TWO-STAGE DECOLOURISATION OF REFINERY LIQUORS BY ION EXCHANGE RESIN

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Abstract

Ion exchange resin has been used at Hulett Refineries to decolourise refinery liquors since 1978. In order to compete on the international markets, it was necessary to reduce the refined sugar colour to meet EEC2 standards. To achieve this extra colour removal, an additional ion exchange decolourisation stage was added in 1987. The results of pilot trials prior to the design of the plant, together with results from the plant itself, are detailed. The operation of the plant is also discussed.

Introduction

Ion exchange resin replaced bone char as a means of decolourising refinery liquors in 1978. The plant consisted of four resin vessels, each with 12,5 m3 bed volumes of resin. This was later expanded to five vessels in order to increase throughput.

To remain competitive in the export market, it became evident that the refined sugar would have to meet EEC2 standards (Table 1). Various options were investigated and pilot plant tests were conducted. As a result of all this work, a second decolourising stage of resin was added in 1987.

Table 1

EEC No. 2 white sugar specification

Pol	99,7° min.
Moisture	0,06% max.
Invert	0,04% max.
(a) Maximum ash	15 points 1 point = 0,0018%
(b) Maximum colour	9 points ½ unit = 1 point
(c) Maximum colour in solution	6 points 7½ units of extinction = 1 point

Total of a + b + c must lie between 8 and 22.

Test work

Prior to the addition of the second decolourising resin stage, the refinery's sugar met most of the EEC2 specifications, the exception being colour. The colour was found to be close to the limit when converted to the EEC2 points system. In order to meet EEC2 colour specifications consistently it was calculated that sugar colour would need to be reduced by about 20 percent. Several options were considered, namely:

1. utilising first boilings for export;
2. decolourising Jet 2;
3. reducing colour in recycling streams;
4. remelting lower boilings;
5. additional decolourising of filtered liquor.
   5.1 by reducing the number of resin cycles;
   5.2 by installing an additional ion exchange vessel;
   5.3 by converting from parallel to two stage series operation.

As more data were collected, ion exchange options were found to be more suitable. Pilot plant studies were instituted in order to assess the three options. Under 5.3 were acrylic/styrene resin versus acrylic/acrylic combinations. The results of these are shown in Table 2. Although the acrylic/styrene combination gave slightly better decolourisations, the acrylic/acrylic combination was the most cost effective and was ultimately adopted.

Plant description and operation

The initial five vessels, A, B, C, D and E, were run in a parallel mode, i.e. brown liquor from the carbonatation station was passed through four of the vessels in parallel, whilst the fifth vessel was being regenerated. The regeneration steps were controlled by timers which were hard wired to the various pumps and valves. The control valves were air actuated Saunders valves. The bed volume was 12,5 m^3.

In changing to a two stage operation, these five vessels and their associated valves and pipework were retained as the first or primary stage. Another set of five vessels was installed as the secondary stage. The primary vessels were re-numbered A1 through to E1 whilst the secondary vessels were numbered A2 through to E2.

Table 2

Comparison of acrylic/acrylic and acrylic/styrene resin combinations over 133 cycles

	Acrylic/Acrylic						Acrylic/Styrene					
	Colours			% Colour Removal			Colours			% Colour Removal		
	Feed	Col. 1	Col. 2	Col. 1	Col 2	Total	Feed	Col. 1	Col. 2	Col. 1	Col. 2	Total
Minimum	573	138	98	37	5	53	605	216	88	17	5	54
Maximum	1179	628	448	77	76	86	1224	964	439	73	76	89
Average	839	319	197	62	37	76	841	363	197	57	46	77

The control system was changed and five Siemens Simatic S5 115U PLCs were installed, each controlling a pair of vessels (one primary and one secondary). A Siemens IM305 Communication Module was also installed to allow communication between the various PLCs for brine make-up as this is controlled for all vessels by the PLC for E vessel. Air actuated Amri valves were installed in the secondary vessels. The bed volume was changed to 16 m^3.

Figure 1 shows the flow of liquor through the vessels. The secondary vessels contain the newer resin which is renewed annually and the resin that was in the secondary vessels is moved across to the primary vessels. At this stage the resin has undergone approximately 220 cycles. The resin that was in the primary vessels is discarded and has undergone approximately 440 cycles. Not only does the older resin in the primary vessels remove colour from the liquor, but it also tends to 'shield' the resin in the secondary vessels from insoluble impurities such as lime leakage coming through from the carbonatation station.

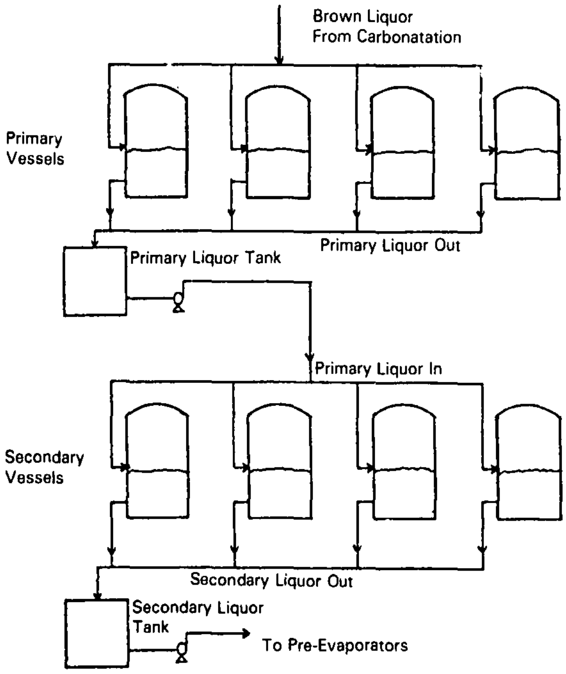

FIGURE 1 Liquor flow through resin vessels

The concentration of the brown liquor feed to the vessels is maintained at 66° to 68° brix, whilst its temperature is controlled at ±83°C. There is no change in these parameters through the vessels. A pressure of 420 kPa is applied to the vessels to drive the liquor through the resin bed.

At any one time, only four pairs of vessels are on-line. The fifth pair is being regenerated. The regeneration takes six hours and as soon as it is complete, the vessel pair is placed on-line and another pair is taken off-line for regeneration. Thus the cycle time for a pair of vessels is a minimum of 24 hours.

Figure 2 shows the direction of flow of regenerant through the vessels. This is counter current to the flow of liquor so that the newer resin gets the benefit of the 'fresh' regenerant. The exception is the backwash step which is carried out with flow through each vessel in parallel. Figure 3 shows the various steps in the regeneration procedure. After every 12 cycles resin is acid washed. Figure 4 shows the various steps involved in this procedure.

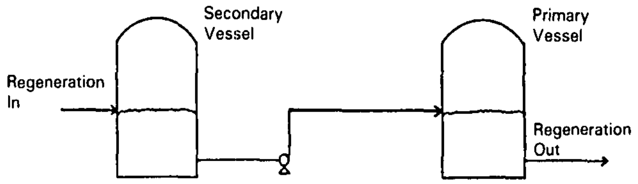

FIGURE 2 Regeneration flow through resin vessels

1. Liquor displacement
2. De-sweeten
3. Fill
4. Air purge
5. Settle
6. Backwash
7. Settle
8. Drain
9. Choose between normal regeneration and acid wash
10. Brine introduction A
11. Brine introduction B
12. Hold
13. Brine introduction B continued
14. Brine displacement A
15. Brine displacement B
16. Brine displacement C
17. Fast rinse A
18. Fast rinse B
19. Sweeten on
20. On-line

FIGURE 3 Regeneration cycle steps

1. Liquor displacement
2. De-sweeten
3. Circulate acid for 2 hours
4. Brine introduction A
5. Brine introduction B starts
6. Vessels go on hold to allow circulation of caustic soda for 2 hours
7. Brine introduction B continues
8. Brine displacement A
9. Brine displacement B
10. Brine displacement C
11. Fast rinse A
12. Fill
13. Air purge
14. Settle
15. Backwash
16. Settle
17. Drain
18. Sweeten on
19. On-line

FIGURE 4 Acid wash cycle

In view of the annual replacement of secondary resin, five new batches are introduced at ten week intervals. Amberlite IR958 from Röhm & Haas is used. Recently, Duolite A173 was also used. However, although its colour removal was very good initially, this was found to deteriorate very rapidly after about 150 cycles and the resin had to be discarded after approximately 300 cycles.

Due to the requirement to acid wash, mild steel vessels must be lined for protection. Both cured and uncured butyl rubber have been used. It has been found that in both cases the rubber above the liquor level deteriorates rapidly. After about a year, bubbles appear under the lining and these have to be cut out and patched as permeation of regenerant and liquor through the rubber occurs at these points causing visible corrosion. After some three to four years, the top half of a vessel's rubber lining needs to be replaced.

In January 1991, it was decided to try corroglass instead of rubber in the top half of the vessels. To date, four vessels have been corroglassed. Inspection after twelve months has revealed that the rubber/corroglass joint in the middle is excellent. However, the corroglass itself developed numerous small bubbles of about 40 mm diameter. Unlike the rubber, these bubbles were found to be only in the first millimeter of the corroglass and not through to the vessel itself. The reason for the formation of these bubbles is not known, but the situation is being monitored carefully. The repair of the corroglass takes a much shorter time than the equivalent repair to the rubber lining and thus has less influence on throughput.

Another problem encountered was severe bending of the pipe configuration and supports inside the bottom of the secondary vessels. Figure 5 shows the layout of the pipework. The laterals are 50 mm in diameter with 5 mm diameter holes 100 mm apart along the length of the lateral. These are covered by a polypropylene mesh which, in turn, is covered by a fine nylon gauze sock to prevent the resin passing through with the liquor. These were clamped onto 100 mm x 100 mm angle sections by U bolts. The angle sections were in turn bolted to lugs welded on the sides of the vessel. All metalwork is stainless steel.

Various solutions were tried in order to solve this severe bending problem. Supports were placed under the outlet header pipe. The angle sections were changed to channel sections as in the primary vessels. The laterals themselves had a second row of holes added to improve the flow into them.

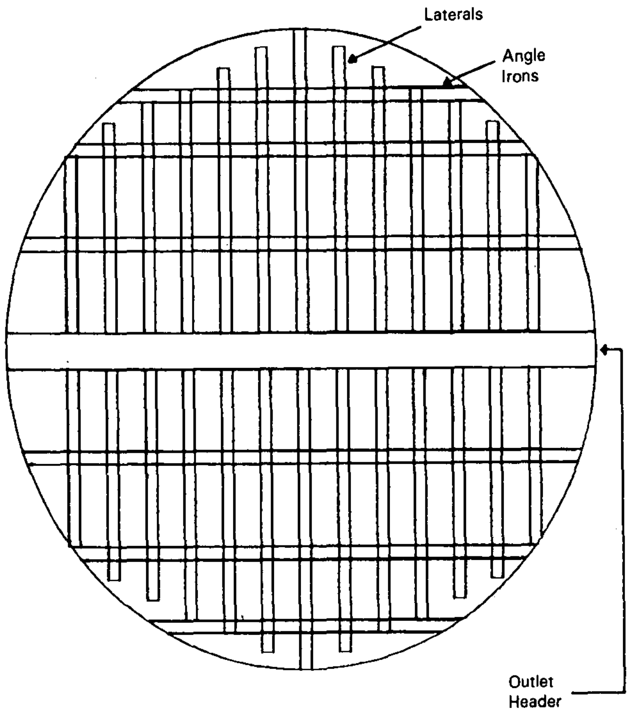

FIGURE 5 Arrangement of laterals and supports inside the resin vessels

In an attempt to determine when this bending occurred, the SMRI installed strain gauges on the channel sections of one of the vessels. Although these failed within a matter of hours, information obtained from them indicated that the bending could have been caused by water hammer when the valves opened or closed. This water hammer was attributed to the fast response of the Amri valves. This did not occur in the primary vessels due to the slower response of the Saunders valves, hence no bending of the pipework occurred

Table 3

Average monthly colours of liquor streams and sugar boilings prior to and after the addition of the second stage 1987–1988 Season

Month	Brown Liquor	Primary Liquor	Secondary Liquor	% Removal Over Resin	1st Boiling	2nd Boiling	3rd Boiling	4th Boiling
April	833	356	-	57,3	29	56	138	213
May	862	379	-	56,1	30	60	137	238
June	1186	471	-	60,7	35	73	138	262
July	702	284	-	59,6	26	53	136	222
August	674	261	-	61,6	26	50	126	212
September	644	264	-	59,0	26	49	124	208
October	722	299	-	58,7	26	57	124	231
November	705	410	246	65,3	22	46	108	214
December	730	513	259	64,5	22	48	111	226
January	786	546	252	68,1	23	48	122	185
February	769	489	235	69,4	20	52	98	157
March	816	503	246	69,9	19	49	96	133

1991–1992 Season to Date

April	570	634	347	64,2	20	58	162	128
May	787	464	233	70,4	19	39	91	114
June	755	444	209	72,3	19	40	91	135
July	792	519	248	68,7	20	45	100	128
August	770	467	246	68,0	19	41	102	130
September	735	453	230	68,7	20	41	97	127
October	637	358	184	71,0	18	38	96	146
November	670	415	195	71,0	19	37	99	134
December	740	487	220	70,3	19	40	100	125
January	746	495	244	67,3	23	49	112	147

in these vessels. Restrictors were placed in the airlines to the Amri valves to slow their response and the subsequent examination of the two vessels indicated that this problem has now been overcome.

Results and discussion

Table 3 gives the decolourisation results before and after the introduction of the second stage. The increase in colour removal is evident with the percent removal over resin increasing from around 60% to about 70% with a corresponding drop in the colours of the white sugar boilings.

In spite of the addition of the second stage, there are still instances when the refined sugar colour increases to above EEC2 specification. These instances are:

(a) Just prior to shutdown. At this point, the proportions of the various jets is such that the required blend of the four boilings cannot be maintained without excessive rejects of the higher boilings. This results in excessive sweetwater which is undesirable to store during a shutdown.

(b) Just after start up. Sweetwater accumulated during the shutdown has a high colour. This is fed on start-up into the melt. The volumes are such that it takes a couple of shifts to consume it all.

(c) Raw sugar colours. The colours of incoming raws affect the colour of the final sugar. The higher colour loading cannot all be removed through the various stages of the refinery. Colours above 1350 result in rejects of fourth boilings. As the colours increase above this figure, so the proportion of rejects increases with part of third boilings being rejected in order to maintain the final mix at the required colour limit. However, there is a limit to the amount of rejects the refinery can handle and if this limit is exceeded, the sugar no longer meets EEC2 specification.

Conclusions

The second stage has now been operational for four years. Colour removals of around 70% are being obtained. This has allowed the refinery to meet consistently the EEC2 specification as intended.

Acknowledgements

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