Chromatographic applications in the cane sugar industry

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Abstract

Industrial chromatography of sucrose containing solutions is a mature and reliable technology. In the United States alone, over 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 metric t/day of 80% dry substance molasses. Two Amalgamated Sugar Co. plants each process more than 455 metric t/day. 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. A variety of possible applications have been proposed and recent innovations which reduce the size of industrial chromatography systems and associated peripheral equipment 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 organized 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 disorganization of the plant material to yield a highly disordered mixture. 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 crystallize 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.

The subject of this paper, 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 media 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 favorable 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.

Figure 1 is a simple illustration of cane syrup chromatography through a column containing a strong cation ion exchange resin. In the illustration, flow through the column is in the downward direction. Note that salts and high molecular weight compounds move more quickly than smaller organic compounds. This is due to an ion

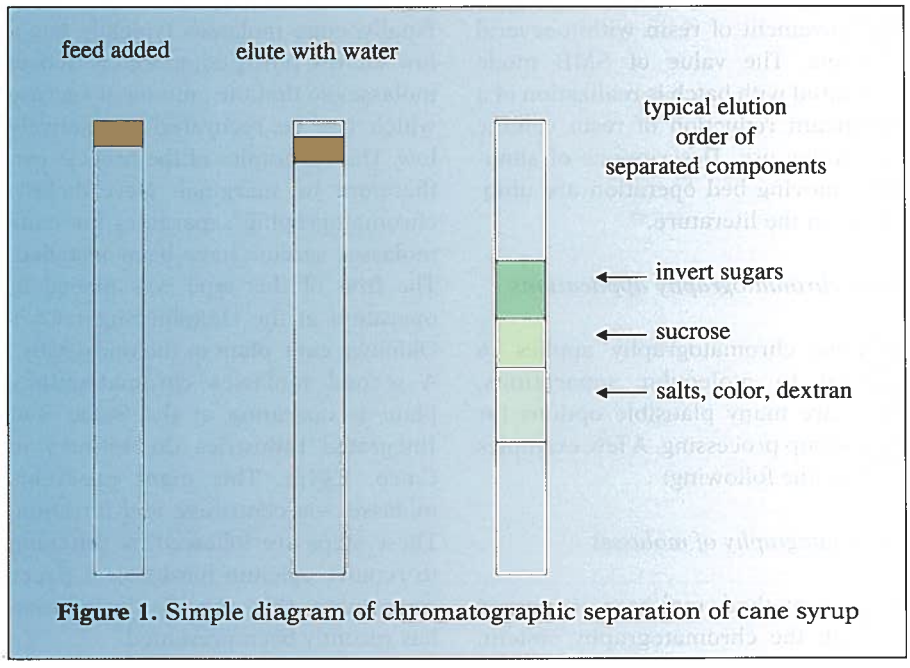

Figure 1. Simple diagram of chromatographic separation of cane syrup

Figure 2. A simulated moving bed system for chromatography of beet molasses

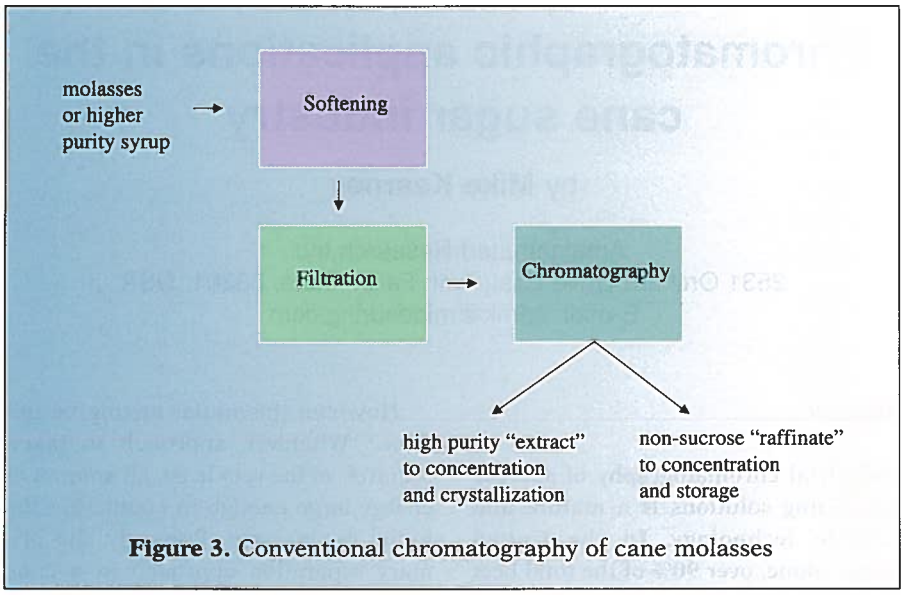

Figure 3. Conventional chromatography of cane molasses

exclusion effect and a partitioning due to molecular weight. Small organics such as invert trail to the greatest extent.

The chromatography of sucrose solutions has a long history. In 1953 it was determined that ionizable compounds could be separated from non-ionic compounds by passage through ion exchange resins.[1] By 1956 it was known that color and ionic materials could be excluded from resin, thus purifying sucrose.[2] Evaluation of the chromatography of blackstrap molasses dates back at least to 1970 and it was recognized at that time that both sucrose and invert could be viable products from such a process.[3] While early work focused on batch chromatography (as in Figure 1), presently the most popular configurations for the industrial separation of sucrose solutions are simulated moving beds (SMB). In this method, valve switching is incorporated to simulate the movement of resin within several columns. The value of SMB mode compared with batch is realization of a significant reduction of resin volume and water use. Descriptions of simulated moving bed operation are ubiquitous in the literature.[4,5]

Cane chromatography applications

Because chromatography applies in general to molecular separations, there are many plausible options for cane syrup processing. A few examples include the following:

Chromatography of molasses

In this method molasses is passed through the chromatography system. Over 90% of the beet molasses produced in the United States is processed in this manner. Figure 2 illustrates such a plant operating at an Amalgamated Sugar Company facility in Twin Falls, Idaho. Why is this technology not common in the cane industry? One reason 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. Some of these suspended solids, such as gums and waxes, can also have characteristics which interfere with filtration. A second drawback is the relatively high level of hardness in cane molasses which must be removed prior to chromatographic separation. Finally, 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.[6] A second 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.[7]

Figure 3 illustrates a simplified flow scheme for conventional chromatography of cane molasses or higher purity syrups. The softening step can be via ion exchange or chemical precipitation. An additional benefit can be obtained by placing the softening step at an upstream location so that advantage is taken of the non-scaling characteristics of the treated juice.

Overall, it is 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.[8] Feed material at about 84 purity can be raised to about 97 purity with 90% color elimination and 96% invert elimination. As with cane molasses, the feed material requires filtration in order to avoid chromatography bed plugging and a softening step must be used to remove divalent cations.

Chromatography of inverted molasses

This method involves the separation of an invert rich fraction from cane molasses.[9,10] The concept is to first invert all of the sucrose in molasses and then separate the invert from the solution. Figure 4 illustrates the

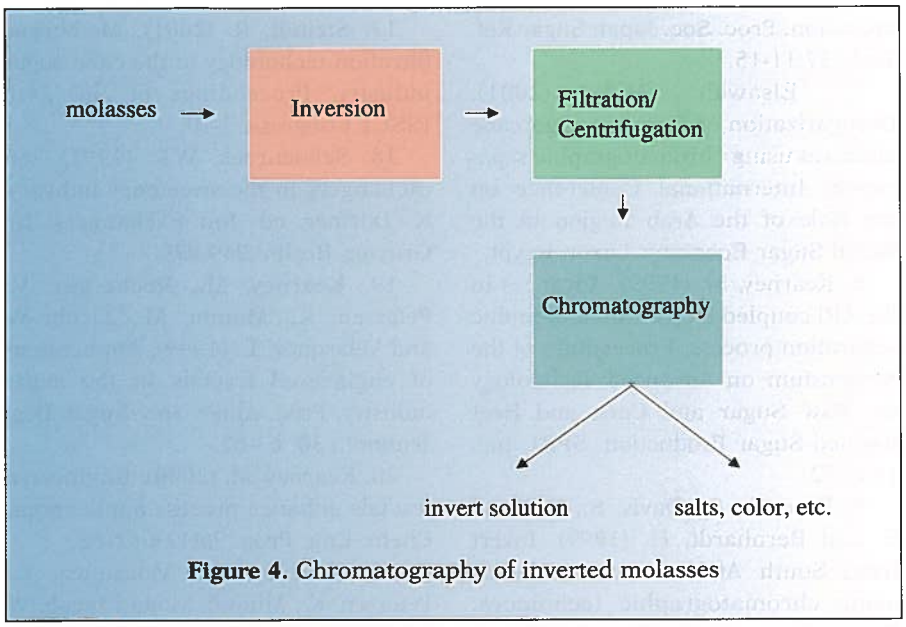

Figure 4. Chromatography of inverted molasses

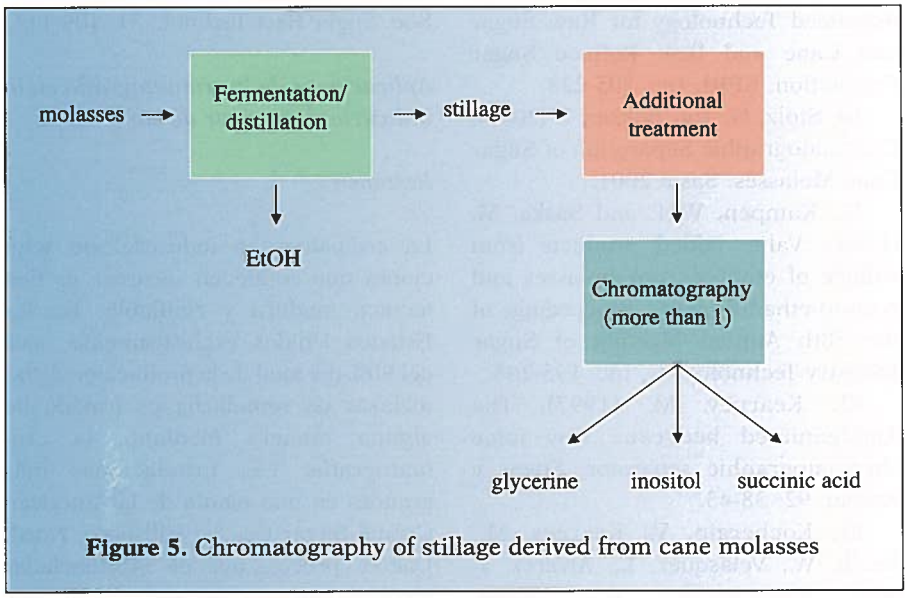

Figure 5. Chromatography of stillage derived from cane molasses

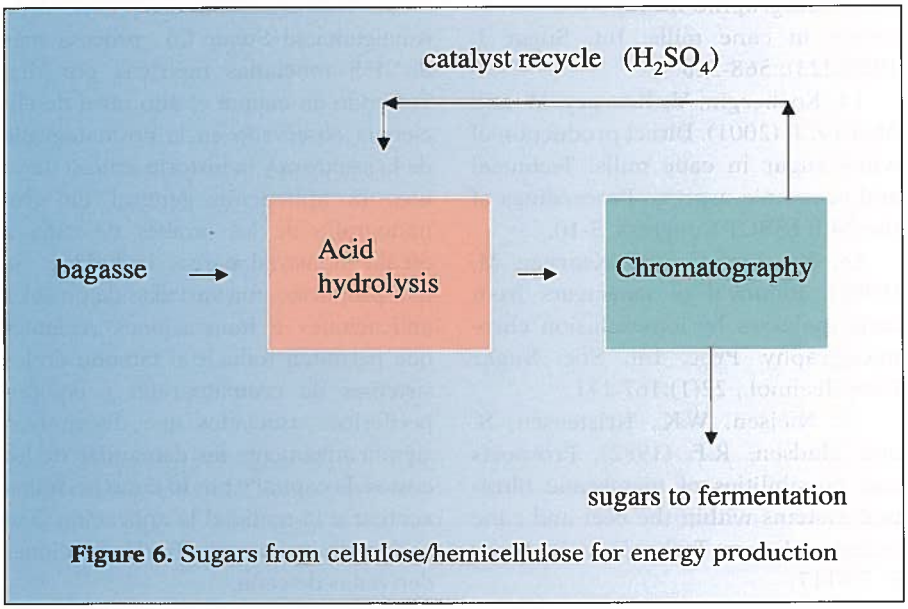

Figure 6. Sugars from cellulose/hemicellulose for energy production

process in general. Inversion is first accomplished, for example, by using sulfuric acid. The resulting precipitate can be removed by centrifugation and/or filtration. As opposed to sucrose separation, it has been found in laboratory and pilot scale studies that the presence of divalent cations in the molasses has no discernable effect on the chromatography step. This is an important characteristic since softening can be a difficult and expensive step. The recovered invert can be cleaned-up for use as a product or used in subsequent processing steps.

Chromatography of cane molasses derivatives

More involved chromatography schemes have been suggested for recovering material other than sucrose or invert. An example is cane molasses fermentation followed by ethanol recovery and subsequent chromatography to recover glycerin and other compounds.[11] Figure 5 illustrates such a process.

Chromatography of hydrolyzed bagasse and fuel alcohol production

Cellulose and hemicellulose can be catalytically hydrolyzed by acid to produce the simple sugars glucose and xylose. Fermentation of these sugars can lead to ethanol for energy use. Although the process of acid hydrolysis of biomass is an old concept, a drawback has been the requirement of neutralization of the hydrolysate and production of a neutralized acid waste. Chromatography can be used to separate the sugars from the acid and therefore allow for re-use of the catalyst without additional chemicals or waste production. Figure 6 illustrates a chromatographically based catalyst recycle loop.

Chromatography of concentrated juice prior to crystallization

This process has been extensively tested and involves the chromatography of syrup obtained from filtered and softened cane juice.[12] An advantage of this process is that sucrose is separated

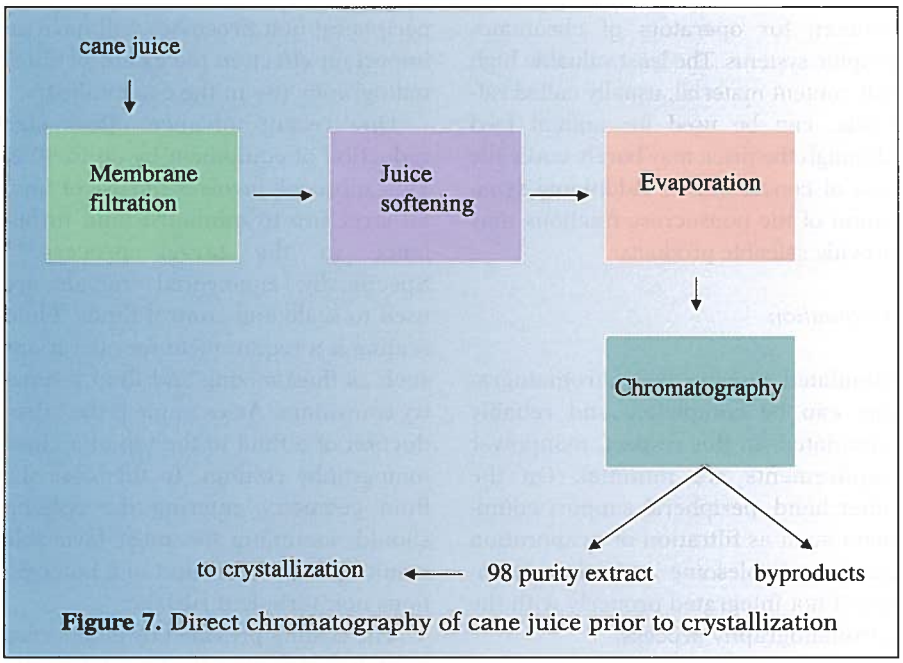

Figure 7. Direct chromatography of cane juice prior to crystallization

from nonsucrose and color prior to crystallization. Chromatography is therefore used as a first step instead of a last step in cane processing. The chromatographic step results in a syrup of about 98 purity. Therefore, when the extract (the sucrose fraction from chromatography) is subsequently crystallized, 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., crystallization is primarily devoted to white sugar production. Figure 7 illustrates this process.

In addition to increased sucrose extraction, certainly one of the most attractive aspects of this method is that white sugar can be produced directly in the cane mill.[13,14] 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.

An alternative use of this technology is for expansion of mill capacity. A slip stream of juice can be treated by this process with the resulting purified sucrose stream added to the existing syrup to crystallization. By this means expansion is possible without alteration of existing equipment and with very little change made to the existing mill crystallization procedure.

Chromatography effects on color, dextran and ash

Chromatography has an important practical effect on color. Chromatography of impure sucrose solutions includes separation of components by molecular size so that a favorable separation of large and small size color compounds can occur. Therefore, applied to chromatography products, conventional statements about the effect of color on crystallization are not necessarily valid. The color compounds in the extract from chromatography have been found to be much less detrimental to crystallization compared to equivalent ICUMSA color in conventionally derived syrups. Therefore, relatively high color syrups obtained from chromatography of cane material can yield very low color crystalline sucrose.[14]

A similar result has been observed in the beet industry where white sugar is produced from chromatographic extract that has a color 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.[15] 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 and a variety of membrane applications for the cane industry have been suggested which do not involve chromatography.[16,17]

However, 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 color 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 strong cation ion exchange resins are generally used for the chromatographic stationary phase and these resins perform properly when they are

in the monovalent form, particularly a mix of Na^+ and K^+. The resins separate poorly if they are converted to divalent 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.

Softening can be accomplished using either chemical precipitation or ion exchange. Ion exchange softening can be accomplished using either weak or strong cation resins . Systems based on both types of resin are presently used in beet chromatography installations. For either type, the avoidance of harmful waste regenerant is a necessity. 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 to 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.[18]

It is generally considered best to place ion exchange 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. Therefore a softener can provide both anti-scaling benefits and provide a syrup which meets 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. The amount of water used is dependent on both the feed syrup brix (lower feed brix requires a lower ratio of water) and the efficiency of the chromatographic separator. Subsequently, this water must be removed from the chromatography products prior to sucrose syrup storage or crystallization and prior to storage or transport of byproducts.

The disposal of the concentrated nonsucrose byproduct(s) is a major concern for operators of chromatographic 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.

Automation

Simulated moving bed chromatography can be completely and reliably automated. In this respect, manpower requirements are minimal. On the other hand, peripheral support equipment such as filtration or evaporation can be troublesome and labor intensive if not integrated properly with the chromatography process.

Reductions in capital cost

Although simulated moving bed chromatography is an efficient method for separating sucrose and other components from solutions, the equipment is relatively large and can have a high capital cost. For example, with chromatography a typical installation will treat 160 to 250 kg nonsucrose/m^3 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 m^3 to 1130 m^3. 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 associated peripherals. Clearly, a significant amount of space is also required along with the expense of a large building.

Support equipment such as softening is also a major cost. A strong cation softener typically operates efficiently at about 10 bed volumes per hour exhaustion flow rate. Therefore, a factory treating 450 m^3/h of juice will require about 45 m^3 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 chromatography use in the cane industry.

One recent advance offers size reduction of equipment by up to 90%. This approach involves the use of fractal structure to minimize fluid turbulence in the target process.[19,20] Specifically, engineered fractals are used to scale and control 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 ordinarily encountered when turbulent or inefficient scaling methods are used. A distribution could represent, for example, a concentration band, fluid velocities, particle/bubble size or eddy size.

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 engineered fractal can be used as an effective functional substitute for turbulence.

In general, fractals can potentially benefit processes via reduction of energy use, decrease in equipment size, uniformity of flow and efficiency of mass and heat transfer.

A comparison test of weak cation exchange softening using conventional and fractal technology serves as an example.[21] The results are from a full scale fractal softener installation 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 conventional 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 chromatography 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 efficient and reliable in the beet sugar industry. 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

1. Wheaton, R.M. and Bauman, W.C. (1953). Ion exclusion, a unit operation utilizing ion exchange materials. Ind. Eng. Chem. 45(1): 228-233.

2. Asher, D.R. (1956). Sugar purification by ion exclusion. Ind. Eng. Chem. 48: 1465.

3. Zievers, J.F., Novotny, C.J. and Selvick, E.A. (1972). Ion exclusion, an overlooked ally. The Sugar Journal. 34(9): 7-10.

4. Rearick, G. and Kearney, M. and Costesso, D. (1997). Simulated moving bed technology in the sweetener industry. Chemtech. 27(9): 36-40.

5. Broughton, D.B. (1968). Molex: Case history of a process. Chem. Eng. Prog. 64(8): 60-65.

6. Kakihana, I. (1989). Sugar recovery from cane molasses by continuous chromatographic separation process. Review of three years commercial operation. Proc. Soc. Japan Sugar Ref. Tech. 37:11-15.

7. Elsawah, M.A. (2001). Desugarization of Egyptian sugarcane molasses using chromatographic separation. International Conference on the Role of the Arab Region in the World Sugar Economy. Luxor, Egypt.

8. Kearney, M. (1999). Advances in the ARi coupled loop chromatographic separation process. Proceedings of the Symposium on Advanced Technology for Raw Sugar and Cane and Beet Refined Sugar Production. SPRI, Inc. 163-172.

9. Peacock, S., Davis, S., Walford, S. and Bernhardt, H. (1999). Invert from South African cane molasses using chromatographic techniques. Proceedings of the Symposium on Advanced Technology for Raw Sugar and Cane and Beet Refined Sugar Production. SPRI, Inc. 205-228.

10. Stolz, N. and Bekker, P. (2001). Chromatographic Separation of Sugar Cane Molasses. Sasta 2001.

11. Kampen, W.H. and Saska, M. (1999). Value added products from stillage of ethanol-from-molasses and corn-to-ethanol plants. Proceedings of the 58th Annual Meeting of Sugar Industry Technologists, Inc. 195-208.

12. Kearney, M. (1997). The Amalgamated beet/cane raw juice chromatographic separator. Sugar y Azucar. 92: 38-43.

13. Kochergin, V., Kearney, M., Jacob, W., Velasquez, L., Alvarez, J. and Baez-Smith, C. (2000). Chromatographic desugarization of syrups in cane mills. Int. Sugar J. 102(1223): 568-578.

14. Kochergin, V., Kearney, M. and Alvarez, J. (2001). Direct production of white sugar in cane mills: Technical and economic aspects. Proceedings of the 24th ISSCT Congress. 3-10.

15. Rearick, G. and Kearney, M. (1995). Removal of nonsugars from cane molasses by ion-exclusion chromatography. Proc. Int. Soc. Sugar Cane Technol., 22(1):167-171.

16. Nielsen, W.K., Kristensen, S. and Madsen, R.F. (1982). Prospects and possibilities of membrane filtration systems within the beet and cane industry. Sugar Technology Reviews. 9: 59-117.

17. Steindl, R. (2001). Membrane filtration technology in the cane sugar industry. Proceedings of the 24th ISSCT Congress. 3-10.

18. Schoenrock, W.R. (1991). Ion exchangers in the sweetener industry. K. Dorfner, ed. Ion Exchangers. De Gruyter, Berlin. 949-979.

19. Kearney, M., Kochergin, V., Petersen, K., Mumm, M., Jacob, W. and Velasquez, L. (1999). Applications of engineered fractals in the sugar industry. Proc. Amer. Soc. Sugar Beet Technol., 30: 63-67.

20. Kearney, M. (2000). Engineered fractals enhance process applications. Chem. Eng. Prog. 96(12): 61-68.

21. Kearney, M., Velasquez, L., Petersen, K., Mumm, M. and Jacob, W. (2001). The fractal softener. Proc. Amer. Soc. Sugar Beet Technol., 31: 109-114.

Aplicaciones de la cromatografía en la industria del azúcar de caña

Resumen

La cromatografía industrial de soluciones que contienen sacarosa es una técnica madura y confiable. En los Estados Unidos exclusivamente, más del 90% del total de la producción de las melazas de remolacha es tratado de alguna manera mediante la cromatografía. Las instalaciones más grandes en una planta de la American Crystal Sugar Co., en Hillsboro, North Dakota, procesa más de 545 toneladas métricas por día del 80% de melazas secas. Cada una de las dos plantas de la Amalgamated Sugar Co,. procesa más de 455 toneladas métricas por día. Teniendo en cuenta el alto nivel de eficiencia observado en la cromatografía de la sacarosa y la historia exitosa de su uso, la aplicación general de cromatografía de los jarabes de caña a escala industrial parece ineludible. Se han propuesto una variedad de posibles aplicaciones e innovaciones recientes que permiten reducir el tamaño de los sistemas de cromatografía y equipos periféricos asociados que disminuyen significativamente las demandas de los costos de capital y por lo tanto permiten acercar a la realidad la aplicación general de la cromatografía de soluciones derivadas de caña.