ION EXCHANGE IN CANE SUGAR PURIFICATION
A PROCESSING AID AND ENERGY SAVER

F. X. McGarvey, F. X. Pollio and John Ungar
Ionac Chemical Division, Sybron-Chemical Group
Birmingham, N.J. USA

ABSTRACT

This paper reviews the advantages of using ion-exchange resin as a processing aid in sugar purification with particular reference to the energy saving aspect in:

a) Softening (removing scale forming components) prior to evaporator and vacuum pans; and

b) Decolorizing mill and/or refinery juices, to avoid need for heat regeneration of activated carbon or bone char and improve product quality.

The economics of the two processes are discussed with some examples.

INTRODUCTION

Ion exchange techniques have played valuable roles as multipurpose tools in cane sugar purification. A previous paper (Pollio and McGarvey) given at the 16th Congress developed two application areas where ion exchange resins were helpful to sugar mills and sugar refiners. This paper serves as an extension of the work reported and provides additional information on sugar juice softening and sugar liquor decolorization. Other processes associated with sugar purification or treatment will be discussed on future occasions.

DISCUSSION

Softening of Sugar Juices and Liquors

The scaling of evaporators and vacuum pans represents a serious problem in cane mills requiring frequent shutdowns for cleanings, as well as mechanical failure of equipment, due to stresses developed from cleaning chemicals and frequent re-heating during startup. Intensification of energy and labor costs makes scale reduction an important goal in mill operation.
The problem of sugar loss in molasses due to increase in molassogenic cations namely, sodium and potassium, continues to be a problem for cation exchange operation since the sodium content will increase during the softening operation and the benefit of divalent calcium and magnesium salts will be lost. In the previous paper this problem was reviewed with a view to minimizing it by means of a special regeneration procedure.

To appreciate some of the problems related to softening, it is necessary to review the composition of typical ash as found in molasses. While these values vary considerably from one location to another, the values shown in Table 1 will serve as a basis for calculation.

**TABLE 1. Typical ash compositions — molasses (Honig²)**

<table>
<thead>
<tr>
<th>Component</th>
<th>Content, %</th>
<th>Amount gms/100 gms H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Ash</td>
<td>—</td>
<td>100</td>
</tr>
<tr>
<td>Potassium % total ash</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Sodium, % total ash</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Calcium and Magnesium</td>
<td>32</td>
<td>32</td>
</tr>
<tr>
<td>Sucrose</td>
<td>—</td>
<td>210</td>
</tr>
<tr>
<td>Invert</td>
<td>—</td>
<td>115</td>
</tr>
<tr>
<td>Brix</td>
<td>93.4</td>
<td></td>
</tr>
</tbody>
</table>

On the other hand, a typical cane liquor would have about 2500 ppm ash with some 1700 ppm hardness expressed as calcium carbonate. This does not give the same ratio of hardness to total ash, as shown in Table 1, because some hardness has been removed during the evaporation and crystallization steps. Considering the difficulty in getting good samples in the mill, the question of material balance on hardness can be answered only after extensive testing.

The effect of various ash components can be evaluated by a review of the molasses composition given in Table 1, with the values likely to be obtained thru a softening cycle. Figure 1 shows the relationship of sucrose solubility to salt content for these compounds commonly found in ash. Anion composition is not expected to exert any appreciable effect. Assuming that the contribution of each of the various salts is cumulative, the following calculation can be made based on information from Table 1.

\[
\text{Combined sugar composition} = 325 \, \text{gms/100 gms H}_2\text{O} \\
\text{Potassium-sodium value} = (60 + 8) \times (420) \times \frac{1}{100} = 286 \, \text{gms/100 gms H}_2\text{O}
\]
**FIGURE 1.** Sucrose solubility as a function of salt type and concentration

\[
\text{Calcium and magnesium value} = \frac{1}{32} (100) (288) = 92 \text{ gms/100 gms H}_2\text{O}
\]

Total sugar solubility (70°C) = 378 gms/100 gms H\text{2O}

A similar calculation at 30°C gives a value of 231 gms sugar/100 gms H\text{2O} lower than that reported in the particular molasses used. Since most mill molasses will show continual crystallization on standing, the model composition is still not at equilibrium. For the purposes of illustration, a comparison can be used recognizing that it is not quantitative.

**TABLE 2.** Effect of softening on equilibrium of sucrose solubility at 70°C

<table>
<thead>
<tr>
<th>Liquor</th>
<th>Solubility, gm sucrose/100 gms H\text{2O}</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard Molasses</td>
<td>378</td>
<td>100</td>
</tr>
<tr>
<td>Softened Completely</td>
<td>420</td>
<td>111</td>
</tr>
<tr>
<td>Calcium Only (No sodium or potassium)</td>
<td>288</td>
<td>76</td>
</tr>
</tbody>
</table>
The calculation was performed assuming that the juice was softened and that the liquor was constituted with calcium and magnesium only. The results are shown in Table 2.

It is apparent that blending back calcium or magnesium into the liquors making up the final molasses will materially affect the ability to exhaust the liquors, but softening does not have as pronounced an effect with about 10% increased solubility. Also, the softened liquors have reduced viscosity and should be expected to crystallize more rapidly than the high hardness liquors. It is expected that the sugar losses will not be as great as indicated from these calculations.

The early ion exchange process with cane sugar juices resulted in serious problems due to bagacillo accumulation in the resin bed. Work in sugar mills showed that the only way to operate the beds was to exhaust by flowing the juice upward thru the bed. At flows approaching 10 gpm/ft², it was found that the bed remained free of bagacillo and consistent results could be obtained. A series of runs at different regeneration levels using a defecated juice at 80°C gave results as shown in Fig. 2.
The pilot runs showed that softening resulted in minor changes in the purity and Brix color. Cycle to cycle variations ranged from -1% to +2% in purity variation and measurable reduction in color was also observed. The runs with expanded beds during the upflow exhaustion gave some hardness leakage due to the tendency for these beds to channel. In most cases between 90 and 95% of the hardness entering the beds was removed. Regeneration was performed with 80°C brine solutions at 10% strength.

The capacity information given in Fig. 2 can be used to calculate the size of a plant to soften a juice containing 2000 ppm (as CaCO₃) of hardness. It will be assumed that the mill can process 3000 tons of cane per day.

\[ \text{Tons sucrose/day} = 3000 \times 0.13 = 390 \text{ tons of cane per day} \]

\[ \text{Tons liquor} = \frac{390}{0.13} = 3000 \text{ tons} \]

\[ \text{Volume liquor/day} = \frac{3000 \times 2200}{8.33 \times 1.05} = 754,600 \text{ gallons} \]

\[ \text{Flow} = \frac{754,600}{24 \times 60} = 524 \text{ gpm} \]

\[ \text{Lbs CaCO₃ to be removed/day at 2000 ppm as CaCO₃} \]

\[ = 2000 \times \left(\frac{3000 \times 2200}{10^6} \times \frac{2 \times 10^3}{10^6} \times 3 	imes 2.2 \times 10^6\right) \]

\[ = 13.2 \times 10^3 = 13,200 \text{ lbs/day} \]

The resin requirements will be a function of the regeneration level (salt consumption). A summary of daily requirement is given in Table 3.

**TABLE 3. Effect of salt consumption on economics**

<table>
<thead>
<tr>
<th>Regenerant level kg NaCl/m³</th>
<th>Capacity kg CaCO₃/m³</th>
<th>Volume m³ of resin used per day</th>
<th>Salt consumption kg/day</th>
<th>$*</th>
</tr>
</thead>
<tbody>
<tr>
<td>64</td>
<td>32</td>
<td>187</td>
<td>12000</td>
<td>528</td>
</tr>
<tr>
<td>96</td>
<td>42</td>
<td>137</td>
<td>13582</td>
<td>598</td>
</tr>
<tr>
<td>128</td>
<td>51</td>
<td>116</td>
<td>16000</td>
<td>660</td>
</tr>
<tr>
<td>160</td>
<td>58</td>
<td>103</td>
<td>16572</td>
<td>729</td>
</tr>
<tr>
<td>192</td>
<td>62</td>
<td>96</td>
<td>18463</td>
<td>812</td>
</tr>
</tbody>
</table>

*cost salt = 0.044 kg
Factors related to cost include cycle time, labor, resin replacement and equipment depreciation. Generally, these costs are about 20% of the salt values. There are various ways to reduce salt consumption as for example, by a two step regeneration where the last portion of the salt is saved for the next cycle.

The availability of salt can be a limiting factor in tropical countries and costs much in excess of two cents per pound may be found. In addition, the quality of salt may be very poor. Source of salt should not be overlooked. In areas where cane is grown near the sea, the ocean, its salty water can be used as a regenerant.

Sea water consists of about 3% sodium chloride with about 0.6% hardness, of which about 85% is magnesium. Cation exchangers regenerated with sea water operate around fixed equilibrium capacities as discussed in another publication (Ungar3). The ion exchange bed after regeneration must be rinsed with good quality potable water to remove excessive amounts of salt prior to the service cycle.

The use of sea water as a regenerant does not mean that the sea water can be taken directly from the sea. Careful filtration and sterilization is necessary to prevent odors from appearing in the liquor and to keep large amounts of bacteria from growing in the beds. If these precautions can be followed, sea water can be used to regenerate softeners with substantial saving over that obtained with regular salt.

**Decolorizing mill and/or refinery juices**

As the prices of the various types of carbons commonly employed at cane sugar refineries for the decolorization of sugar liquors have progressively increased, alternative ways to reduce decolorization costs associated with a refinery operation have been considered. The need for increased decolorization capacity has been met by ion-exchange resin decolorization systems after an economic evaluation of bone char of granular carbon installations. There is also the benefit of paving the excessive energy used for regenerating the carbon (or bone char).

The use of ion-exchange resins for decolorizing cane refinery liquors is an established unit operation that is practiced at cane sugar refineries throughout the world. Anion exchange resins, particularly those having a styrene-divinylbenzene matrix, are employed for polishing-decolorization of clarified liquors resulting from treatment with activated carbon powder, granula vegetable carbon, or animal bone char decolorization systems. These strongly basic anion-exchange resins are normally operated in fixed columns to polish the carbon decolorized 60° to 65° Brix liquors producing very light-colored liquors. The anion-exchange resins are usually operated warm (70° to 75°C) in the chloride cycle for maximum efficiency and are regenerated with NaCl solutions once a predetermined maximum color leakage is observed or slightly exceeded. The regenerated resins are then used to decolorize additional cane sugar liquors.
With proper conditions and handling, polishing decolorization resins for sugar, can be used repeatedly for hundreds and even a few thousand decolorization cycles to give the highly decolorized liquors required to produce refinery-grade sugars. During the treatment of typical carbon-treated cane liquors, as processed by North American, Asian, European, and Latin American refineries, it is possible to decolorize up to one metric ton of sugar solids per cubic foot of resin per decolorization cycle at an incremental cost well below $0.01 per kilogram of refined sugar produced. This incremental cost is attributable to the polishing decolorization of the particular carbon system being employed at the refinery.

Anion exchange resins produced by the Ionac Chemical Company are sold worldwide for this purpose. In the United States alone, 75% of the cane sugar refineries utilizing ion exchange resins, currently use Ionac sugar grade ion exchange resins in their refinery operations.

During recent years, acrylic type decolorizing anion-exchange resins have received much attention due to the ability of these resins to effectively decolorize the darker, clarified cane sugar refinery liquors. Though not currently used in the U.S.A., acrylic type decolorizing anion resins have been showing considerable promise in decolorizing darker colored refinery liquors at several refineries in Brazil and South Africa.

The use of acrylic type decolorizing resins has been also suggested for decolorizing refinery cane liquors which have not been treated by any type of carbon, in the hope of eliminating the need for carbon altogether. Though attractive in principle, there are numerous problems and much care must be exercised. Even in the best of cases, a reduced resin life must be accepted as a reality due to the fouling tendency of waxes and high molecular weight colored organic matter present in the liquors which are normally removed by the carbons. Needless to say, the performance characteristics of the acrylic type decolorizing anion resins during the processing of refinery liquors without prior carbon treatment, will be a function of the quality of the feeds, the clarification techniques used to produce turbidity free liquors, and the handling of the resins by the refinery technicians, particularly with regard to the regeneration practices utilized. To produce granulated refined sugar without the use of carbon, it is most desirable to feed turbidity free liquors characterized by a color not exceeding 600 ICUMSA units (at 420 mu) in order to achieve maximum economics of operation and increased resin life.

Figs. 3 and 4 illustrate typical decolorizing performance of a macroporous styrene-DVB matrix anion exchange resin (Ionac D-182) and a macroporous acrylic-DVB matrix anion exchange resin (Ionac A-688) during the treatment of clarified refinery liquors produced from Philippine raw sugars. The data are presented to illustrate the remarkable decolorization ability of both styrene and acrylic based-DVB anion exchange resins.
FIGURE 3. Decolorization of refinery clarified liquor with Ionac D-182 (Styrene-DVB Matrix Resin)

- Raw Sugar Source - Philippines
- Clarified Liquor - 63 Brix
- Feed Color: 150 ICUMSA units at 400 µu
- Ash - 0.09% (Dry Basis)
- Invert - 0.29% (Dry Basis)
- Processing Temperature 73°C
- Processing Flow - 4BV/hour

FIGURE 4. Decolorization of Refining Clarified Liquor with Ionac A-685 (acrylic DVB matrix resin)
Cost Analysis

In order to gain some insight into the incremental costs that will result by adding ion exchange decolorization resins into an existing cane sugar refining operation, two systems have been considered.

System 1. Acrylic-DVB/Styrene-DVB anion units in series (without carbon pretreatment)

System 2. Styrene-DVB anion unit (with carbon pretreatment)

1. Acrylic-DVB/Styrene-DVB Anion Units (without the use of carbon pretreatment).

Plant size = 200 tons refined sugar/24 hours.

Plant type = No carbon/gross decolorizer/polishing decolorizer.

Assume 60 Brix clarified liquors feed 600 ICUMSA color to Ionac A-685.

Assume 3 trains: 2 on – 1 off.

Assume each train has a unit of Ionac A-685 and a unit of Ionac D-182 operated in series.

Assume 3 bedvolume (BV)/hr. flow through Ionac A-685 unit.

Assume 6 bedvolume (BV)/hr. flow through Ionac D-182 unit.

Assume A-685 treats 24 BV/8 hr. cycle (3 BV/hr.).

Assume D-182 treats 48 BV/8 hr. cycle (6 BV/hr.).

\[
\frac{200 \text{ tons}}{0.60 \text{ Brix}} \times \frac{1}{1.20 \text{ g/cc}} = 278 \text{ m}^3 \text{ clarified liquor (60BX) treated/day}
\]

For Ionac A-685:

\[
\frac{278 \text{ m}^3}{24 \text{ hrs.}} = 11.6 \text{ m}^3/\text{hr.}
\]

\[
11.6 \text{ m}^3/\text{hr.} \times \frac{\text{hr.}}{3 \text{ BV}} = 3.9 \text{ m}^3 = 3.9 \text{ m}^3 \times \frac{35.3 \text{ cu. ft.}}{\text{m}^3} = 140 \text{ cu. ft.} + (70 \text{ cu. ft.}) = 210 \text{ cu. ft.}
\]

There will be 3 units, each having 10 cu. ft. of Ionac A-685. In other words, 140 cu. ft. of resin will be on stream at all times.

3 regeneration per day at 15 lbs. NaCl/cu. ft. level
\[
210 \text{ cu. ft.} \times 15 \text{ lbs} = 3160 \text{ lbs. NaCl/day}
\]

cu. ft.

For Ionac D-182:

\[
\frac{278 \text{ m}^3}{24 \text{ hr.}} = 11.6 \text{ m}^3/\text{hr.}
\]

\[
\frac{11.6 \text{ m}^3}{\text{hr.}} \times \frac{\text{hr.}}{6 \text{ BV}} = 1.93 \text{ m}^3
\]

\[
1.93 \text{ m}^3 \times 35.3 \text{ cu. ft.} = 68 \text{ cu. ft.} + (34 \text{ cu. ft.}) = 102 \text{ cu. ft.}
\]

There will therefore be 3 units Ionac D-182, each containing 34 cu. ft. of resin, two units always on stream – 3 regenerations/day.

Regeneration @ 15 lbs. NaCl/cu. ft.

\[
102 \text { cu. ft.} \times 15 \text{ lbs.} = 1540 \text{ lbs. NaCl/day}
\]

cu. ft.

Total resin cost 312 cu. ft. \times $150 = $46,800
cu. ft.

Total equipment cost $46,800 \times 3.00 = $140,400

Operating Cost:

Assume 10 years amortization of equipment = $14,040/yr. =

\[
\frac{\$14,040}{365\text{ days}} = \$38.47/\text{day}
\]

Resin life: 500 tons/cu. ft.

\[
\frac{365\text{ days} \times 200\text{ tons}}{\text{yr.}} = 73,000\text{ tons/yr.}
\]

\[
\frac{73,000\text{ tons} \times 1\text{ cu. ft.} \times \frac{\text{yr.}}{500\text{ tons}} \times \frac{\$150}{365\text{ days} \times \text{cu. ft.}} = \$60/\text{day}}{\text{yr.}} = \$60/\text{day}
\]

Daily Costs:

Equipment = $38.47/day

Resins = $60.00/day

Regenerants

Assume NaCl $0.02/lb.
\[
\$0.02 \times 4600 \text{ lbs. NaCl} = \$92.00/\text{day}
\]
\[
\text{lb./day}
\]
Total daily cost $190.47/day
Cost/ton sugar = \(\frac{190.47/\text{day}}{200}\) = $0.95/ton sugar
Cost/kg sugar = 0.095 cents/kg sugar ($0.001/kg sugar)

Capital Investment:

Equipment $140,400
Resin 46,800
Total $187,200

System II Styrene-DVB Anion Unit (with carbon pretreatment)

Plant size = 200 tons refined sugar/24 hrs.
Plant type = carbon/polishing decolorizer.
Assume 60 Brix clarified liquor feed 100 ICUMSA color to Ionac
A—642 unit
Assume 3 trains: 2 on — 1 off.
Assume each train consists of a single Ionac D-182 unit.
Assume 4 BV/hr. flow through Ionac D-182 unit.
Assume Ionac D-182 treats 32 BV/hr. cycle (4 BV/hr.)

\[
\frac{200 \text{ tons}}{0.60 \text{ Bx}} \times \frac{1}{120 \text{ g/cc}} = 278 \text{ m}^3 \text{ clarified liquor (60 Bx)/day}
\]
\[
\frac{278}{24 \text{ hrs.}} = 11.6 \text{ m}^3/\text{hr.}
\]
\[
11.6 \text{ m}^3/\text{hr.} \times \frac{hr.}{4 \text{ BV}} = 2.9 \text{ m}^3
\]
\[
2.9 \text{ m}^3 \times 353 \text{ cu. ft.} = 102 \text{ cu. ft.} + (51 \text{ cu. ft.}) = 153 \text{ cu. ft.}
\]

Total for 3 units

There will therefore be 3 units each having 51 cu. ft. of Ionac D-182. In other words 102 cu. ft. will be on stream at all times.
3 regeneration per day at 12 lbs. NaCl/cu. ft. level

153 cu. ft. x 12 lbs. NaCl/cu. ft. = 1836 lbs. NaCl/day

Total equipment cost 22,950 x 3.00 = $68,850

Total resin cost 153 cu. ft. x $150/cu. ft. = $22,950

Operating Cost:

Assume 10 year amortization of equipment = $6885.00/yr.

\[
\frac{6885.00}{365} = $18.86/day
\]

Resin life: 500 tons/cu. ft.

\[
\frac{365 \text{ days} \times 200 \text{ tons}}{\text{year}} = 73,000 \text{ tons/yr.}
\]

\[
\frac{73,000 \text{ tons}}{\text{year}} \times \frac{1 \text{ cu. ft.}}{500 \text{ tons}} \times \frac{\text{yr.}}{365 \text{ days}} \times \frac{150}{\text{cu. ft.}} = $60/day
\]

Daily Cost:

Equipment = $18.86/day

Resin = $60.00/day

Regenerants

Assume NaCl $0.02/lb.

\[
0.02 \times \frac{1836 \text{ lbs. NaCl}}{\text{day}} = $36.72/day
\]

Total daily cost $115.58/day

Cost/ton sugar $115.58 = $0.085/ton sugar

Cost/kg sugar = .068 cents/kg ($0.001/kg sugar)

Capital Investment:

<p>| | |</p>
<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>Equipment</td>
<td>$68,850.00</td>
</tr>
<tr>
<td>Resin</td>
<td>22,950.00</td>
</tr>
<tr>
<td>Total</td>
<td>$91,800.00</td>
</tr>
</tbody>
</table>

It should be noted that the cost calculations for System I do not take into account the refinery operations savings (equipment and operating cost) due to the
elimination of the carbon decolorization system. Likewise, increased savings achieved due to increased yield of granulated sugar resulting from the operation of either system are not taken into account in the cost calculations. Finally, labor, utility, energy, and overhead economies have not been purposely considered either, since these costs can be quite variable depending on the country and the administrative costs unique to each region.

SUMMARY

It can be stated that as the true value of ion exchange as a unit operation becomes better understood by cane sugar processors worldwide, there will be a greater acceptance of these type systems by cane sugar processors. Not only have sugar decolorizing anion-exchange resins allowed the refiner to improve the overall operation and economics of the refining process, but also have brought about a general improvement in the sugar quality that is now available commercially.

REFERENCES


INTERCAMBIO IONICO EN LA PURIFICACION DE AZUCAR DE CANA – UNA AYUDA EN EL PROCESO Y UN AHORRADOR DE ENERGIA

F.X. McGarvey, F.X. Pollio y John Ungar

RESUMEN

En este trabajo se hace una revision de las ventajas que tiene el uso de resinas de intercambio ionico como ayuda en el proceso de purificacion de azucar con referencia especial al ahorro de energia en:

a) Ablandamiento (remocion de compuestos incrustantes) antes de la evaporacion y el cocimiento.

b) Decoloracion de jugos del ingenio o licores de la refineria para evitar la necesidad de la regeneration termica del carbon activado o carbon de huesos y mejorar la calidad del producto.

Se discute el resultado economico de los dos procesos con algunos ejemplos.