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Pilot-Scale Studies of Sugar Separations by Continuous Chromatography

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ABSTRACT

A pilot-scale continuous chromatograph has been developed for optimization studies and scaling factor evaluations. The continuous annular chromatograph consists of a slowly rotating annular bed of ion exchange resin to which feed is continuously introduced at a stationary point at the top of the bed while eluent flows over the remainder of the annulus. The rotation of the sorbent bed coupled with the simultaneous elution chromatography causes the separated components of the feed stream to appear as helical bands, each of which has a characteristic, stationary exit point.

The separation of sucrose, glucose, and fructose, using the calcium form of cationic ion exchange resin, uses water as the isocratic eluent. A synthetic mixture of the sugar was explored in fixed columns, then on a bench scale unit. The results almost perfectly scaled to the pilot unit when loading was low and feed mixtures were of low viscosity. Factors such as column loading, feed-to-eluent ratio, and feed concentration were explored. An industrial sugar mixture containing the three sugars and a number of higher molecular sugars was successfully separated. Based on these results, recommendations are made concerning an optimized scaling of the process.

Index Entries: Chromatography; ion exchange; sugars; separations; scaleup.

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NOMENCLATURE

a Particle-fluid interfacial area, cm^2
c Liquid-phase solute concentration, g/cm^3
c_F Feed solute concentration, g/cm^3
c^* Equilibrium concentration, g/cm^3
D_z Axial dispersion coefficient, $g/cm^2/s$
D_θ Angular dispersion coefficient, g/cm^2
k_o Global mass transfer coefficient, cm/s
K Equilibrium distribution coefficient
q Sorbent solute concentration, g_{solute}/g_{solid}
Q Column loading of solute, g_{solute}/g_{solid}
Q_F Feed flowrate, g/s
Q_T Total flowrate, g/s
R_o Outside radius of annular bed, cm
t Time, s
$\hat{t}$ Chromatographic time, s
u Superficial velocity, cm/s
z Bed axial position, cm
ϵ Bed void fraction
θ Displacement from feed point, radians
θ_E Elution angle, radians
θ_F Feed angle, radians
ω Rotation rate, radians/s

INTRODUCTION

Largescale separation of the materials that are produced as mixtures in bioprocessing is necessary to successful operation. Sugar stereoisomers provide an example of such a system in which an improved separation method is sought, and in which an improved continuous chromatographic method would contribute significantly to the progress. The glucose–fructose separation, in particular, is an industrially significant fractionation. The most common type of fructose syrup, usually called a high-fructose corn syrup (HFCS), contains 42% fructose, 52% glucose, and 6% oligosaccharides on a dry-wt basis. It is used as a sucrose replacement in some foods and beverages, since fructose is 1.3–1.8 times sweeter than sucrose.

The method of choice for the separation of sugars used a calcium-exchanged, strong-acid-type, cation exchange resin as a chromatographic medium. The separation occurs as a result of the combined effects of size exclusion and restricted diffusion, as well as by virtue of specific interactions between calcium ions held by the resin and the hydroxyl groups of different sugars.

Glucose and fructose can freely penetrate the matrix of resins with a 4–12% degree of crosslinking, and a coordination complex with calcium ions may be formed that determines their distribution coefficient. Both

glucose and fructose are cyclic sugars (pyranoses) and exist as different anomers, the α- and β-forms, which exist in solution as an equilibrium mixture. β-D-fructose is the predominant fructose form, but glucose exists as one-third α- and two-thirds β-D-glucose. Thus, one observes three peaks in the glucose–fructose chromatogram, with the α-D-glucose appearing as a shoulder on the β-D-glucose, and the β-D-fructose following as a fully resolved peak. Sucrose and other higher-molecular-weight oligosaccharides interact only very weakly with the hydration sphere of calcium ions, and because of their larger molecular size they are excluded from the resin matrix.

Finnish Sugar Co. has designed and built several chromatographic systems for the separation of sucrose from beet molasses and the recovery of crystalline fructose. American Xyrofin has a plant in Thomson, IL, which produces 27.5 million pounds of crystalline fructose per year; the chromatographic separation system used in this plant is made up of 17 separation columns and 8 crystallizers. This system converts a high-dextrose syrup to fructose by using immobilized glucose isomerase; fructose is then isolated from other sugars in chromatographic columns. In all commercial operations to date the chromatographic separation is *semicontinuous,* since the feed solution and eluent enter the column in a cyclical sequence.

Because of the large scale of the operation, a *continuous* operation would be desirable from the viewpoints of efficient adsorbent utilization and simplicity of operation. An efficient fructose–glucose separation may be achieved in a sample simulated countercurrent adsorption system, but the fructose product, although high in purity, is greatly diluted relative to the feed concentration, making it necessary to expend energy on reconcentration of the product. In the more practical UOP "Sorbex" process, a simulated recycled moving-bed system, an effective countercurrent operation is achieved by the sequential movement of the feed and exit ports through the bed in the direction of fluid flow. It has been successfully applied to the separation of glucose–fructose mixtures on a calcium-form ion exchange resin. However, the process allows only two products, thus allowing the purification of only one specie. Further, the process is mechanically complex. Recently, some studies have been initiated to explore the separation of sugars, using the continuous annular chromatograph CAC, which operates at steady state, is mechanically simpler, and potentially allows the full range of features that have been developed for the liquid chromatograph. This study also traced the development of the concept. Of importance to this study is the ability to perform multicomponent separations and simultaneous chromatographic purification of the products in a single operation. Efficiency of adsorbent utilization is dependent on experimental design.

A conceptual drawing of the CAC operated in isocratic mode is given in Fig. 1. The CAC consists of an annular bed of adsorbent particles, packed in the space between two concentric cylinders. As the column assembly

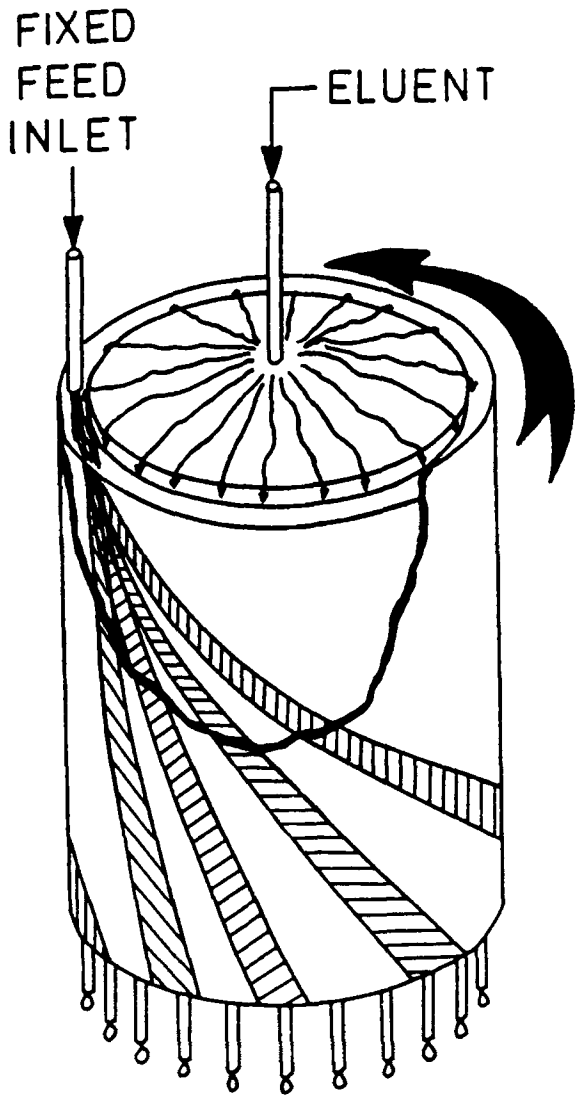

Fig. 1. Conceptual diagram of the continuous annular chromatograph (CAC) operating in isocratic mode.

slowly rotates around its axis, eluent and feed solutions are continuously fed into the top of the annular bed. The eluent is uniformly fed to the entire circumference, whereas the feed mixture is introduced in only a sector of the circumference that is stationary in space. As time progresses, helical component bands develop from the feed point, with slopes redependent on eluent velocity, rotational speed, and the distribution coefficient of the components. These bands are stationary in space and exit at fixed exit points at the bottom of the annular bed. Under constant conditions, the angular displacement of each component exit band from the feed point

remains constant. Hence, the rotating annular chromatograph is a truly continuous, steady-state process. A more detailed description of the bench scale apparatus is given elsewhere.

In the previous study, we showed the feasibility of the sugar separation, and performed some low-to-medium concentration experiments on a bench scale unit. The objectives of the current study are as follows.

1. The scale-up of the glucose–fructose separation to pilot scale, based on the information from a small batch column;
2. The use of industrial feedstocks from corn and sugar beet sources, comparing these results with those of synthetic mixtures;
3. The testing of the capacity of the unit with high feed concentrations and flowrates.

From these results, a prediction of the capacity and separating capacities of industrial size CAC units is evaluated.

EXPERIMENTAL

Since the objective of the investigation was the comparison of results from a fixed column with a pilot scale CAC, both types of facilities are described in this section. A typical fixed column was used, consisting of a straight 0.95 cm ID tube, 106.7 cm long, equipped with a sample loop isolated by a multiposition valve and pumping system. A bed of calcium-form Dowex 50W-X8 resin with a narrow particle size range (average 50 μm) was used for the pilot scale experiments and packed to a depth of 107 cm. At zero time the feed sample was injected by the diversion of the eluent that is continuously pumped by an Altex Model 104 pump. To minimize tailing effects in the feed, the loop was bypassed at the end of the nominal sample time. The column the pressure drop was continuously monitored.

Figure 2 is a schematic drawing of the construction details of the 445-mm-diam pilot scale CAC used in this study. The annulus is formed from two concentric open cylinders, both of which are flanged at the bottom and constructed of Carpenter 20 steel and pressure rated for 1.15 MPa (165 psia). The inner cylinder which is 100 mm shorter than the outer cylinder, is closed at the top, allowing head room for stationary feed and eluent lines. The resin is packed within the 31.7-mm-wide annulus to a depth of 107 cm with 8.5-cm-thick layer of 0.18-mm glass beads is placed on top of the resin, filling the remaining annular depth. If the feed is imbedded in the resin, the stationary feed tubes plow up the resin, significantly disrupting the top layers of the bed. If the feed tubes end in the glass layer, the beads flow around the tubes without significantly disturbing the bed. Secondly, distribution of feed and eluent occurs within the bead layer without significant convection, thus minimizing mixing of adja-

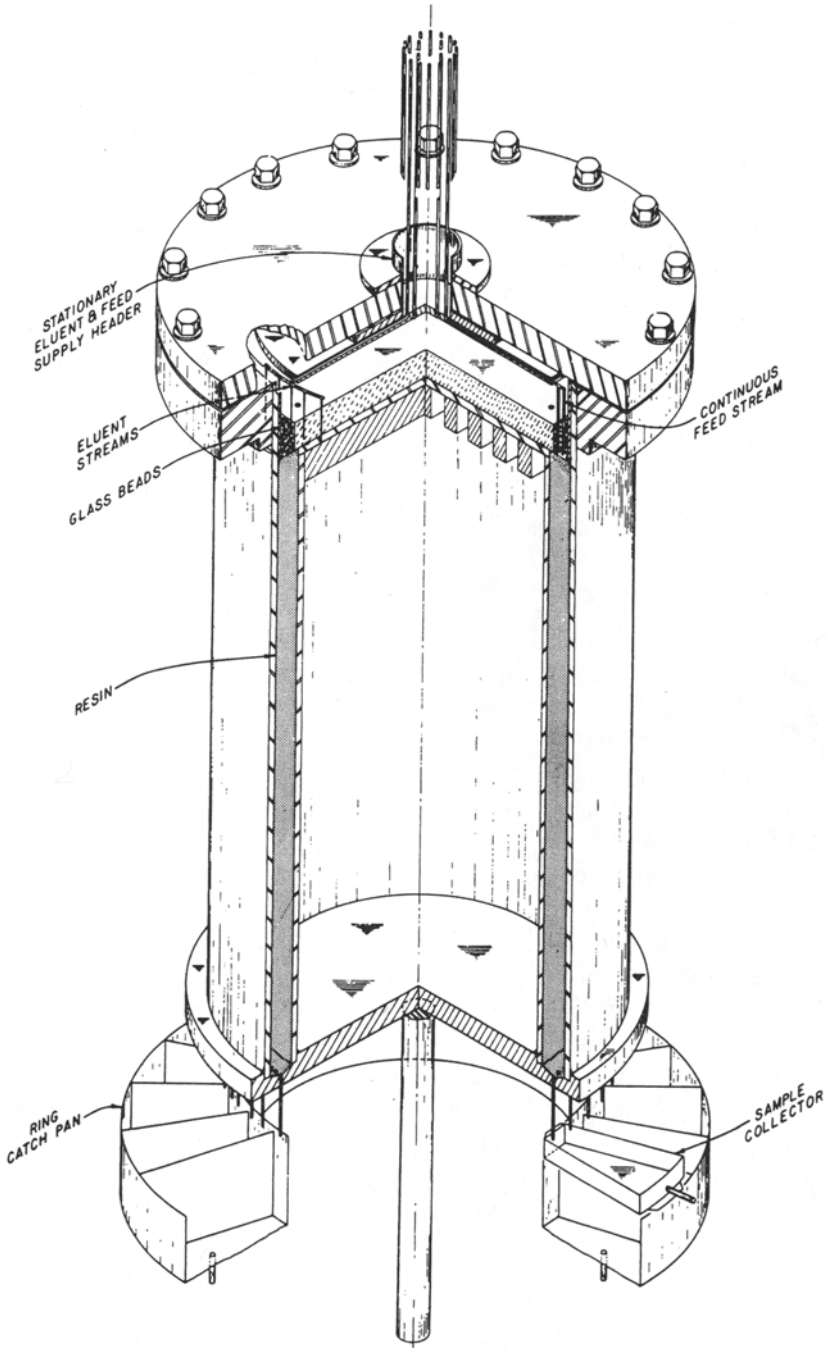

Fig. 2. Construction detail of the continuous annular chromatograph illustrating the 445-mm-pilot scale unit.

cent streams. This approach has given bed inlet band widths for streams of similar viscosities that are proportional to the inlet streams. Eluent and feeds are introduced through a stationary inlet distributor that extends through the top flange and is sealed by two O-rings contained in the flange. In the isocratic mode used in sugar separations the head space is flooded with the eluent. All entering streams are controlled by metering pumps to within 1%. A digitally-controlled drive system causes slow rotation of the column, including the exit tubes. Porous, high-density polyethylene plugs located at the top of each exit hole provide support for the sorbent bed while permitting the effluent to exit through 120 individual exit tubes.

A preliminary monitoring of the separation performance of the CAC unit can be readily determined by connecting an in-line, continuous detection instrument with a single eluate exit tube. As the CAC rotates, the the eluate tubes also rotate, and the detector receives eluate from all circumferential points as the apparatus completes a 360° turn. Thus, if the concentration-detection instrument is attached to a timer, an apparently conventional (i.e., concentration vs time) chromatogram is recorded. Angular concentration profiles are immediately obtained, considering that the angular displacement from the feed point, θ, is related to the recorded time, t, and to the rotation rate, ψ, by $\theta = \psi t$. In practice, the connection between one of the eluate exit tubes and a Waters Model R401 Differential Refractometer was provided by a digitally controlled Constametric pump to insure constant flow, equal to 1/120 of the total eluent flowrate. In some of the experiments it was necessary to dilute the sugar stream from the CAC to remain within the response range of the refractometer. Diluent water was mixed into the sample line, with its flow controlled by a metering pump. The millivolt signal from the detector was converted to a digital signal by an A/D conversion board (Data Translation Model 2801) interfaced to a microcomputer (NCR Model PC8) for graphical display and digital data storage. Calibrations were obtained for two materials Blue Dextran 2000 (a high mol wt polysaccharide used to determine bed void fraction), and glucose. The response of the sugars used in this study are the same. A photograph of the experimental operation showing the control panel and data acquisition equipment appears as Fig. 3.

Three mixtures were used to explore the separation of glucose-fructose mixtures. First, a dilute synthetic mixture containing reagent grade glucose (25 g/L), fructose (25 g/L), sucrose (10g/L), and Blue Dextran (1.0 g/L). The latter is a polysaccharide is used in this case to evaluate void fraction and the sucrose simulates the behavior of the oligosaccharides in the typical industrial mix. Two industrial sugar mixtures were used in the scaling studies. First, a corn based glucose–fructose mixture containing 60 wt% solids, about 5% of which were unknown high molecular weight material. The second mixture, which again contained a predominance of glucose and fructose, was an inverted beet sugar. Of the 80% solids in the as-received mixture impurities accounted for approximately 10%. The

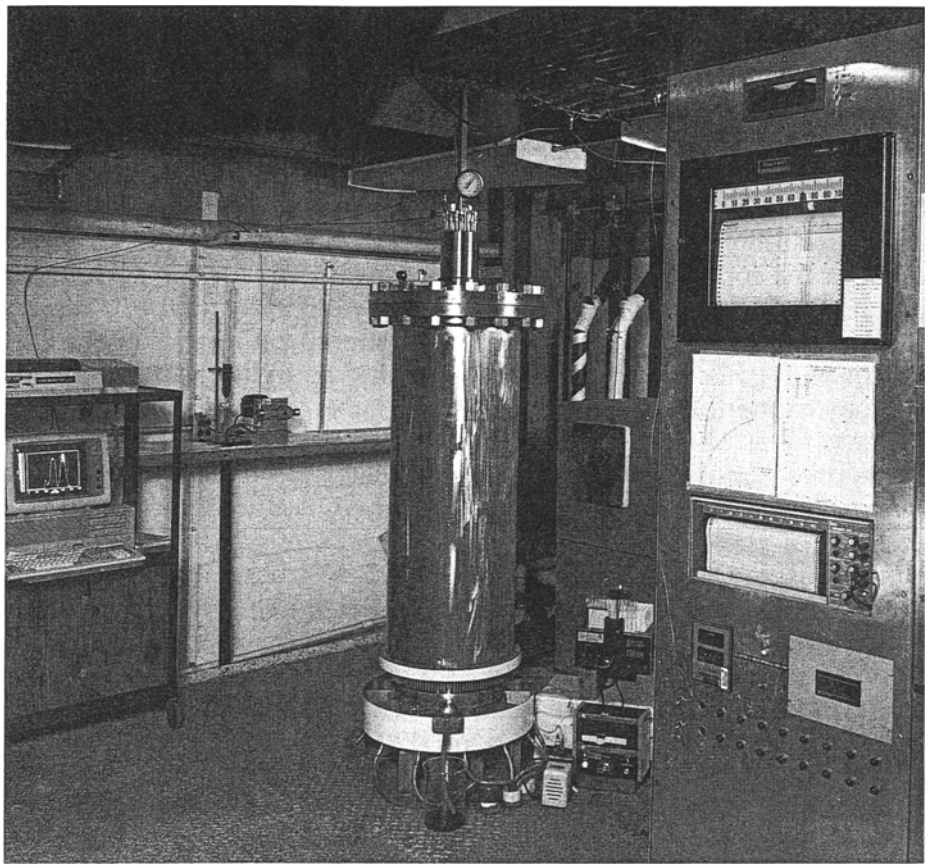

Fig. 3. A photograph of the 445-mm pilot scale CAC, showing data acquisition and auxiliary equipment.

latter two mixtures were provided by industrial interests. Feed mixtures were diluted with deionized distilled water without further purification. The isocratic eluent was deionized distilled water.

The method selected for analyzing the concentrations of the three main species, glucose, fructose, and sucrose depended on whether there was complete resolution of the species in the continuous chromatograph. A liquid chromatography (Perkin Elmer Series 410) using an Biorad Aminex HPX-87C column at 85°C was the favored method where there was overlap of the peaks. This involved taking samples during the continuous separation and subsequently injecting these samples into the Perkin Elmer chromatograph. In cases where complete resolution of the species was obtained in the continuous chromatograph, a continuous trace of total sugar concentration as a function of angular position was based on the calibrated response of a differential refractometer. The latter technique could also be used in cases where there was incomplete resolution to

monitor the total sugar concentration in real time. This allowed monitoring of the runs in all instances, as well as providing a check on the closure of the material balance.

THEORETICAL DISCUSSION

As has been previously shown, a uniformly-packed annular sorbent bed with void fraction ϵ, the following steady-state continuity equation may be written for a solute with concentration c

$$\epsilon D_z \partial^2 c / \partial z_2 + \epsilon D_\theta / R_0^2 \partial^2 c / \partial \theta^2 = \omega \epsilon \partial_c / \partial \theta + \omega(1-\epsilon) \partial_q / \partial \theta + u \partial c / \partial z \quad (1)$$

where D_z and D_θ are the axial and angular dispersion coefficients, ω is the rate of rotation, R_0 is the outside radius of the annular chromatograph, u is the fluid superficial velocity, and z and θ the axial and angular coordinates, respectively. This is similar to the equivalent fixed-packed bed case with the exception that in the latter case there can be no angular dispersion, and time t is related to θ through the angular velocity, as follows

$$t = \theta / \omega \quad (2)$$

The concentration of solute in the sorbent, q, and the fluid phase concentration, c, are related by a rate equation. Following Sherwood, Pigford and Wilke, a film model equation to describe fluid-particle mass transfer may be written as follows.

$$\omega(1-\epsilon) \partial q / \partial \theta = k_0 a(c-c^*) \quad (3)$$

where $k_0 a$ is an overall mass transfer coefficient and c^* is the fluid concentration in equilibrium with the solid. This relationship applies to both the fixed-bed and continuous chromatographs.

If the angular dispersion term in Eq. (1) is neglected and the time transformation given in Eq. (2) is made, Eqs. (1) and (3) become

$$\epsilon D_z \partial^2 c / \partial z^2 = \epsilon \partial c / \partial t + (1-\epsilon) \partial q / \partial t + u \partial c / \partial z \quad (4)$$

$$(1-\epsilon) \partial q / \partial t = k_0 a(c-c^*) \quad (5)$$

Thus, as pointed out by Wankat, under conditions of negligible angular dispersion, the *unsteady-state, one-dimensional* chromatographic process is equivalent to the *steady-state, two-dimensional* CAC process. Solutions of Eqs. (4) and (5) available in the literature may be directly applied to predict the steady state performance of CAC operations. For systems exhibiting a linear adsorption isotherm, various analytical solutions are available to describe isocratic elution.

Two possible differences in resin behavior exist between the fixed bed and the CAC. First, D_z could be somewhat different because of geometric and packing factors. Second, there exists the possibility of angular disper-

Table 1
Equilibrium Distribution and Mass Transfer Coefficients[a]

Sugar	Distribution coeff., K	Mass transfer coeff., $k_o a(s^{-1})$
Sucrose	0.130	0.0042
β-D-glucose	0.228	0.0143
α-D-glucose	0.294	0.0184
β-D-fructose	0.657	0.0409

[a]Dowex 50W-X8, Calcium form, $T=25°C$, results of Howard et al. (1987).

sion in the CAC, whereas none is possible in the fixed bed analog. Since it is usual practice to assume that D_θ is negligible, a significant contribution from this source would be manifested in a difference in D_z between the fixed column chromatograph and the CAC.

Howard et al. have demonstrated that at the flowrates typically encountered in liquid chromatography applications, when fluid and intraparticle mass transfer resistances are present, both angular and axial dispersion are only moderately important in the CAC. In this case, for an infinitesimally small feed pulse, the solute concentration profile is described by

$$c(z,\hat{t}) = Q / 2\sqrt{\pi}\,\{ (k_o a)^2 / u^3 z\hat{t}[(1-\epsilon)K]^3 \}^{0.25}$$
$$\exp\{ - [\sqrt{k_o a z / u} - \sqrt{k_o a \hat{t} / K(1-\epsilon)}]^2 \} \quad (6)$$

where K is the distribution coefficient for the solute, and

$$\hat{t} = \theta / \omega - \epsilon z / u \quad (7)$$

Equation (6) applies as an approximation where the number of transfer units available in the bed is greater than 5. The amount of solute introduced per unit cross-sectional area of the sorbent bed, Q, may be calculated from

$$Q = c^F u Q_F / Q_T 360^o / \omega \quad (8)$$

where c_F is the solute concentration in the feed mixture, Q_F is the feed flowrate, and Q_T is the total flowrate of fluid through the annular bed.

In previous experiments, Howard et al. have shown that the distribution coefficient, K, is a constant for the species investigated here to concentrations of 300 g/L in both glucose and fructose. This allows the use of the theoretical approach discussed here. The results of the previous work are given in Table 1.

Equation (6) predicts that the resolution of two species is independent of loading. This is a good approximation for low bed loadings, but is obviously unrealistic at high loadings. When the feed occupies a significant sector of circumference, and, hence, acts as a square concentration wave rather than a sharp pulse, the following series solution may be used to compute concentration profiles.

Table 2
Equilibrium Distribution and Mass Transfer Coefficients[a]

Sugar	Distribution coeff., K	Mass transfer coeff., $k_o a(s^{-1})$
Sucrose	0.0079	0.0021
α- & β-D-glucose	0.253	0.0111
β-D-fructose	0.590	0.0163

[a]Dowex 50W-X8, Calcium form, $T=25°C$, current study—fixed bed.

$$c(z,t) = c_F\theta_F / \theta_F + \theta_E + 2/\pi \sum_{j=1}^{\infty} \{ 1/j \exp[-j^2 k_o a z / j^2 + r^2)u] \times \sin[j\pi\theta_F / \theta_F + \theta_E] \times \cos[j\pi\theta_F / \theta_F + \theta_E + 2j\pi\theta / \theta_F + \theta_E - 2j\pi z w / u(\theta_F + \theta_E) - jrk_o az / (j^2 + r^2)u] \} \quad (9)$$

where θ_F is the arc over which feed is applied to the column θ_E is the elution arc, and r is given by

$$r = k_o a(\theta_F + \theta_E) / 2\pi(1-\epsilon)K\omega \quad (10)$$

For systems which exhibit nonlinear isotherms a numerical solution of Eqs. (4) and (5) is in general required to predict the performance of chromatographic separations (Ruthven 1984).

RESULTS AND DISCUSSION

In considering the objectives of the study it was deemed necessary to repeat runs we had previously made to check the reproducibility of the bed packing. Then we explored on a fixed bed the nature of the two industrial feedstocks that were used in the study. Based on these findings, we were able to design CAC scaleups of low capacity experiments. Finally, moderate and high capacity experiments were executed on both the fixed bed and the CAC. The objective in the final series was to assess the capacity of a CAC unit for sugar separation.

Fixed Bed Experiments

Fixed bed experiments began with a low-concentration synthetic mixture (25 g/L glucose, 25 g/L fructose, and 10 g/L sucrose). A 0.57 mL sample was injected into the 107 cm-long column, and eluted with water at a superficial velocity of 0.2 cm/s. Based on Eq. (6) and a computation of K based on the position of the peak maxima, results for K and $k_o a$ are given in Table 2. It will be noted that the glucose moieties were combined into a single peak for the purposes of this study, following the usual industrial practice. Distribution coefficients agree well between the two experimen-

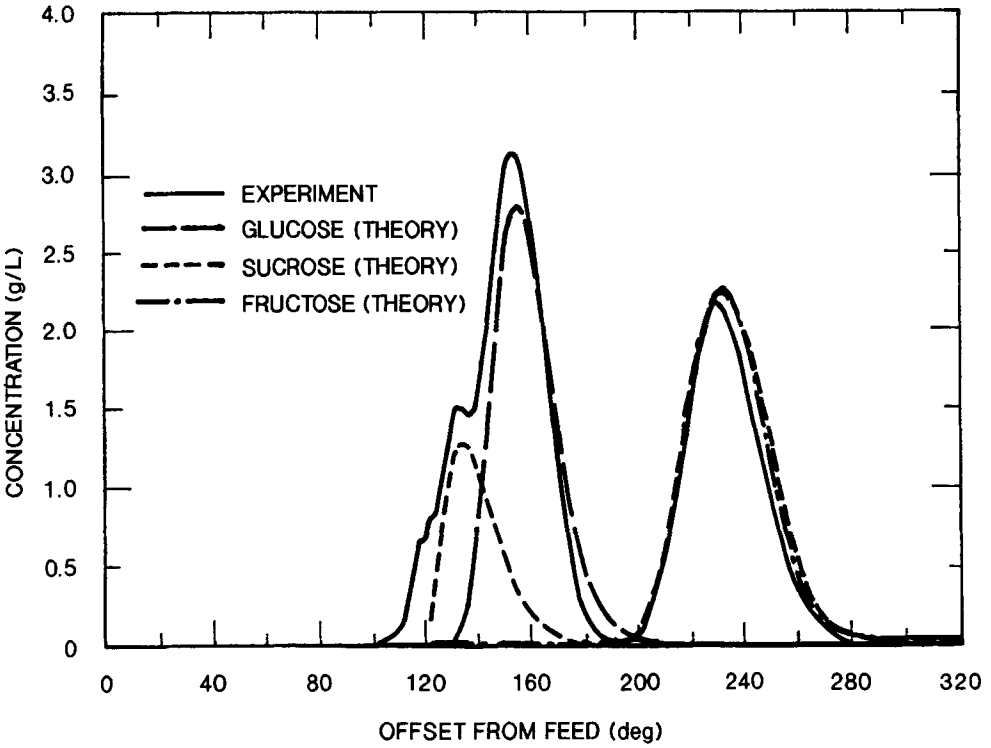

Fig. 4. Comparison of experimental fixed bed results with the prediction of the simple mass transfer resistance theory. Feed material is 25 g/L glucose, 25 g/L fructose, and 10 g/L sucrose.

tal series, especially in the cases of glucose and fructose. However, there is significant disagreement between the two series in the value of the mass transfer coefficient. This is possibly attributable to differences in the equipment used in the two experiments and to difficulty of reproducibly packing columns. The discrepancy in sucrose is most likely the result of the sensitivity of the numerical results to small differences in experiments in the region where little sorption occurs.

A comparison of the theoretical results and the experimental concentration profile indicate that there is significant difference in peak shape between the two traces (Fig. 4). A material balance on the components indicates that there is less than a 2% discrepancy between feed and exit in sucrose and glucose and 11% in fructose. In the latter case, it is possible that problems were experienced with refractometer calibration. Since the theory assumes that we can neglect dispersion, and the theoretical curves include these in the estimation of the effective mass transfer coefficient, k_0a, an imperfect fit of the data results.

Two industrial samples from different sources were evaluated on the fixed bed column to assess the possible differences between these samples, one of which was a corn syrup and the second was an inverted beet sugar molasses. It is important to observe the influence of the impurity

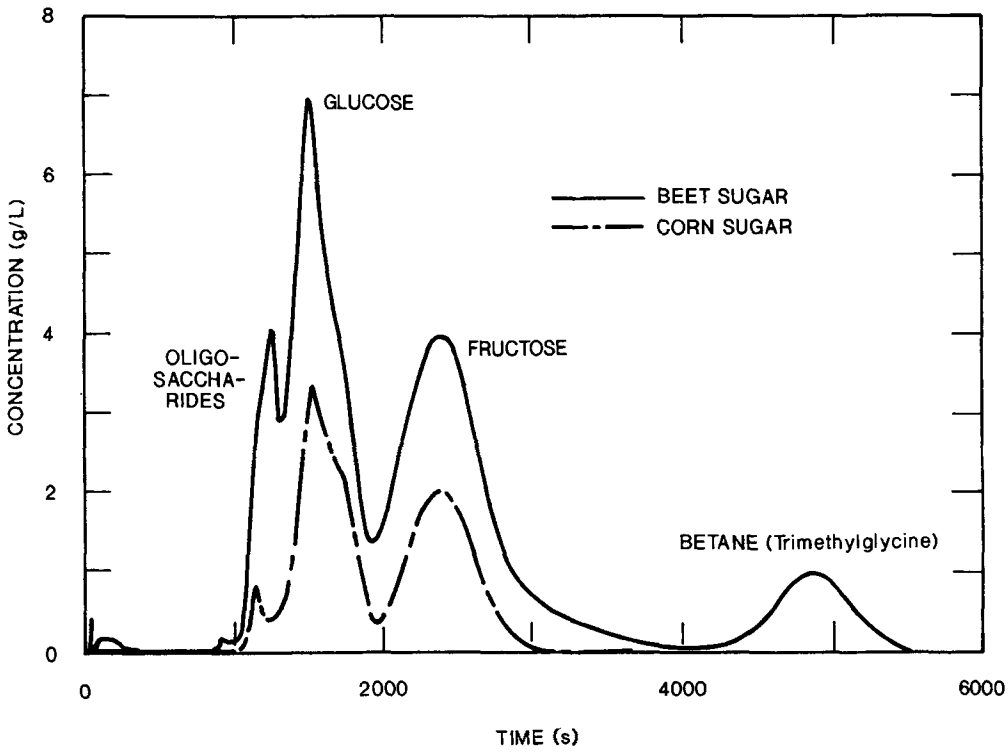

Fig. 5. Comparison of experimental fixed bed results for diluted industrial corn syrup with industrial beet sugar.

components on the ultimate separation. Figure 5 is a direct comparison of two runs, in which a 0.57 mL sample of diluted feeds (10:1) were injected into the column. Since the starting concentration of the beet sugar was significantly higher than the corn syrup, its exit peaks are substantially higher. It is evident that the mixtures are quite different. The corn syrup's only apparent impurities are oligosaccharides that exit the column early in the process. These amount to about 5% of the total solids. Thus, the angular span of the separation on the CAC will be compact. On the other hand, the beet sugar contains, in addition to the oligosaccharides, a component that is known as betaine (trimethylglycine), which is strongly held by the resin, resulting in a chromatogram that is 1.75 times longer than that of the corn syrup. This effectively reduces the capacity of a CAC separation to about 56% of that realized with the corn syrup. Aside from that difference and the fact that in the case of the beet sugar the oligosaccharide fraction is somewhat larger, the two sugars should be scaled in a similar fashion. Therefore, only the corn syrup was used in the CAC.

Low Capacity CAC Experiments

To assure that the results of a fixed bed could be scaled to the pilot scale CAC, the low-concentration run reported in Fig. 4 was scaled to the

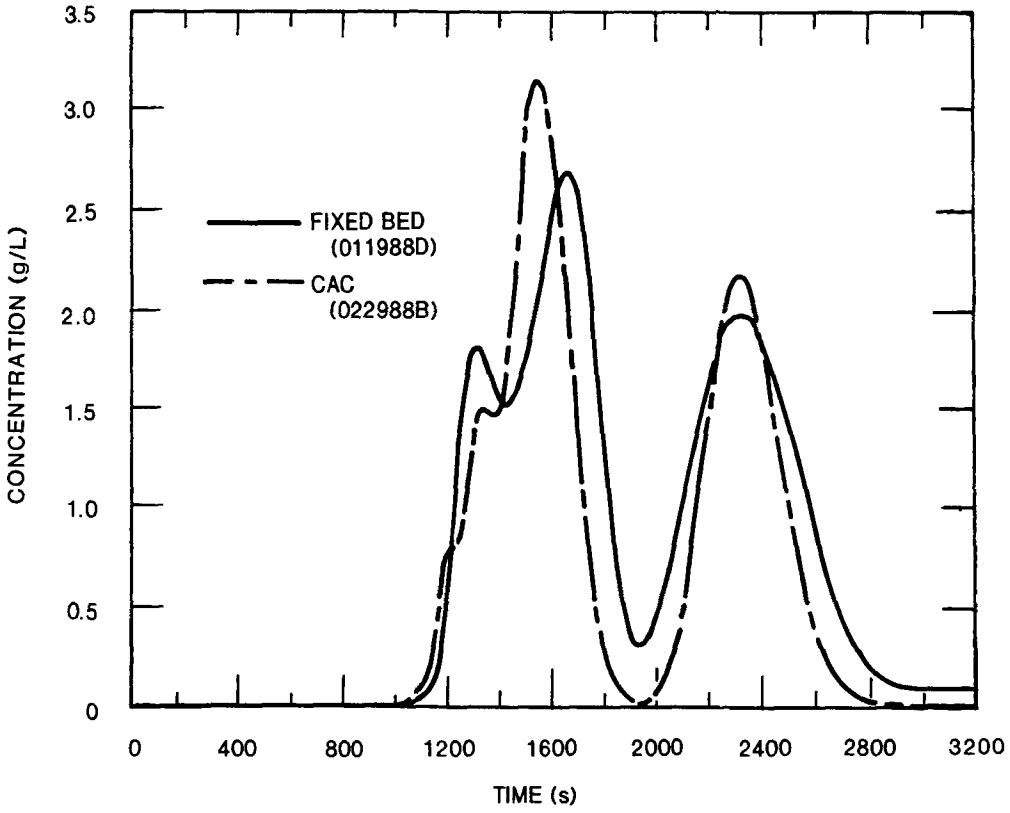

Fig. 6. Comparison of experimental fixed bed results with the equivalent run on the pilot scale CAC. A synthetic sugar mixture was used containing 10 g/L sucrose; 25 g /L glucose and 25 g/L fructose was used in both cases.

pilot scale CAC as precisely as possible. A comparison of the two runs is given in Fig. 6, with the time in the case of the CAC being relative to the feed position of the column. It is evident that there is a significantly better resolution in the CAC experiment, caused primarily by an earlier elution of the glucose and apparently better mass transfer than in the fixed bed run. However, it is obvious that matching of the two peaks is quite good and that we can effectively use the scaling relationships to predict the behavior of the pilot unit. The differences between the two runs may be ascribed to differences in packing of the two beds, and, possibly, additional tailing associated with flushing out a sample loop in the fixed bed experiment.

It is of interest to compare the constants that were found for the fixed bed experiment with those that were obtained from the CAC experiment. The results of this exercise are given numerically in Table 3 as the constants K and $k_o a$ and in Fig. 7 as comparative chromatographic traces. The results in this case were much closer to those of Howard et al., indicating a possible difficulty with the fixed bed experiments.

Table 3
Equilibrium Distribution and Mass Transfer Coefficients[a]

Sugar	Distribution coeff., K	Mass transfer coeff., $k_o a(s^{-1})$
Sucrose	0.078	0.0014
α- & β-D-glucose	0.1883	0.0064
β-D-fructose	0.594	0.0414

[a]Dowex 50W-X8, Calcium form, $T = 25°C$, current study—CAC experiment.

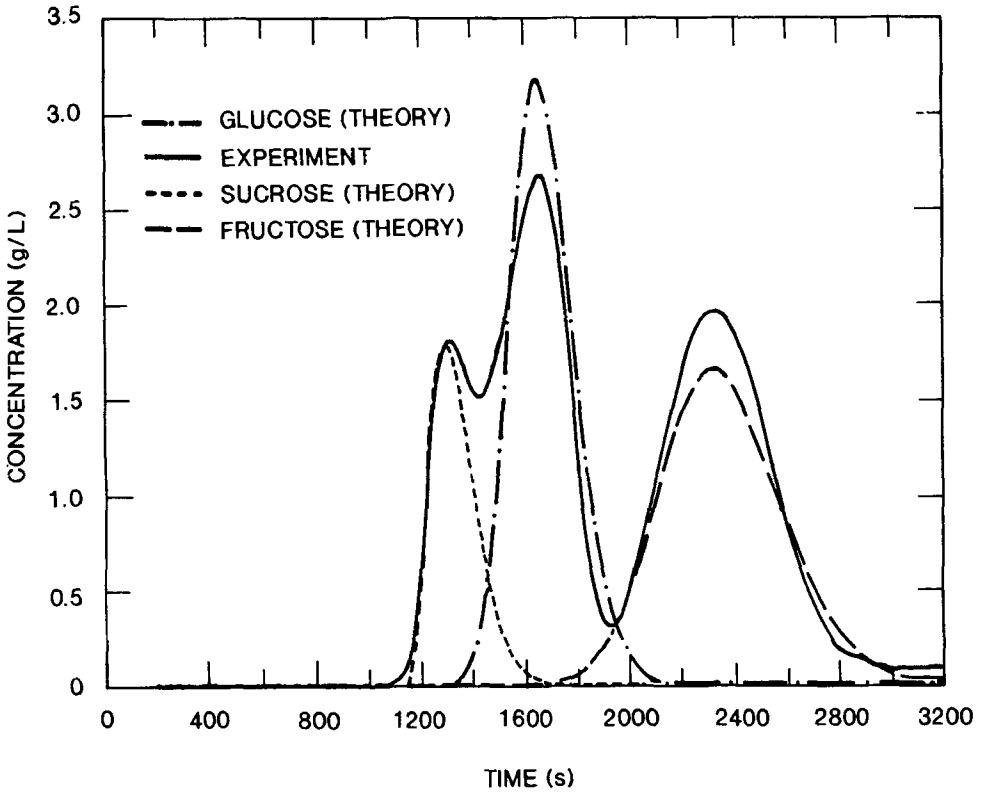

Fig. 7. Comparison of experimental pilot scale CAC results with the predictions of Eq. (6). A synthetic sugar mixture was used containing 10 g/L sucrose; 25 g/L glucose and 25 g/L fructose was used in the experiments.

The performance of the CAC using an industrial mixture at full strength (600 g/L of solids) under lightly loaded conditions was compared with the equivalent run on a fixed bed. In the latter case the feed was injected at 0.4 cc/min for 2.5 min and eluted completely in 9500 s. The feed sector in the CAC was 5.6 degrees, with a similar superficial velocity to the fixed bed run. This run, although considered light, represents a 20-fold increase in loading over the synthetic runs previously discussed. It will be noted that there is a significant difference between the fixed-bed and the CAC experiments. It appears as if angular dispersion might be active in the

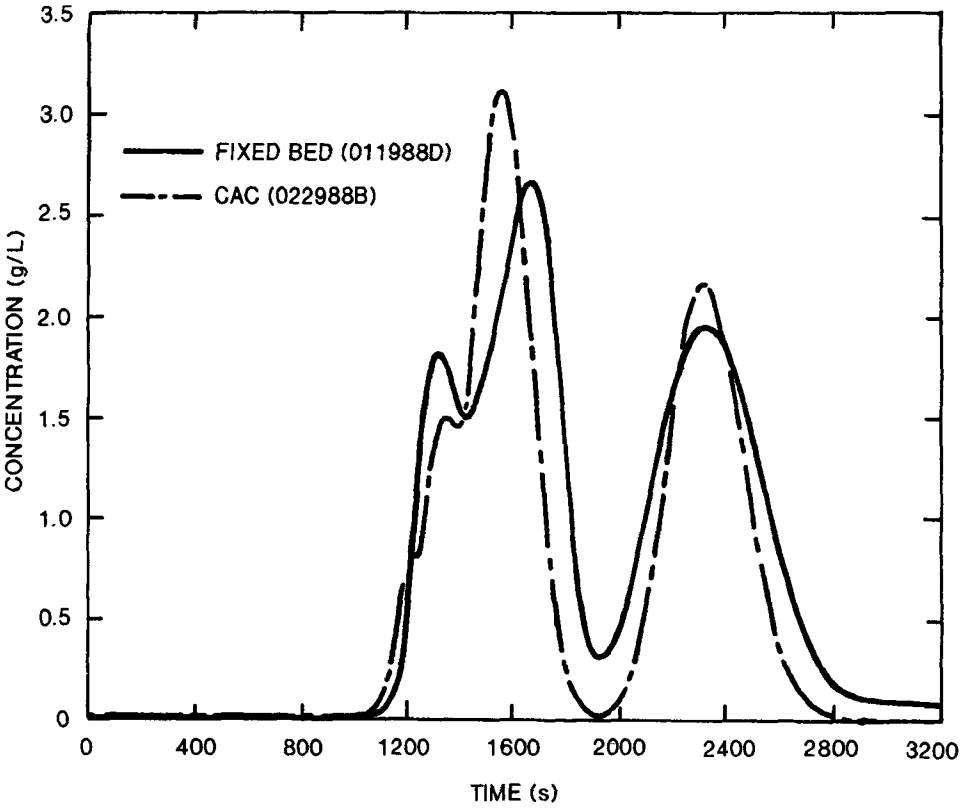

Fig. 8. Comparison of experimental pilot scale CAC results with an equivalent fixed bed run. An industrial corn syrup mixture was used containing 26.7 g/L oligosaccharides, 343 g/L glucose, and 304 g/L fructose.

CAC, causing broadening of the peaks and, thus, poorer resolution. The probable cause of this dispersion is the viscosity of the feed material, which at the concentration level of the feed is approximately forty times that of the water that is used as an eluent. As this feed enters the bed, it slows and spreads, because metering pumps assure a constant flow. The eluent, on the other hand, takes up a narrower sector than one would at first predict, causing a higher interstitial velocity in its sector. This leads to an appearance of axial dispersion and deteriorated performance. The results of high viscosity feeds in the fixed column are higher pressure drops while the material passes through the column, but here the geometry does not allow angular dispersion. Therefore, a significant difference in performance develops between the two modes of operation.

High Capacity Fixed Bed and CAC Experiments

Using the relationship in Eq. (8), it is possible to predict the behavior of chromatographs under high feed loading. Based on the predictions of this model it was shown that one could load the column with approximately 12 cc of feed at 0.4 cc/min using a full strength sugar, and elute the

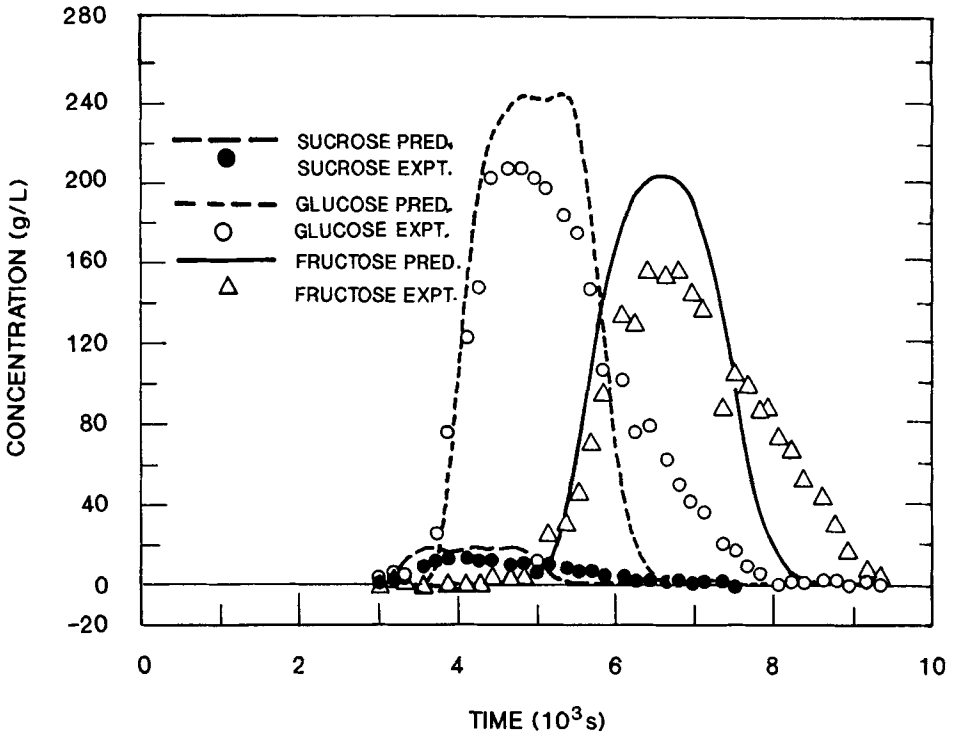

Fig. 9. High capacity fixed bed run using as-received industrial corn syrup as feed. The theoretical prediction is compared with experimental data. Comparison of experimental pilot scale CAC results with an equivalent fixed bed run. The feed mixture contained 26.7 g/L oligosaccharides, 343 g/L glucose, and 304 g/L fructose.

last material in 9500 s. Therefore, a 12-cc sample loop was prepared. Unfortunately, the high viscosity feed was not swept out of the tube as a plug by the water, leading to a great deal of tailing. The material balance indicated that only about 66% of the feed left the sample loop during the feed period. Therefore, we assumed that the concentration of the feed square pulse was reduced by 34% in all components in computing the predicted exit concentration using Eq. (9). Obviously, the shape was probably not square but more like a decaying exponential, leading to some inaccuracy in the prediction. The constants that we generate in Table 2 were used in the prediction. A comparison of the theory and the experimental data (Fig. 9) indicated that the theory predicts the general shape of the experimental data, particularly along the leading edges of the peaks. A proper separation is shown, whereas the tailing nature of the trailing edges are probably attributable to the feed peak shape.

The capacity of an industrial scale CAC unit, based on the feed mixture used and the theoretical predictions shown in Fig. 9 are given in Table 4. Obviously, the result is dependent on the functioning of the CAC in the same manner as the fixed bed. The calculation assumes a fairly typical industrial scale CAC. It includes a scaling feature that has been previously

Table 4
Scaleup of a Typical Industrial Mixture

Feed material: corn based glucose/fructose mix (630 g/L solids)
Feed: 300g/L glucose 300g/L fructose
Impurities: Approx. 5% oligosaccharides
Product Specification
90% Fructose recovery: 90% purity
Column Specifications
Bed diameter: 10 ft (3.05 m) 95% resin-filled
Depth: 4 ft (1.4 m); Pressure: 50 psig(0.45 MPa); Temp: 25°C
Rotation rate: 600 degrees/h
Feed rate: 81,600 L/d
Fructose product: 22,500 kilo/d
Total fructose + glucose: 17,500 tons/y or ~ 16 M kilo/y

tested—a wide annulus. This allows the use of over 95% of the volume of the vessel for separations. A 10-ft (3.05 m) diameter chromatograph was selected as a typical size. There appears no impediment to making larger units. The capacity figure is based on a 90% time utilization.

An attempt to reproduce the high capacity fixed column run on the CAC indicated that the capacity of the CAC was somewhat exceeded, again because of the viscosity effect, which added angular dispersion to the picture. The resulting fructose peak, although showing separation, required more than 306° to exit and, thus, came out with the leading edge of the glucose. As an immediate resolution to the problem, the feedrate was reduced to give a 30-degree sector, somewhat less than half the original capacity. The results are given in Fig. 10. The separation here is adequate and probably represents the capacity of the CAC under the conditions of the experimental program. Significant improvement may be expected in performance if the temperature is increased to the 60–80°C range. Two advantages accrue to this change. First, the difference in the K values is greater and, second, the viscosity difference is significantly reduced at higher temperatures, reducing effective angular dispersion. Finally, the resin in this study is 8% crosslinked. A 5% crosslink would probably be optimal for this mixture. All of the changes will probably allow us to approach the predictions of capacity in Table 4.

CONCLUSIONS

Synthetic and industrial mixtures of glucose, fructose, and sucrose may be separated using the calcium form of Dowex 50W-X8 cation exchange resin with distilled deionized water as the isocratic eluent in both a fixed-bed column and a pilot scale CAC. Equilibrium and mass transfer

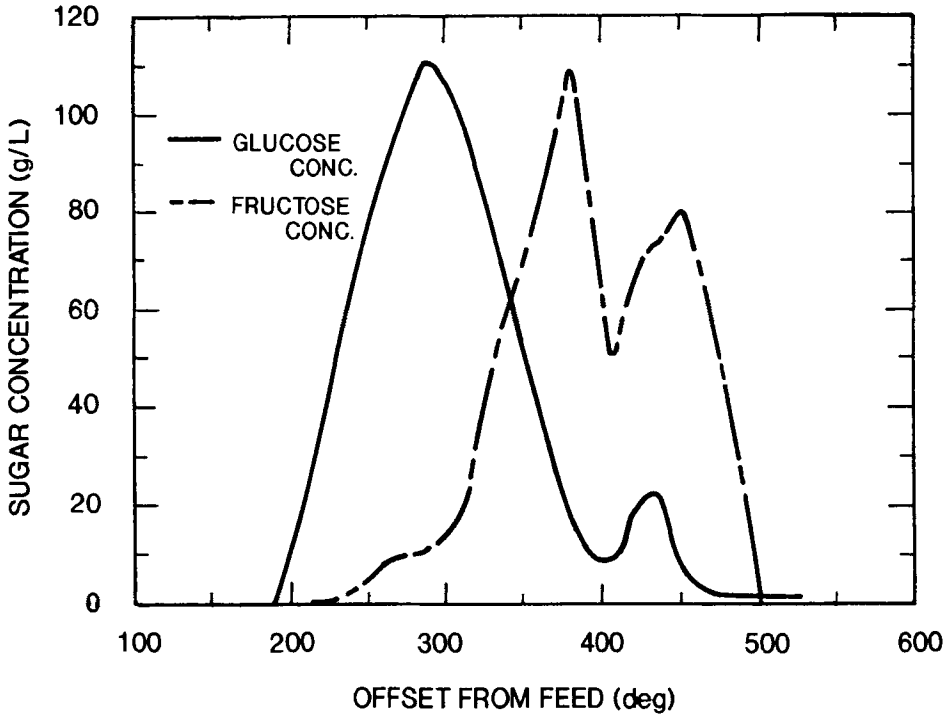

Fig. 10. High capacity pilot unit separation of industrial corn syrup.

parameters evaluated in the fixed-bed column were used to predict the behavior of the CAC. Since earlier studies had determined effects of feedrate, feed concentration, eluent velocity, and rotation rate on CAC performance, the primary purpose of the current study was to observe the permissible loading of the feed solution on the CAC.

The following conclusions can be drawn from the studies conducted:

1. Operation of the pilot scale CAC for the separation and purification of binary and multicomponent aqueous sugar mixtures has been demonstrated. Long runs were made to illustrate typical conditions.
2. The scaling of sugar separations from a fixed column to a pilot scale CAC was demonstrated at low and moderate sugar loadings. At high loadings, angular dispersion, presumably caused by the effect of feed solution viscosity degraded the performance of the CAC relative to the fixed bed.
3. The theory for both low and high loadings gave excellent agreement with results. Again, the effect of feed viscosity appears to have effectively added angular dispersion to the CAC case.
4. Future investigations will include the effects of feed viscosity on high throughput performance, and the effect of operating temperature.

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