

AN INVESTIGATION INTO THE USE OF ION-EXCHANGE RESINS FOR DECOLORISING CARBONATED BROWN LIQUOR IN A SUGAR REFINERY

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Abstract

Tests carried out on three ion-exchange resins for decolorising refinery brown liquor have shown that the process is economically justifiable under local conditions. To optimise resin life, it is important that brown liquor colour values do not exceed 850 ICUMSA colour units for a single bed system, otherwise a two bed system would be required.

Introduction

The use of ion-exchange resins is well known throughout the sugar industry for a number of different processes,^{3, 6} but the most widely utilised function is that of decolorising concentrated sugar solutions to produce very high quality liquid sugars. Since ion-exchange resins are prone to fouling by organic matter even at low concentrations, it has not been possible, until recently, to replace char with resins as a primary decolorising agent in the refinery. Furthermore, resins were not very robust mechanically and pressure drops across the beds had to be limited for this reason. There have been, however, considerable advances made in resins in the last few years, particularly in the realm of macroporous, macroreticular resins. A recent survey of patent literature has also indicated that further advances, which have not yet found application on an industrial scale, have been made in this field.

Decolorisation of sugar liquor after bone char, as a gross decoloriser, by ion-exchange is well documented.⁵ A description of the use of Permutit FS-IP resin as a gross decoloriser is given by Cunneen & Hawkins.¹ In this case three ion-exchange beds in series were used to decolorise carbonated liquor with resin being moved countercurrently to liquor flow at periodic intervals, i.e. when performance was unacceptable the last bed was renewed and moved to the second last position, etc.

A full scale ion-exchange plant using Rohm & Haas SDC 301 resin⁴ has been installed to decolorise considerable tonnage per day of white sugar equivalent using a flow rate of 3 bed volumes per hour on a single pass (75-80% decolorisation).

In view of the preceding and particularly in the light of recent fuel oil price increases, it was felt that ion-exchange might well be capable of replacing the char process completely under local conditions. This depends entirely on the comparative costs and an attempt was made to calculate these. For this purpose a twin stream pilot plant was constructed to test the performance of two resins in parallel, in order to ensure that both resins were tested under identical conditions. This was necessary since the carbonated brown liquor input varies continuously both in colour and ash level. The resins were run through a number of cycles and their relative performance measured.

Plant description

The flow diagram for one of the two parallel flows is shown in Fig. 1. This enabled the following six essential steps to be carried out every cycle.

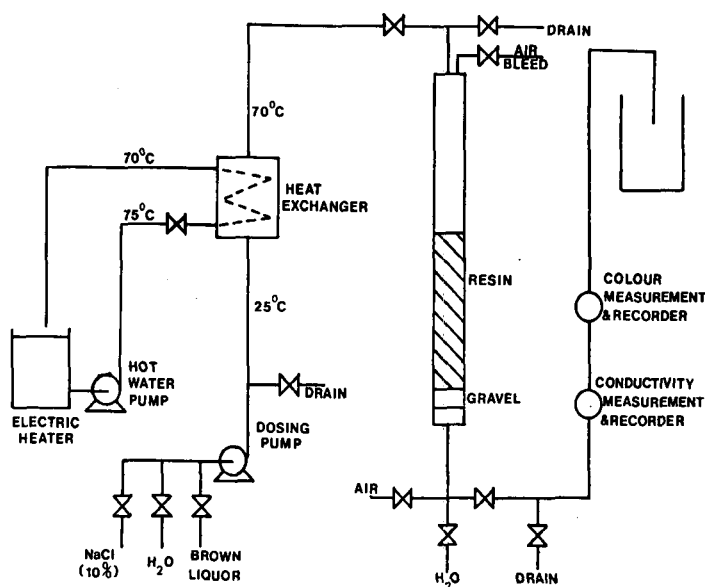


FIGURE 1 Simplified pilot plant flowsheet.

- (i) *Sweeten on* — brown liquor heated to 70°C is pumped through the system displacing water. The beginning of the cycle is judged according to the brix of the liquid leaving the column.
- (ii) *Normal decolorising run* — brown liquor is metered through the column at a pre-determined flow rate (2 bed vol/hr) for a specified length of time (48 hrs). Samples of brown liquor and fine liquor are taken for accurate laboratory analysis. Continuous measurement of colour and conductivity is recorded during the run to give an approximate idea of the profile.
- (iii) *Sweeten off* — at the end of the cycle water is passed through the column to displace sucrose to a pre-determined level.
- (iv) *Back wash* — the resin is backwashed with water to break up the bed and separate particles, and also to remove fines resulting from resin degradation which otherwise is the cause of increased pressure drop.
- (v) *Regenerate* — NaCl (10%) is metered through the resin in a pre-determined volume (determined by manufacturers recommended regeneration quantities).
- (vi) *Rinse* — the resin is rinsed to remove the remaining chloride ions.

The important parameters are:

Resin volume	51
Flowrate	2 BV/hr
Temperature	70-75°C
Cycle length	96 BV
Regenerant	10% NaCl (240 kg NaCl/m ³ resin)
Regenerant temp.	70°C

Since flowrates used are low, the whole apparatus after the heat exchanger has to be thermostatically heated to prevent any decrease in temperature. Brown liquor is metered through the column by a stainless steel dosing pump, with an adjustable stroke, enabling flowrates to be controlled exactly, independently of viscosity changes.

Experimental and results

The two columns were charged initially with Rohm & Haas SDC 301 resin and Permutit FS-IP resin respectively. The intention was to run the pilot plant on a continuous basis, to ascertain the life of the resin and the drop in performance due to irreversible fouling of the resin by colour bodies.

Three 48 hour runs were carried out each week (apart from when mechanical problems intervened). This gave a cycle length of 96 BV which was the maximum feasible length obtainable as a result of the time constraint.

A sample of brown liquor was taken at the beginning of the run and three samples of decolorised liquor during the run (this was later reduced to two). An accurate analysis of colour and conductivity (ICUMSA methods) were carried out.

Results for typical cycles are shown in Tables 1, 2 and 3.

TABLE 1
Rohm & Haas SDC 301 Resin

Cycle No.	BV	pH	Cond. Ash %	Colour
9	Brown liquor	7,3	0,19	840
	16	7,4	0,18	160
	48	7,2	0,19	230
	96	7,2	0,20	300
22	Brown liquor	8,7	0,38	1 220
	48	8,2	0,27	280
	86	8,4	0,38	480
23	Brown liquor	8,5	0,40	1 290
	96	8,3	0,40	640
24	Brown liquor	8,5	0,38	1 230
	10	7,3	0,43	250
	57	8,6	0,38	440
	94	8,6	0,37	610
	37	Brown liquor	8,7	0,26
46	Brown liquor	8,4	0,26	430
	93	7,2	0,24	930
53	Brown liquor	7,2	0,19	450
	9	7,0	0,33	1 530
	54	7,2	0,38	430
	96	7,0	0,33	750
			0,33	980

TABLE 2
Permutit FS-IP Resin

Cycle No.	BV	pH	Cond. Ash %	Colour
7	Brown liquor	7,7	0,21	820
	8	8,0	0,14	140
	54	7,6	0,20	220
	98	7,4	0,21	250
13	Brown liquor	7,2	0,27	1 010
	37	7,1	0,24	420
	70	7,4	0,26	440
	115	7,3	0,27	460
17	Brown liquor	8,0	0,18	670
	96	7,6	0,20	630
18	Brown liquor	8,0	0,20	740
	9	7,2	0,25	460
	50	7,2	0,21	510
	95	7,8	0,20	530

TABLE 3
Duolite A 171 P Resin

Cycle No.*	BV	pH	Cond. Ash %	Colour
1	Brown liquor	8,0	0,20	680
	35	7,8	0,21	90
	92	7,9	0,20	220
6	Brown liquor	8,5	0,38	1 230
	10	7,2	0,44	390
	57	8,5	0,38	620
	94	8,5	0,38	760
8	Brown liquor	8,9	0,35	910
	9	7,3	0,39	630
	94	8,6	0,33	840

* These cycles are equivalent to cycles No. 19, 24 and 28 in Fig. 2.

Colour of brown liquor as well as of fine liquor at the end of each cycle is plotted in Fig. 2. After 18 cycles the Permutit resin was completely fouled and was replaced by Duolite 171 P. This resin gave a very poor performance, being irreversibly fouled after 8 cycles.

An analysis of ash was carried out to ascertain whether the ion-exchange resin removed any of the ash or merely a selective portion. These figures are shown in Table 4. A frequency scan, from 360 to 740 nm, was carried out on fine liquor, brown liquor, and ion-exchange decolorised liquor at 50° Bx and pH 7 to establish whether the ion-exchange resin removed different colour components when compared to the fine liquor off char. The results are shown in Fig. 3.

TABLE 4
Analysis of Ash Constituents (all results are ppm on syrup)

No. of BV	Mg ⁺⁺	K ⁺	Ca ⁺⁺	Na ⁺	Cl ⁻
<i>Run 7 — R & H Resin</i>					
Brown liquor	15	232	148	61	133
8	14	220	7	41	98
54	15	223	148	42	124
98	15	225	148	42	142
<i>Run 9 — R & H Resin</i>					
Brown liquor	18	226	126	36	115
16	14	186	105	26	329
48	17	213	114	31	178
96	18	220	120	33	160
<i>Run 18 — R & H Resin</i>					
Brown liquor	12	233	145	25	107
Equiv. fine liquor off char	11	236	89	27	115
9	12	239	143	29	471
50	12	230	140	27	178
95	12	230	144	26	151
<i>Run 60 — R & H Resin</i>					
Brown liquor	11	218	271	<25	107
47	11	220	272	<25	163
96	10	216	228	<25	131

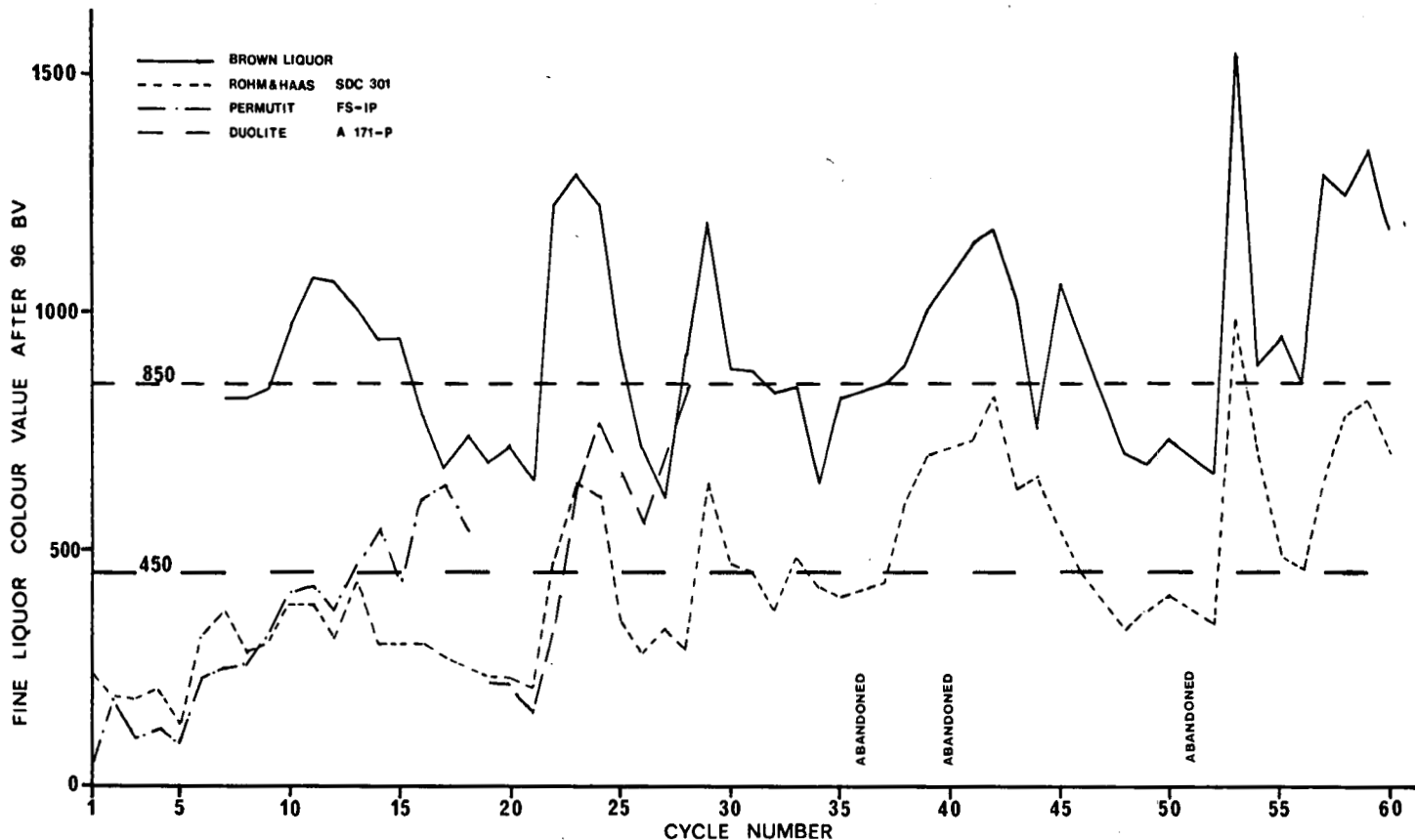


FIGURE 2 Colour of brown liquor and fine liquor after 96 BV for various resins versus cycle number.

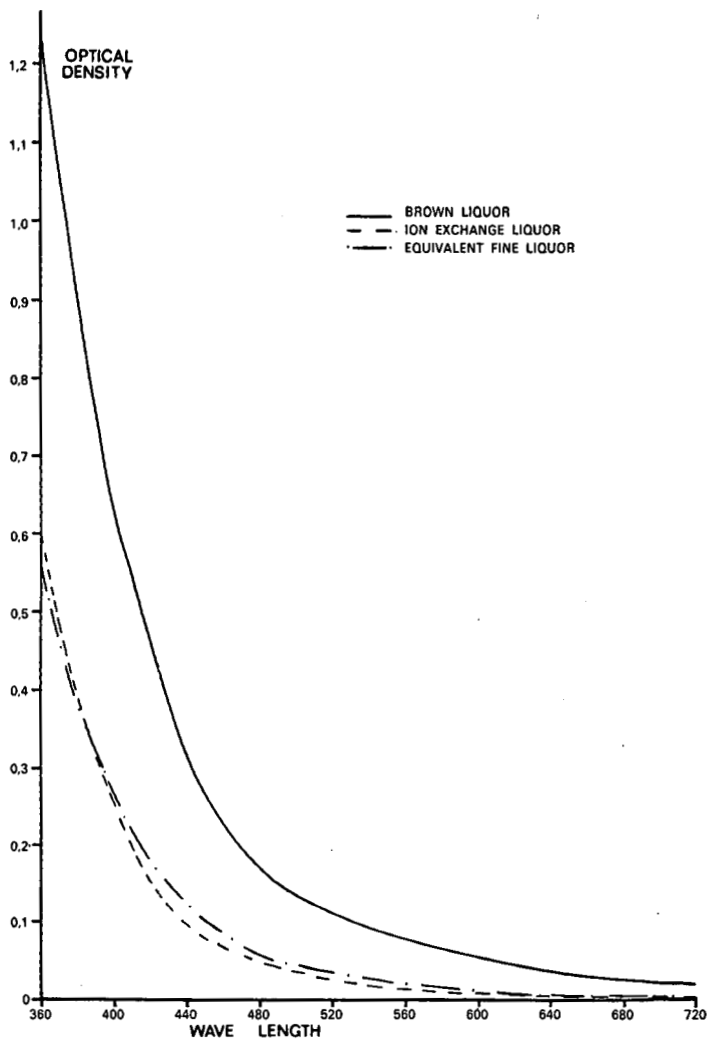


FIGURE 3 Frequency scan for fine liquor and brown liquor.

Preliminary tests carried out at Huletts Refinery had indicated that ion-exchange decolorised liquor might produce needle crystals on boiling. The kestose levels in brown liquor, fine liquor and ion-exchange liquor were therefore determined by GLC² and are presented in Table 5. First crop boilings were carried out on the ion-exchange decolorised liquor and the equivalent fine liquor off char in the SMRI pilot vacuum pan and showed no signs of needle grain. A photograph of the grain obtained from the ion-exchange liquor is shown in Fig. 4.

TABLE 5
Analysis of Liquors for Total Kestoses

	% Total Kestoses
Brown liquor (Run 18)	0,047
Equivalent fine liquor off char	0,030
Ion-exchange decolorised liquor (Run 18)	0,049

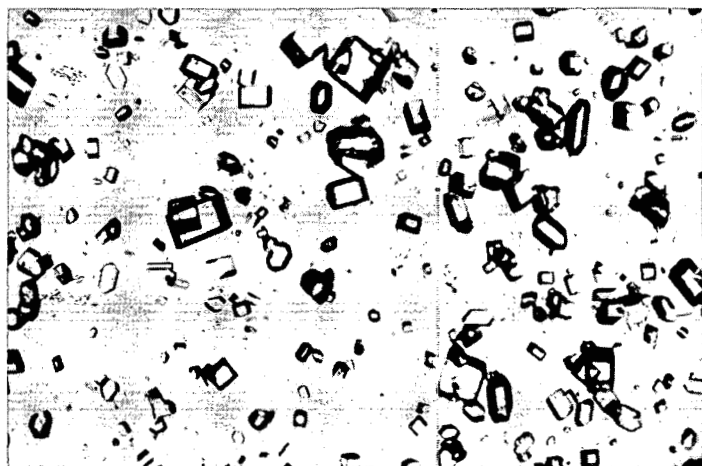


FIGURE 4 Crystals boiled from ion-exchange liquor.

Discussion

The brown liquor colour values have varied between 700 and 1 500 (Fig. 2) and with a fixed run length, as can be expected, the fine liquor colour value at the end of the run varies in accordance with the brown liquor colour value. Apart from isolated runs, the composite fine liquor colour value of the cycle has normally been below 450, which is the maximum allowable by the refinery.

Reference to Table 1 and Fig. 2 shows that the Rohm & Haas resin underwent irreversible fouling during roughly the first ten cycles, but thereafter the performance stabilised despite frequent high organic loads due to the colour of brown liquor. The Permutit and Duolite resins became irreversibly fouled after very small numbers of cycles as seen from Tables 2 and 3.

A plot of colour value of the fine liquor vs the number of bed volumes passed through the resin gives a curve of the form shown in Fig. 5. From classical ion-exchange theory, the normal S breakthrough curve as indicated in the figure would be expected. However, the actual situation is considerably different with the colour value increasing rapidly over the first few bed volumes and then tapering off to a slow but steady increase.

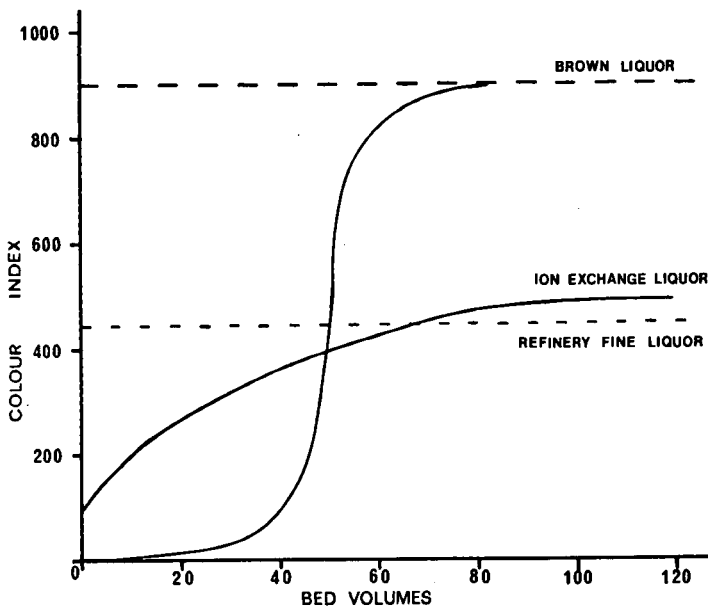


FIGURE 5 Theoretical and practical breakthrough curves.

It would therefore appear best to run with a cycle length such that the highest tolerable colour value is obtained. As shown in Fig. 5, this would be of the order of 100 BV if the colour of brown liquor does not exceed 850 units. However, the longer the cycle length the greater the organic loading of the resin between regenerations. Since the level of irreversible fouling is dependent on this organic loading, longer cycles lead to decreased resin life. There is thus an economic optimum between cycle length and resin life, but, since each series of tests on resin life would take approximately two years, it was not possible to vary the parameters experimentally to obtain this optimum.

This resin life is also dependent on different techniques of regeneration. It has been found that regeneration with a 10% NaCl solution, the pH of which has been adjusted to pH 12, removes substantially larger quantities of organic colour bodies and consequently increases the resin capacity as shown in Fig. 2, cycles 45 to 52. Regeneration with sodium hypochlorite (1% free chlorine) after run 52 removed considerable quantities of otherwise irreversibly absorbed organic bodies, so much so that the resin, which is white when new, was returned almost

to its original colour. However, subsequent runs, at very high brown liquor colour values, have masked any beneficial result. It can be seen, though, that this means of regeneration certainly did not reduce the activity of the resin. It is generally considered that the oxidising effect of the hypochlorite removes approximately 5% of the active ion-exchange sites and as a result should not be used under normal circumstances. A balance between the cost of chemicals and resin will determine which techniques should be used.

It should be noted that the effluent from regeneration, while high in organic matter, is of low volume and can be treated at a modest cost either by municipal sewage works or by mixing with the factory effluent. The effluent volume is approximately 1-2% of the total liquor throughput. Tests have shown that the oxygen absorption is about 7 500 mg/ml.

The analysis of the ash constituents in brown liquor, fine liquor off char and decolorised liquor from ion-exchange (Table 4) has shown that the char removes greater quantities of Ca. However, since this is very probably recycled in the char sweetwaters it is likely that ash removal by char and resin is comparable.

Boilings made from ion-exchange decolorised liquor (Fig. 4) have shown no signs of needle grain. This is supported by the results of kestose analysis (Table 5). An absorption frequency scan (Fig. 3) carried out on brown liquor, fine liquor and ion-exchange fine liquor showed that both char and resin remove essentially the same colour components.

Cost studies, which include depreciation on capital plant, maintenance, labour, decolorising materials, cost of regeneration, effluent cost, etc, indicate that decolorisation by ion-exchange is roughly half the cost of decolorisation by char under present conditions. This is dependent on a reasonable resin life. The breakeven point would be a resin life of 75 cycles under the conditions of the experiment. Overseas experience indicates, however, that a resin life of up to 500 cycles is possible provided that cycle lengths are not greater than 45 bed volumes.

In order to maximise the resin life it is important that brown liquor colour values do not exceed 850 colour units. Since it is unlikely that this is practically achievable (Fig. 2) a two bed series system (Fig. 6) would ensure that liquor contacting the second resin bed has a reasonable colour value.

As the resin in column 2 approaches the end of its useful life it is replaced with new resin, and the old resin replaces that of column 1. Regeneration is in the opposite direction so that the old resin in column 1 is regenerated by the effluent from column 2. It is thus clear that column 1 acts as a gross decoloriser and protects the resin in column 2 from overloading.

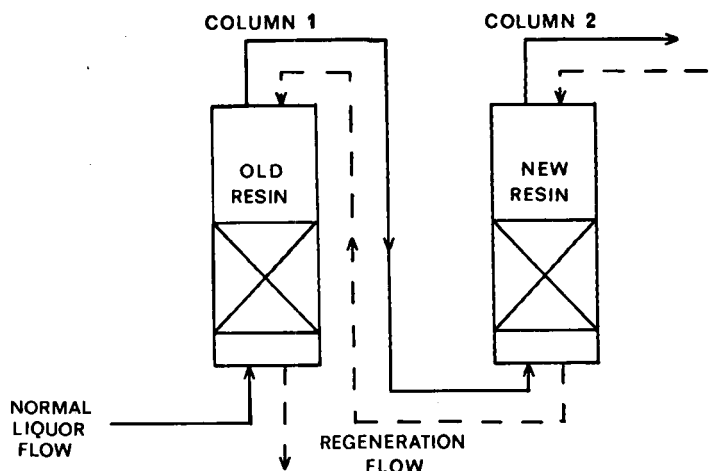


FIGURE 6 Proposed two bed ion-exchange flowsheet.

Conclusions

Under local conditions it would appear that gross decolorisation by ion-exchange is economically and technically feasible. If brown liquor colour values are consistently below 850 colour units a single bed can be used. The optimum configuration for brown liquors exceeding 850 colour units is probably two columns in series (Fig. 6).

The advantages, aside from purely economic ones, of an ion-exchange plant are:

- (1) The capital plant is very inexpensive when compared to a char system (roughly 5 to 10% of the cost).
- (2) The ion-exchange plant can be utilised on any scale whereas a char system requires a large throughput to be economical.
- (3) Salt prices are unlikely to escalate at the rate of oil prices.
- (4) The resin does not have to be removed from the columns for regeneration, which is done in situ. In fact the whole cycle of sweetening off and regeneration, etc, can be completely automated.
- (5) The plant requires very little labour.
- (6) The ion-exchange plant is physically very much smaller than the char plant.

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