. As sucrose is the most prevalent compound in the jet, this peak is the largest. The third and final visible peak in Figure 2 is the monosaccharide peak, containing fructose and glucose. These components, being the smallest non-charged molecules in the feed, have the highest affinity for the resin beads and are thus retained the longest within the column. Not visible as a distinct peak on the elution profile (due to its low concentration) is the oligosaccharide peak. Owing to their intermediate size, these molecules are eluted between the sucrose and polysaccharide peaks.

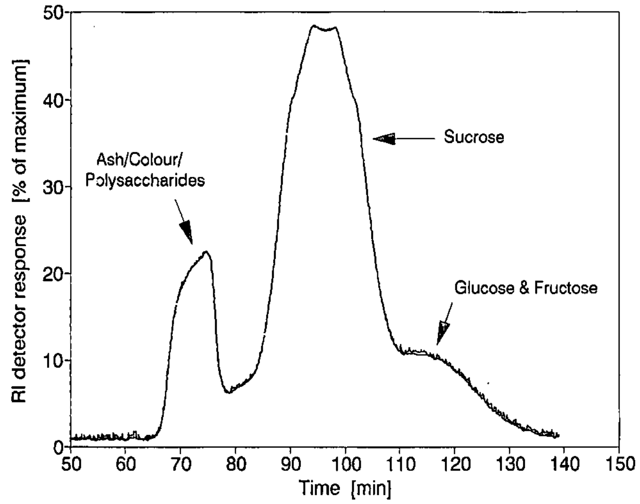

FIGURE 2: A typical jet 4 elution profile.

By observation of the elution profile during operation of the pilot plant, the various fractions emerging from the column may be diverted, by a series of valves, into separate product tanks. The sucrose product fraction may be further processed to recover crystalline sugar, the monosaccharide fraction may be processed to produce a saleable invert syrup, and the excluded ash/colour/polysaccharide fraction may be used as a feedstock for fertiliser production, due to its high potassium ion content. It should be noted that, due to the nature of the ion exclusion process (ie elution of a relatively small quantity of feed with large quantities of water), the product fractions eluted from the bottom of the column are more dilute than the original feed.

While the mechanism of ion exclusion is completely independent of ion exchange, a limited amount of ion exchange does occur during the process. Divalent cations in the feed, notably Ca^{2+} and Mg^{2+}, replace the sodium ions in the resin. The large size of these cations, as compared to the size of the sodium ion, results in a decrease in the sizes of the pores within the resin beads. This effect decreases the efficacy of the resin in separating components by ion exclusion. Thus, in order to maintain the efficiency of separation, it is necessary to pretreat the feed to the ion exclusion pilot plant for the removal of divalent cations. This is achieved by sulphitation, producing an insoluble precipitate of calcium and magnesium compounds which is removed by defecation and filtration. The low concentrations of divalent cations still remaining in the feed result in a slow decline in the column efficiency, requiring periodic regeneration of the resin beads with a brine rich in monovalent cations. The excluded ash/colour/polysaccharide fraction obtained from the column during ion exclusion separation may be utilised for this purpose, due to its high potassium ion concentration.

Technical feasibility

Experimental design

The governing criterion for the technical feasibility of the ion exclusion process is the ability to recover a greater quantity of higher quality sugar from the separated sucrose product fraction than would have been possible from the original, untreated jet 4 feedstock. On the basis of laboratory scale tests (Thompson, personal communication) and the results obtained from earlier experiments on the pilot plant, an experiment was designed to test the technical feasibility of the ion exclusion process, using this criterion. It was planned to produce sufficient sucrose product fraction for pilot pan crystallisation at the SMRI. The results of this test would then be compared to the results of a similar test crystallisation performed on the untreated jet 4 feedstock.

A computer program was developed in order to facilitate analysis of the pilot plant performance. Analytical data regarding the elution profiles obtained during earlier experimentation were manipulated by the program to develop a full description of the system performance under the conditions used for the tests. This allowed the computer to predict the composition of any product fraction from the column, given details of the "cut" to be made (ie the times of opening and closing of the valve to the product tank in question). The ability to predict such information is critical to any economic evaluation of the ion exclusion process.

The set of operating conditions chosen for the experiment was that for which the most reliable analytical data were available from previous experimentation (see Table 1). It was decided to recover 90% of the sucrose in the original jet 4 to the sucrose product fraction.

Table 1
Experimental operating conditions

Column temperature	80°C
Elution water flowrate	60 kg/h
Loading of jet 4	1 kg per batch

With the aid of the computer program, it was predicted that the sucrose product fraction thus obtained would contain 26% of the original oligosaccharide content and 5% of the original monosaccharide content of the feedstock. The predicted component concentrations in the product fraction (given a typical Malelane jet 4 feedstock as shown) are displayed in Table 2. Upon comparison with oligosaccharide concentrations previously measured in refinery products by the SMRI, the predicted oligosaccharide content of the sucrose product fraction was found to be similar to that normally encountered in jet 1 (Morel du Boil and Walford, 1995).

Table 2
Predicted component concentrations in the sucrose product fraction

	Feed jet 4	Product
Brix [°]	64,72	2,95
Purity [%]	≈ 90	98,82
Monosaccharides [%]	≈2	0,24
Oligosaccharides [ppm]	8895	2312

Experimental method

Under the conditions described in Table 1 above, 36 batches of jet were required to produce sufficient product fraction for a pilot pan boiling. The time taken for each batch to elute from the column was approximately 140 minutes. The ion exclusion separation of these batches .produced 517 kg of dilute sucrose product fraction (at 2,9° brix), which was concentrated to 55° brix in the SMRI pilot evaporator. During processing, the dilute product fraction was preserved by freezing, or by the addition of formaldehyde and subsequent chilling. The excluded and monosaccharide fractions were discarded. The concentrated product fraction was boiled in the SMRI pilot pan under the conditions normally used for jet 4 boiling. For the purposes of comparison, a sample of untreated jet 4 feed was boiled in the pilot pan under identical conditions.

Results and discussion

Samples of the feed, massecuite, sugar and molasses from each of the boilings were collected and analysed, yielding the results listed in Table 3. Potassium ion content, conductivity ash, glucose, fructose and oligosaccharide concentrations are all reported on brix.

Table 3
Results of the comparative boiling tests

	Feed to pan		Massecuite		Sugar		Molasses	
	Raw Jet 4	Product fraction	Raw Jet 4	Product fraction	Raw Jet 4	Product fraction	Raw Jet 4	Product fraction
Brix [°]	58,15	57,35	89,85	88,90			83,05	78,25
Purity [%]	91,96	97,89	91,38	97,69			83,07	95,60
Pol [°Z]	53,48	56,14	82,10	86,85			68,99	74,81
Colour [ICUMSA]	11360	1418	12266	1729	122	41	19744	3641
Potassium [ppm]	5021	349	2315	90	9,8	0,5	7225	204
Conductivity ash [%]	1,45	0,42	2,25	0,67	0,013	0,007	3,88	1,20
Glucose [%]	1,22	0,45						
Fructose [%]	1,07	0,38						
Oligosaccharides [ppm]	3701	968						
Scaled oligosaccharides [ppm]	8895	2326						

The benefits of the ion exclusion process are immediately apparent. With 90% recovery of sucrose from the feed, a decolourisation of 88% was achieved in the product fraction fed to the pilot pan, resulting in 66% less colour in the crystalline sugar. The reductions in conductivity ash achieved were 71% for the pan feed and 46% for the affinated sugar. The sucrose product fraction fed to the pan contained 64% less oligosaccharides and 74% less monosaccharides than were present in the original jet 4. For this particular test, the feed jet to the ion exclusion process contained a lower concentration of oligosaccharides than had been previously measured in jet 4 from Malelane. This was not thought to be unusual, given the high degree of inherent variability in the jet. In order to facilitate comparison between the results of this test and the predicted results discussed above (the latter being based upon the earlier oligosaccharide measurements), the oligosaccharide levels in this test were scaled by the ratio of the normal oligosaccharide concentration to the actual feed oligosaccharide concentration, thus making the feed concentration equivalent to that previously measured in jet 4 from Malelane (see the last row of Table 3). This gave a resulting oligosaccharide concentration in the product fraction of 2326 ppm on brix. As predicted, this value was found to be similar to that previously measured in refinery jet 1. Table 4 shows the results obtained in this test as compared to those predicted by the computer program. From this comparison, it is evident that the computer program can predict the performance of the ion exclusion pilot plant with a reasonably high degree of accuracy. The unexpectedly high monosaccharide levels observed in the *actual* figures may be attributed to the occurrence of inversion in the product fraction during evaporative concentration and storage.

Table 4
Comparison of actual and predicted results

	Predicted	Actual
Brix of dilute product [°Brix]	2,95	2,86
Purity [%]	98,82	97,89
Monosaccharide level [% on brix]	0,24	0,83
Oligosaccharide level [ppm on brix]	2312	2326

Crystal size distribution analyses were performed on the sugars crystallised from the untreated jet 4 and the sucrose product fraction (see Figures 3 and 4). The effect of the decreased oligosaccharide concentration in the product fraction is immediately apparent, with less crystal elongation being observed. The measured elongation ratios were 2,3 for the untreated jet 4 sample and 1,4 for the sucrose product fraction.

Assuming, as a rough approximation, a 50% recovery of sugar from each refinery boiling, a diversion of 90% of the sucrose in jet 4 back to jet 1 (by application of the ion exclusion process) would result in the recovery of more than 78% of the original sucrose in the jet 4 as sugar *"in the bag"*. Additional benefits to processing would also accrue as a result of the reductions in ash and colour achieved. Furthermore, a saleable monosaccharide syrup fraction may be produced as a by-product of the ion exclusion process.

It is important to note that the operating conditions used in the above experiment were chosen, on the basis of reliability of previous experimental data, to demonstrate the technical feasibility of the ion exclusion process. It is highly improbable that these conditions would be those chosen as economi cally optimum for the operation of a full scale plant, and thus no undue importance should be placed on the absolute numerical values of the system parameters.

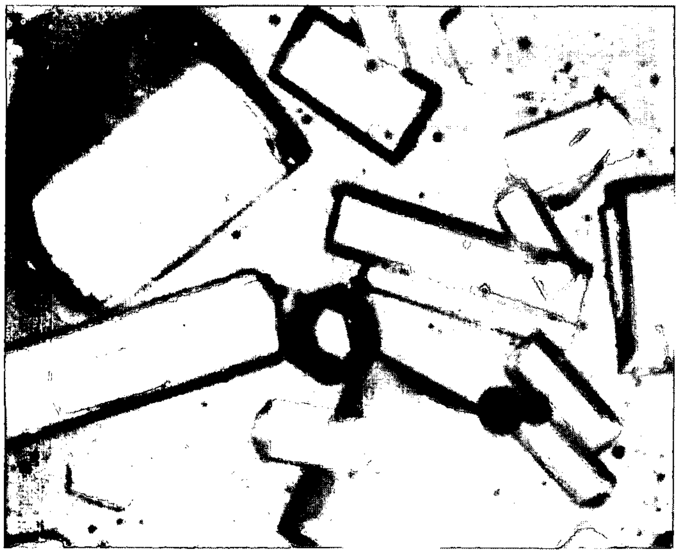

FIGURE 3: Crystals grown from untreated jet 4.

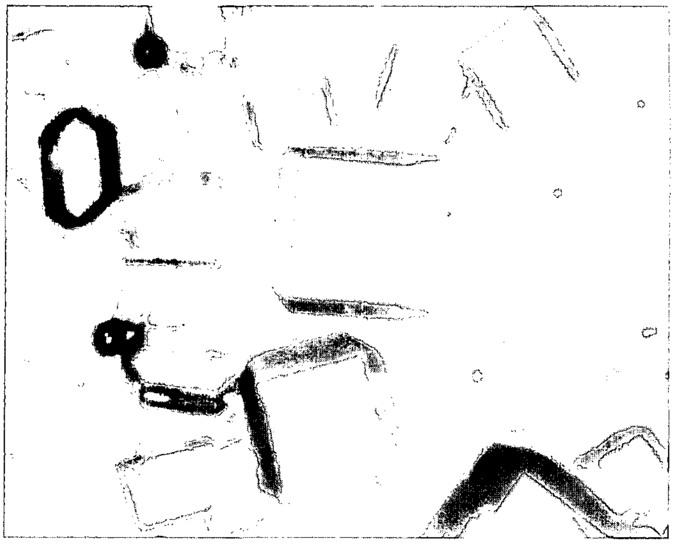

FIGURE 4: Crystals grown from the sucrose product fraction.

Analysis of operating conditions

Experimental method

Knowledge of the variation of the quantity and quality of the sucrose product fraction with changes in operating conditions is of vital importance to any economic feasibility study of the ion exclusion process. An experiment was thus designed to determine the effect of changing operating conditions on the performance of the ion exclusion pilot plant.

Six tests were performed on the pilot plant, with two key operating parameters being varied during the experimentation:

- elution water flow rate to the top of the column: (1, 2, 3 and 4 litres per minute)
- mass loading of feed per separation: (1 and 2 kg per batch)

The precise operating conditions used for each test are shown in Table 5.

Table 5
Operating conditions for experimentation

Run number	Temperature [°C]	Elution water flow rate [l/min]	Mass loading of feed [kg]
1	80,4	0,94	1,0
2	80,0	2,33	1,0
3	80,0	2,84	1,0
4	80,0	4,23	1,0
5	80,1	1,51	2,0
6	80,1	2,26	2,0

Before the commencement of each test, the column was heated to 80°C and flushed with large quantities of hot water. To begin the separation, a weighed batch of jet 4 was fed to the top of the column. Immediately after introduction of the feed batch, the automatic data logger and a stopwatch were simultaneously started. In order to minimise the number of samples to be analysed, the collection of effluent samples from the column was only commenced once the top of the ash/colour/polysaccharide peak was observed on the RI detector. Sample collection was continued until most of the monosaccharide peak had eluted from the column. This technique ensured that the entire sucrose peak was collected during each test. Samples were collected in one litre plastic bottles, with typically 60 to 80 samples being collected per test. The time of collection of each sample was noted, thereby facilitating the exact determination of the volumetric flow rate of the elution water through the column. The samples from the column were frozen and analysed for sucrose, glucose, fructose and oligosaccharide concentrations by high performance liquid chromatography. Every third sample was analysed for brix, colour, and sulphated ash.

The analytical results of the experimentation were evaluated with the assistance of the computer program discussed earlier. The computer program was used to determine the composition of the theoretical sucrose product fraction that would be obtained, given sucrose recoveries of 50, 60, 70, 80, 90 and 95% of the original sucrose in the feed jet to the product fraction. For the purposes of the results described here, the sucrose product fraction to be collected was that which centred around the middle of the sucrose peak eluting from the column.

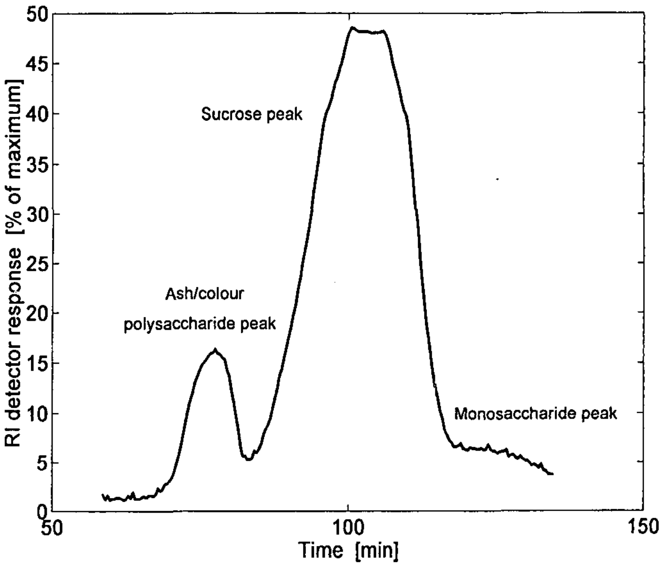

FIGURE 5: Elution profile at low flow rate.

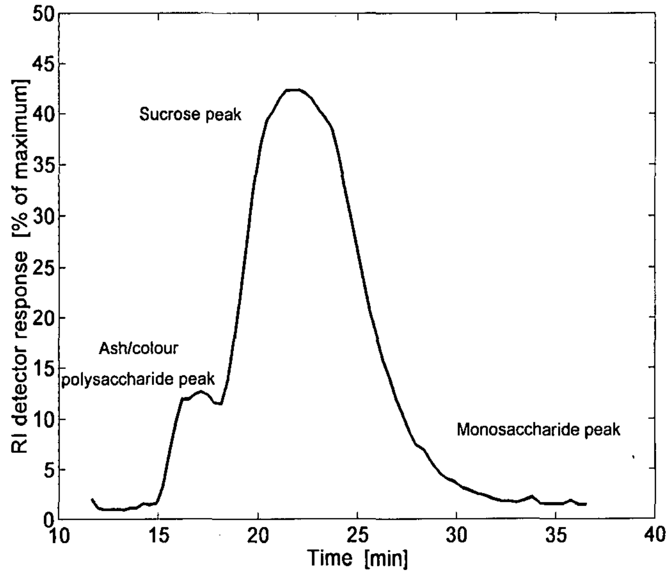

FIGURE 6: Elution profile at higher flow rate.

Results and discussion

It is well known that an increase in elution water flow rate or an increase in column loading (mass of feed per batch) results in poorer resolution of the components to be separated by the ion exclusion process. This effect can be observed in Figures 5 and 6. Figure 5 shows an elution profile for 1 kg of jet 4 at a flow rate of 0,94 l/min, while Figure 6 shows a similar profile for a flow rate of 4,23 l/min. The difference in resolution is immediately apparent, with a poorer degree of separation being observed on the elution profile for the higher flow rate.

The results of the evaluation of the ion exclusion process by the computer program are displayed in Figures 7 to 12, with the numerical labels on the curves referring to the test number (see Table 5 for the conditions of each test). The following observations may be noted:

- Ion Exclusion Desugarisation of Refinery Jet 4. The brix of the product fraction decreases with increasing sucrose recovery (see Figure 7). This is due to the inclusion of greater quantities of low-brix, non-sucrose components in the sucrose product fraction at higher recoveries. The product fraction brix increases with increasing column loading, due to the greater quantity of material eluting from the column at higher loadings. It can be seen that a doubling of the loading of feed per batch results in an approximate doubling of the brix of the product fraction.
- Ion Exclusion Desugarisation of Refinery Jet 4. The sucrose purity of the product fraction decreases with increasing recovery, as more impurities are included in the product fraction at higher recoveries (see Figure 8).
- The oligosaccharide concentration of the sucrose product fraction increases with increasing sucrose recovery (see Figure 9). This observation is also true of the monosaccharide concentration (Figure 10), ash content (Figure 11) and colour (Figure 12) of the product fraction. This phenomenon is a result of the inclusion of more of the impurities from the feed jet into the sucrose product fraction at higher recoveries. It should also be noted that the concentrations of oligosaccharides, monosaccharides and colour in the product fraction increase with elution water flow rate and column loading, due to the decrease in separation efficiency which is encountered under conditions of higher flow rates and column loadings. The ash concentration of the product fraction (on brix) decreases with column loading.

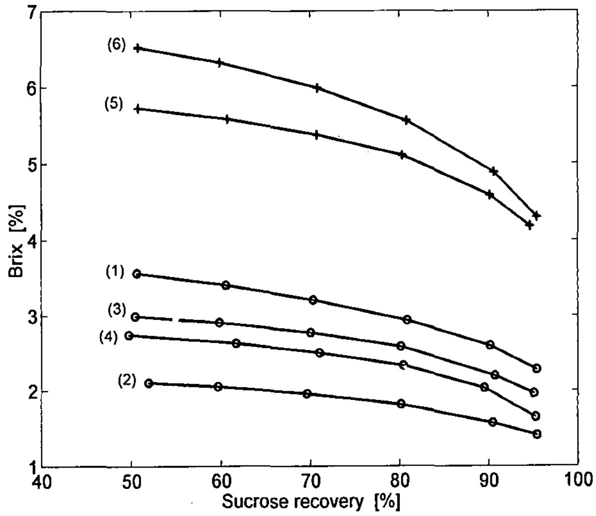

FIGURE 7: Product fraction brix as a function of operating conditions.

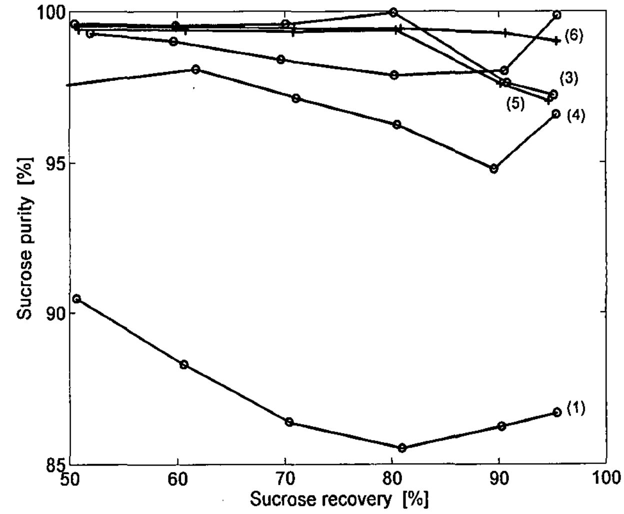

FIGURE 8: Product fraction purity as a function of operating conditions.

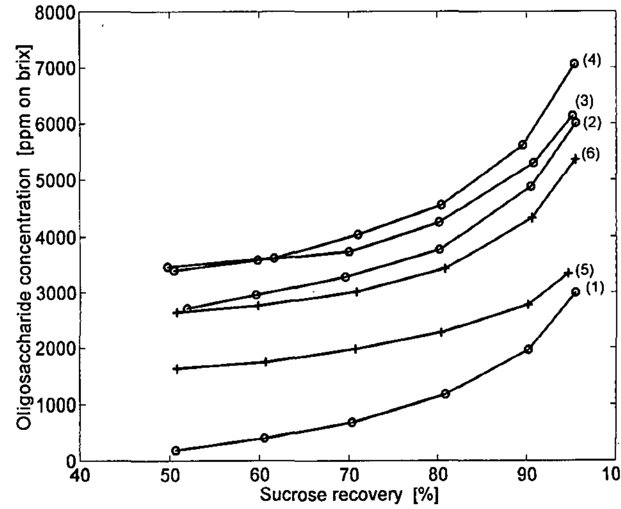

FIGURE 9: Oligosaccharide content of product fraction as a function of operating conditions.

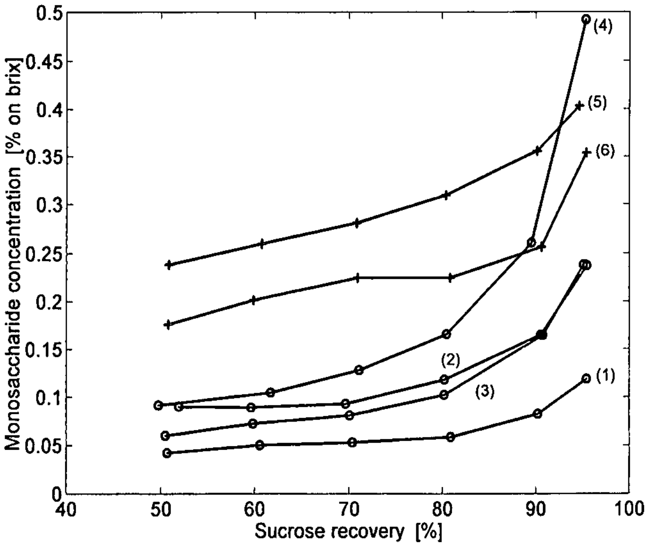

FIGURE 10: Monosaccharide content of product fraction as a function of operating conditions.

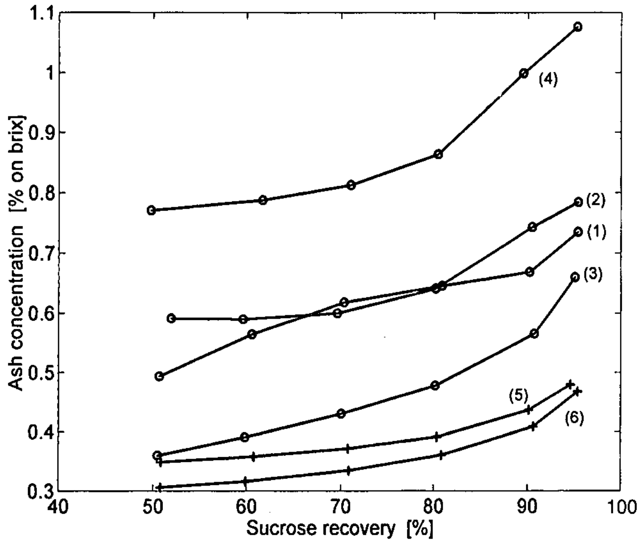

FIGURE 11: Ash content of product fraction as a function of operating conditions.

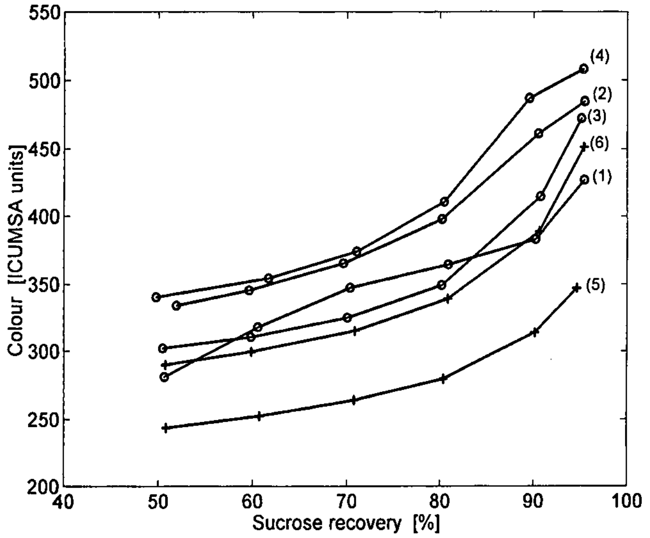

FIGURE 12: Colour of product fraction as a function of operating conditions.

Conclusions

Extensive tests were performed in order to evaluate the technical feasibility of the ion exclusion process for the desugarisation of refinery jet 4. The effects of the pilot plant operating conditions on the quantity and quality of sugar recovered by ion exclusion were examined. It was found that the ion exclusion process was technically feasible on a pilot plant scale. Sugar boiling trials on the product fraction recovered from the ion exclusion pilot plant separator showed considerable improvements in crystal morphology, recoverable sucrose and crystal colour. It was found that the brix of the sucrose product fraction obtained by ion exclusion decreased with increasing sucrose recovery, but increased with column loading. It was also found that the sucrose purity of the product fraction decreased with increasing recovery, as more of the impurities from the feed jet were found to be included in the product fraction at higher recoveries. Impurity concentrations within the product fraction were found to increase with sucrose recovery, column loading and elution water flow rate (with the exception of ash concentration, which was found to decrease with column loading). It would be necessary to take all of these factors into consideration in the design of a full scale ion exclusion plant, trading the advantages of higher recoveries, brixes and throughputs against the disadvantages of increased impurity concentrations in the sucrose product fraction, to determine the optimum operating conditions for the system.

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