CHROMATOGRAPHIC APPLICATIONS IN THE CANE SUGAR INDUSTRY

By

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Abstract

Industrial chromatography of sucrose containing solutions is a mature and reliable technology. In the United States alone, more than 90% of the total beet molasses production is treated in some manner via chromatography. The largest facility at an American Crystal Sugar Co. plant in Hillsboro, North Dakota processes over 545 t/d of 80% dry substance molasses. Two Amalgamated Sugar Co. plants each process more than 455 t/d. Because of the high level of efficiency observed for the chromatography of sucrose and the successful history of use, the general application of industrial scale chromatography to cane syrups appears inevitable. Recent innovations which reduce the size of industrial chromatography systems and associated peripheral equipment using fractal technology will significantly reduce capital cost requirements and, therefore, bring general applications of chromatography of cane derived solutions closer to reality.

Chromatography as a key purification step

In cane, or any other plant, the chemical components such as sucrose are highly organised in a manner appropriate for the processes required for a living organism. It is interesting in this respect that the first steps of cane processing involve a near complete disorganisation of the plant material to yield a highly disordered mixture and that the primary goal in the mill in these initial turbulent steps is to undo what nature has done. Of course, with present technology, this rather contradictory aspect of sugar processing is the most practical approach.

How can this initial mixing be undone? Whatever approach is taken requires, at the very least, an amount of energy large enough to counteract the initial mixing step. Presently, the primary separation approach in a cane mill is to crystallise the sucrose from the mixture. This requires a number of preliminary steps and is ultimately dependent upon manipulating solution concentrations to take advantage of the solubility characteristics of sucrose.

In contrast, chromatography is dependent upon a quite different mechanism. This mechanism is easily described. If an impure sucrose solution is placed in contact with ion exchange resin and, if the solution components are allowed to come to a concentration equilibrium, it is found that a given chemical component exhibits a different concentration within the resin and in the surrounding solution (for industrial sucrose applications, the typical chromatographic medium is an ion exchange resin). This difference, expressed as a ratio of concentration between the solid and liquid phase is called the distribution coefficient. In a favourable case, each component has a different distribution coefficient. Differences in distribution coefficient between components can be very small for chromatography to work successfully.

Passing an impure sucrose solution through a column of ion exchange resin is equivalent to allowing many individual equilibrium steps to occur, one after another. The components are therefore partitioned between the liquid and resin over and over and with each equilibrium step, the components with a greater preference for the solid phase are left further and further behind. A useful term for this effect is “differential migration”. The passage of a solution mixture through a column of resin magnifies the partitioning observed for a single equilibrium step and, with proper design of the chromatography system, the components will be separated from one another.

While industrial chromatography can be accomplished in a simple batch manner, the most popular chromatography configurations for the industrial separation of sucrose solutions are of the simulated moving bed (SMB) type where valve switching is incorporated to simulate the movement of resin within several columns. The value of the SMB type operation is a significant reduction of resin volume and water use. Descriptions of SMB operation are ubiquitous in the literature (e.g., Broughton, 1968; Rearick et al., 1997).

Cane chromatography applications

There are many plausible options for cane syrup processing via chromatography. A few examples include the following:

- Chromatography of molasses.

  In this method, molasses is passed through the chromatography system. A drawback of this process is the difficult to achieve pre-treatment, particularly the necessary removal of suspended solids which are typically at a very high level in cane compared to beet molasses. A second drawback is that cane molasses typically has a low sucrose purity compared with beet molasses so that the amount of sucrose which can be recovered is relatively low. The economics of the process can therefore be marginal. Nevertheless, chromatographic separators for cane molasses service have been installed. The first of this type was placed in operation at the Hokubu Sugar Co.'s Okinawa cane
plant in the mid-1980s (Kakihana, 1989). Little information is available about this system, and it may no longer be in operation.

A molasses chromatography plant is operating at the Sugar and Integrated Industries Co. refinery in Cairo, Egypt. This plant pre-treats molasses via centrifuge and filtration. These steps are followed by softening to remove calcium hardness. A paper concerning this specific installation has recently been presented (Elsawah, 2001).

It appears proper to conclude that the application of chromatography to cane molasses has been rare and has not met with the same wide acceptance accorded beet molasses separation.

- Chromatography of refinery syrups.

It has been demonstrated that cane refinery (recovery house) syrup can be successfully purified via chromatography (Kearney, 1999). Feed material at about 84 purity can be raised to about 97 purity with 90% colour elimination and 96% invert elimination.

- Chromatography of cane molasses derivatives.

Chromatography has been suggested for recovering material other than sucrose. An example of this type of process is cane molasses fermentation followed by ethanol recovery and subsequent chromatography to recover glycerin and other compounds (Kampen and Saska, 1999). Another example is the separation of an invert rich syrup fraction from cane final molasses (Peacock et al., 1999). As opposed to sucrose separation, it was found in these laboratory and pilot scale studies that the presence of divalent cations in the molasses had no discernable effect on the chromatography step. The economic viability of the process was determined to be most sensitive to the product selling price.

- Chromatography of concentrated juice prior to crystallisation.

This process has been extensively tested and involves the chromatography of syrup obtained from filtered and softened cane juice (Kearney, 1997). An advantage of this process is that the sucrose is separated from nonsucrose and colour prior to crystallisation. The chromatographic step results in a syrup of about 98 purity. Therefore, when the extract (the sucrose fraction) is subsequently crystallised, the extraction of sucrose is much greater than with conventional processing. Although not always true, suspended solids which contaminate low purity sugar end syrups or molasses may be absent or at least present at much lower levels in high purity feed. Therefore, the chromatographic step may be less hindered by this material. Also, because of the upfront purification, the small amount of nonsucrose remaining in the product extract means that little low end equipment capacity is needed, i.e., crystallisation is primarily devoted to white sugar production.

In addition to increased sucrose extraction, certainly one of the most attractive aspects of this process is that white sugar can be produced directly in the cane mill (Kochergin et al., 2000, 2001). This represents a key difference from the chromatographic goals in the beet sugar industry where white sugar is already produced in the factory without an extra refining step.

Chromatography effects on colour, dextran and ash

Chromatography has an important practical effect on colour. Chromatography of impure sucrose solutions includes separation of components by molecular size so that a favorable separation of large and small size colour compounds can occur. Therefore, applied to chromatography products, conventional statements about the effect of colour on crystallisation are not necessarily valid. The colour compounds in the extract from chromatography have been found to be much less detrimental to crystallisation compared to the colour in conventionally derived syrups. Relatively high colour syrups obtained from chromatography of cane material can yield very low colour crystalline sucrose (Kochergin et al., 2000).

A similar result has been observed in the beet industry where white sugar is produced from chromatographic extract that has a colour very much higher than that required to obtain white sugar from conventional liquors.

Other beneficial characteristics of chromatography include its ability to eliminate ash and dextran from feed material (Kearick and Kearney, 1995). Sodium and potassium salts typically exhibit over 95% elimination while over 99% of dextrans can be removed. Salts are eliminated by an ion exclusion effect, while dextrans are removed by size exclusion.

Chromatography support equipment

In addition to the chromatography process itself, additional peripheral processes are required.

- Filtration

Cane derived solutions can contain large amounts of suspended solids which are detrimental to the long-term operation of resin-based chromatography systems. While several methods of solids removal are available (e.g., drum filtration, pressure leaf filtration and centrifugation), there is presently a strong interest in membranes. The detailed evaluation of membranes for cane processing has a long history (e.g., Nielsen et al., 1982) and a variety of membrane applications for the cane industry have been suggested which do not involve chromatography.

With respect to chromatography, membranes become of interest for the simple reason that membrane treated juice or syrup can prevent the long-term plugging of a chromatographic resin bed. Additional benefits such as colour reduction or partial nonsucrose elimination are desirable but not required for the chromatography process. This fact reduces the requirements of the membranes to suspended solids removal, a task which can be accomplished with relatively high flux, low-pressure micro-filtration.

- Juice or syrup softening

Softening is a conventional requirement for the chromatographic separation of sucrose syrups. The reason is that ion exchange resins are generally used for the chromatographic stationary phase and these
resins perform properly when they are in the mono-
valent form, particularly a mix of Na⁺ and K⁺. The 
resins separate poorly if they are converted to diva-
lent form. Furthermore, it has been observed that if 
the feed to a chromatography system is properly 
softened, it will not be necessary to regenerate the 
chromatographic resin during the life of the process.

Ion exchange softening can be accomplished 
using either weak or strong cation resins (Schoen-
rock, 1991). Systems based on both types are 
presently used in beet chromatography installations. 
For either type, there is no harmful waste regenerant. 
For example, weak cation softening typically returns 
a calcium sulfate regenerant waste to diffusion where 
it acts as a beneficial pulp pressing aid. For strong 
cation softening, the regenerant waste can be returned 
carbonation where the calcium is removed as a 
precipitate. Other strong cation softening methods 
include the use of internal streams such as molasses 
or raffinate for regeneration.

It is generally considered best to place softeners 
on low brix juice rather than subsequent syrups. The 
reason is that advantage can be taken of the softened 
 juice via evaporator scale reduction and, therefore, a 
softener can have both anti-scaling benefits and meet 
the subsequent chromatography requirements.

Evaporation

Because water is used as an eluent for the 
chromatography process, the products are dilute 
compared with the feed syrup. Typical water addition 
volume ratios on syrup are 2 water/syrup up to 
7 water/syrup. Subsequently, this water must be 
removed from the chromatography products prior to 
sucrose syrup storage or crystallisation and prior to 
storage or transport of byproducts.

The disposal of the concentrated nonsucrose 
byproduct(s) is a major concern for operators of chro-
matographic systems. The least valuable high salt 
content material, usually called raffinate, can be used 
for animal feed although the price may barely 
cover the cost of concentration. Additional separation of 
the nonsucrose fractions may provide saleable products.

Fractal technology and reductions in capital cost

Although simulated moving bed chromatography 
is an efficient method for separating sucrose from 
solutions, the equipment is relatively large and can 
have a high capital cost. For example, with chroma-
tography, a typical installation will treat 160 to 
250 kg nonsucrose/m³ of resin per day. For a plant 
treating 450 tonnes of 50 purity molasses per day at 
80% dry substance, the associated resin quantity 
required is about 765 m³ to 1130 m³. This large 
quantity of resin is generally distributed across several 
columns. Therefore, there is a major expense for the 
chromatographic resin, the large columns and associ-
ated peripherals. Clearly, a significant amount of space 
is also required along with the expense of a large 
blding.

Support equipment such as softening is also a 
major cost. A strong cation softener typically operates 
efficiently at about 10 bed volumes per hour exhaust-
ion flow rate. Therefore, a factory treating 450 m³/h 
of juice will require about 45 m³ of resin. However, 
this quantity typically will be much more because it is 
necessary to have a column in regeneration/standby 
and, additionally, it may be necessary to have more 
than one column exhausting in series in order to meet 
decalcification requirements.

A significant reduction of the size and cost of 
chromatography and peripheral unit processes will 
have an important effect on the extent of chromato-
graphy use in the cane industry.

One very recent advance offers size reduction of 
equipment by up to 90%. This approach involves the 
use of fractal structure to minimise fluid turbulence 
in the target process (Kearney et al., 1999; Kearney, 
2000). This method involves using engineered frac-
tals to scale fluids. Fluid scaling is a requirement for 
operations such as fluid mixing and fluid geometry 
transitions. An example is the introduction of a fluid 
to the top of a chromatography column. In this case, 
the fluid geometry entering the column should, 
assuming the most favorable result, quickly transition 
to a homogenous non-turbulent surface.

The scaling provided by engineered fractals can 
narrow the broad distribution of fluid properties ordi-

narily encountered when turbulent or inefficient 
scaling methods are used (Figure 1). Fractals can also 
 scale fluids with reduced energy loss compared with 
scaling via turbulence (turbulence is inherently an 
energy dissipation process). In this manner, an engi-
neered fractal can be used as an effective functional 
substitute for turbulence.

In general, fractals can potentially benefit pro-
cesses via reduction of energy use, decrease in equip-
ment size, uniformity of flow and efficiency of mass 
and heat transfer.

Table 1 lists the results of a comparison test of 
weak cation exchange softening using conventional 
and fractal technology (Kearney et al., 2001). The 
results are from a full-scale fractal softener instal-
lation in Paul, Idaho, USA operated over the 
2000–2001 campaign. Of particular importance is that 
the softener cells are only 10% of the size used in con-
ventional weak cation softening systems and about 
2% to 4% of the size used in conventional strong 
cation softening systems (fractal technology can, of 
course, also be applied to strong cation softening). 
Although operating at 10 times the flow rate used on 
a conventional weak cation softener, the pressure 
drop is very much lower—essentially insignificant.

The benefits observed with the fractal softener 
include a relatively low capital cost, a very small 
column, a correspondingly smaller amount of resin, 
a small amount of building space, a low-pressure cell 
design, small peripheral equipment and relatively low 
energy consumption.

Fractal technology is applicable to chromatog-
raphy systems as well, and to other factory processes 
which can benefit from precise control of fluid mixing, 
multi-fluid reactions, or fluid geometry transitions.

Conclusions

Industrial scale chromatography has been proven 
to be efficient and reliable in the beet sugar industry.

The progressive narrowing of the distribution of a fluid property as a fractal is iterated to smaller and smaller scale. The distribution could represent, e.g., a concentration band, fluid velocities, particle/bubble size or eddy size.

Table 1—An example of process size reduction using fractal technology.

<table>
<thead>
<tr>
<th></th>
<th>Conventional weak cation softener</th>
<th>Fractal weak cation softener</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin bed depth (m)</td>
<td>1.0 or more</td>
<td>0.15 or less</td>
</tr>
<tr>
<td>Exhaustion flow rate (bed volumes per hour)</td>
<td>50</td>
<td>500</td>
</tr>
<tr>
<td>Bed pressure drop exhaustion (kPa)</td>
<td>350–550</td>
<td>7 or less</td>
</tr>
<tr>
<td>Relative process size</td>
<td>1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Only a few chromatography installations have been operated in cane plants and these have been devoted to conventional molasses separation. A number of current studies have demonstrated that entirely new chromatography schemes may offer much more favorable methods of using this technology in the cane sugar industry. Recent significant reductions in the size and cost of chromatography equipment and chromatography support equipment add to the viability of these new concepts.

REFERENCES


APPLICATION DE LA CHROMATOGRAPHIE EN SUCRERIE DE CANNE

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Résumé
L'utilisation de la chromatographie, avec des solutions de saccharose, est bien établie. Aux USA plus de 90% des mélasses de bettraves sont traitées par chromatographie, d'une façon ou d'une autre. La plus grande unité (American Crystal Co, Hillsboro, North Dakota) traite 545 tonnes de mélasses avec 80% de matières sèches par jour. Deux autres unités (Amalgamated Sugar Co) traitent plus de 455 tonnes par jour. Les sucres obtenus et l'efficience de cette approche indiquent qu'il est possible de traiter des sirops de canne. Les couts d'installation et de l'équipement peuvent être réduits grâce à des innovations récentes, comprenant la technologie basée sur les fractals. Ces développements devraient faciliter l'utilisation de la chromatographie.

Mots clefs: Chromatographie, Fractals, Adoucissement, Membrane, Couleur.

APLICACIÓN DE LA CROMATOGRAFÍA EN LA INDUSTRIA AZUCARERA DE LA CAÑA DE AZÚCAR

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Resumen
La cromatografía industrial aplicada a soluciones de sacarosa se ha constituido en una tecnología moderna y confiable. Solamente en los Estados Unidos, más del 90% de la producción total de mieles de remolacha se trata de alguna manera por vía cromatográfica. La mayor aplicación de esta técnica se encuentra en una planta de la American Crystal Sugar Co, localizada en Hillsboro, North Dakota. Está planta procesa más de 545 t/d de mieles con un 80% de materia seca. Por otra parte dos plantas de la compañía Amalgamated Sugar Co. que procesan cada una más de 455 t/d también utilizan esta tecnología. La alta eficiencia observada en el uso de la cromatografía en el proceso de la sacarosa y el histórico éxito de su empleo llevarán necesariamente a la aplicación general de la cromatografía a escala industrial para jarabes y maladuras. Recientes innovaciones que reducen el tamaño de los sistemas industriales de cromatografía y equipos periféricos asociados usando tecnología fractal reducirán significativamente los costos y necesidades de capital que conducirán a aplicaciones generales más aproximadas a la realidad de la cromatografía en el análisis de soluciones provenientes de la caña.

Palabras claves: cromatografía, fractal, suavizamiento, membranas, color.