An Improved Adsorption Process for the Production of High-Fructose Syrup

By applying a temperature profile to the system, the concentration of the extract product in a countercurrent adsorption separation process may be increased relative to the maximum concentration attainable under isothermal conditions. To achieve the required temperature profile in a simulated countercurrent system it is necessary to heat and cool the columns in sequence as the feed and product draw-off points are switched through the bed. The practical feasibility of operating the system in this way has been demonstrated experimentally for the separation of glucose-fructose mixtures. By maintaining a temperature difference of 30-35°C across the bed an extract product containing 28% fructose and about 1% glucose was obtained, at steady state, from a feed containing 25 wt. % of each sugar.

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Introduction

The large-scale separation of fructose-glucose mixtures is generally carried out by a simulated countercurrent adsorption process in which countercurrent contact between fluid and adsorbent is simulated by switching the feed inlet and product draw-off points, at fixed time intervals, through the bed. Such a system retains the basic advantage of a countercurrent process (driving force for mass transfer is maximized so that the size of the adsorbent bed and the eluent flow rate are minimized) while avoiding the problems associated with actual recirculation of the adsorbent. In previous studies (Ching and Ruthven, 1985a; Ching et al., 1985) we have shown that the behavior of such simulated countercurrent systems may be modeled by considering the equivalent true countercurrent process. The equivalent countercurrent system for the most commonly employed mode of operation, exemplified by the UOP Sarex process (deRosset et al., 1981), is illustrated in Figure 1. Processes of this type are widely used for many industrially important separations, but the glucose-fructose system is particularly useful as a model since the equilibrium is essentially linear over a rather wide concentration range. This allows the basic features of the process to be elucidated without the complications that may arise from nonlinear, interacting equilibria.

The essential requirement to achieve separation in such a process is that the flow rates in the four sections must be adjusted in such a way as to achieve a net flow of the more strongly adsorbed species (fructose) toward the extract point, and a net flow of the less strongly adsorbed species (glucose) toward the raffinate point.

For a linear system this leads to the following inequality constraints:

$$\begin{array}{lll} \text{Section} & & \\ \text{I} & \gamma_F < 1, & \gamma_G < 1 \\ \text{II} & \gamma_F > 1, & \gamma_G < 1 \\ \text{III} & \gamma_F > 1, & \gamma_G < 1 \\ \text{IV} & \gamma_F > 1, & \gamma_G > 1 \end{array} \qquad (1)$$

If we specify that the limiting constraints in all four sections should be satisfied by the same margin ($\alpha > 1.0$), Eq. 1 translates to a set of four simultaneous equations defining the relative flow rates throughout the system:

$$\begin{aligned} D/S &= K_F\alpha \\ E/S &= K_F\alpha - K_G\alpha \\ F/S &= K_F/\alpha - K_G\alpha \\ R/S &= K_F/\alpha - K_G\alpha \end{aligned} \qquad (2)$$

By choosing a high value of α it becomes relatively easy to satisfy the flow rate constraints and to obtain pure raffinate and extract products, but the higher the α value, the greater is the dilution of the products. This is undesirable since costly evapora-

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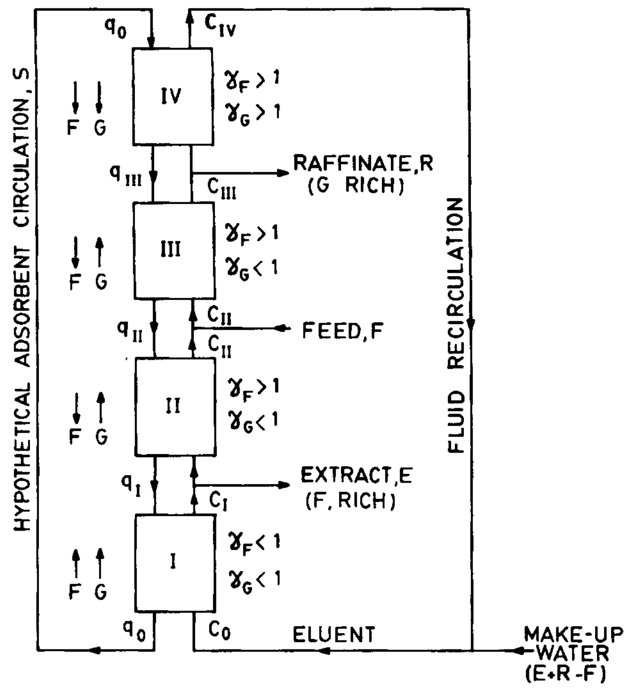

Figure 1. Equivalent countercurrent system showing required net flow directions and values of γ within the four sections of the bed.

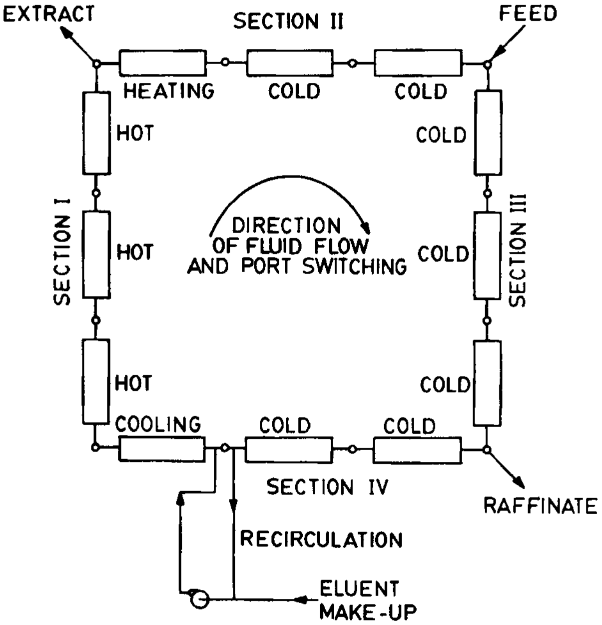

Figure 2. Diagram of experimental system showing feed and product ports and arrangement of hot and cold columns.

tion steps are then required to obtain the products at the desired concentration. The number of theoretical stages (i.e., column length) required to achieve any specified degree of separation also increases as α approaches unity, but this constraint is generally economically less severe than the requirement to minimize dilution of the products. In practice it is therefore generally desirable to operate with a relatively small margin.

By reference to the McCabe-Thiele diagram and to the constraints imposed by Eq. 1, it is easy to show that in an isothermal linear system of this type the product concentration can never exceed the feed concentration (Ching et al. 1985; Ching and Ruthven, 1985b). The limiting case in which product and feed concentrations are equal occurs as $\alpha \rightarrow 1.0$. Under these conditions the operating and equilibrium lines are coincident, requiring an infinite number of stages in all sections of the bed. In a practical system, the products will therefore always be significantly diluted relative to the feed. In a nonisothermal system, however, this constraint no longer applies and it is shown here that by a judicious choice of temperature profile it is possible to obtain the extract product at a concentration significantly higher than the feed.

Experimental

The basic experimental system consists of 12 identical columns, each 100 cm long × 5.1 cm ID, packed with Duolite ion exchange resin in Ca^{++} form. The columns are connected in series through pneumatically operated switch valves that allow the introduction of feed or withdrawal of product at the junctions between each pair of columns. The flow rates of eluent, extract, and raffinate were controlled by metering pumps. The general arrangement is shown schematically in Figure 2. Countercurrent flow is simulated by advancing the eluent, extract, feed, raffinate, and recirculation points by one column in the direction of fluid flow, at fixed time intervals.

Each column is fitted with a water jacket that is connected through a manifold to either a hot water or cold water supply system. In previous isothermal studies the water jackets were all maintained at a constant temperature throughout the system. However, in the present mode the heating and cooling water valves were operated synchronously with the flow switching in order to maintain columns 2–4 (section I) hot and the rest of the system at ambient temperature. (Column 1 is therefore always cooling while column 5 is heating).

To determine the concentration profile, samples were withdrawn by syringe, at the midpoint of the switch period, from sample points at the junctions between each pair of columns, and were analyzed by HPLC using a Sugarpak column. Cumulative samples of extract and raffinate products were also collected over the entire switch interval.

The adsorption equilibrium constants and the chromatographic HETP were measured by pulse chromatography with two representative columns isolated from the rest of the system. The voidage of the adsorbent bed was determined from the retention volume of starch.

Results and Discussion

The adsorption equilibrium constants for fructose and glucose were calculated in the usual way from the first moments of the chromatographic response peaks:

$$\mu \equiv \frac{\int_0^\infty ct \cdot dt}{\int_0^\infty c\, dt} = \frac{\ell}{v}\left[1 + \left(\frac{1-\epsilon}{\epsilon}\right)K\right] \qquad (3)$$

The temperature dependence of K_F and K_G is shown in Figure 3. The equilibrium constant for glucose is essentially independent of temperature, suggesting that this species is not significantly

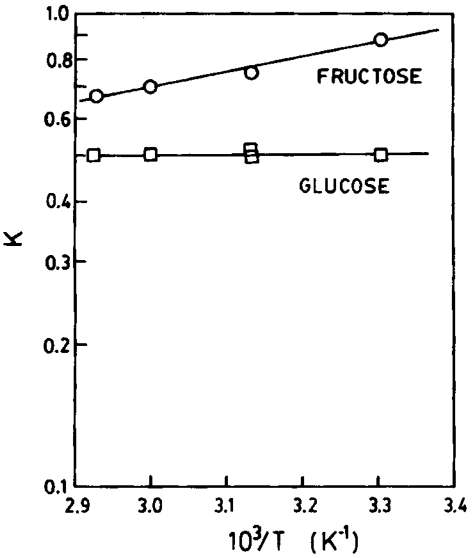

Figure 3. vant' Hoff plot showing temperature dependence of adsorption equilibrium constants for fructose and glucose.

adsorbed but merely held within the pores of the resin particle. The equilibrium constant for fructose decreases, as expected, with increasing temperature, corresponding to a modest exothermic heat of adsorption.

Since the starch molecule is too large to penetrate the pores of the resin its retention time is given simply by the ratio of the free liquid volume in the column to the liquid flow rate. The voidage of the adsorbent bed is thus obtained directly. The values obtained for the two test columns were both close to 0.40.

Two experimental runs were carried out under the flow conditions given in Table 1, with equimolar mixtures of fructose and glucose as feed. In run 1 the feed was dilute (5% glucose + 5% fructose by weight) whereas the feed for run 2 was at a concentration typical of the commercial process (25 wt. % of each sugar). The columns of section I (columns 1–4) were maintained at a temperature of about 65°C while the columns in the rest of the system were maintained at about 29°C with cooling water. Approximately four complete cycles were required to approach the cyclic steady state. The resulting concentration profiles, measured at the midpoint of the switch interval, are shown in Figure 4. It is evident that the fructose concentration in the region of the extract point is substantially higher than the feed concentration. The analysis of the cumulative extract and raffinate samples, given in Table 2, is seen to be consistent with the profile.

The profiles from Figure 4 are plotted in Figure 5 on a dimen-

Table 1. Summary of Experimental Conditions

Switch Time, τ = 19.5 min

Flow Rate (mL/min)	Equiv. C-C Flow Rate
Eluent 89	S = 62.5 cm³/min
Extract 5.6	D = 47 cm³/min
Feed 9.0	
Raffinate 25.2	

Feed

Run 1: 5% fructose + 5% glucose
Run 2: 25% fructose + 25% glucose

Section	No. of Columns	T °C	K_F	γ_F	K_C	γ_G
I	4	65	0.68	0.9	0.5	0.66
II	3	29	0.88	1.33	0.5	0.75
III	3	29	0.88	1.09	0.5	0.62
IV	2	29	0.88	2.18	0.5	1.24

Hypothetical solid velocity $u = \ell/\tau$,
Actual liquid flow rate = $A\,\epsilon(u + v)$
Equiv. C-C flow rate = $A\epsilon v$
Equiv. C-C solid flow rate(S) = $A(1 - \epsilon)\,u$

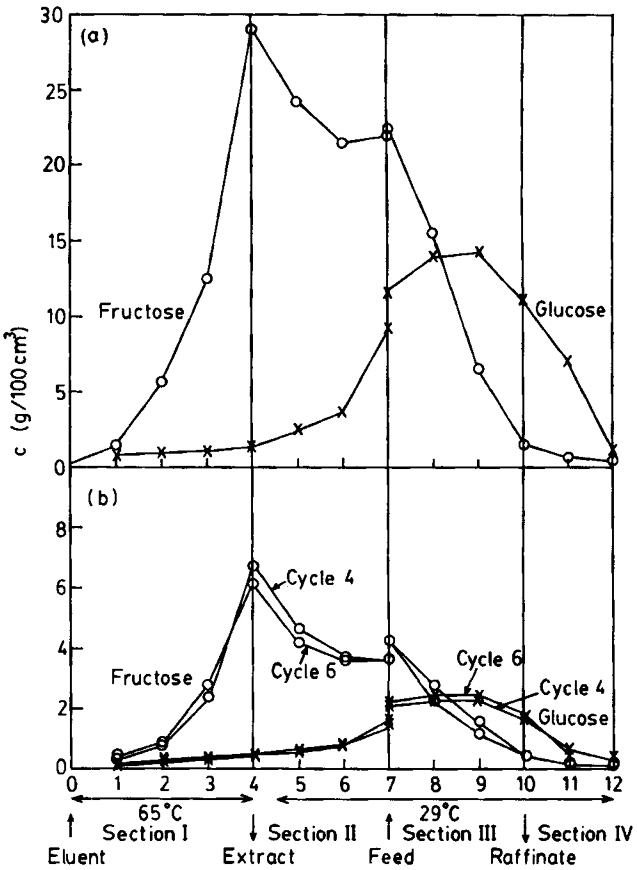

Figure 4. Experimental concentration profiles measured at middle of switch interval.

(a) Feed containing 25 g/100 cm³ each of fructose and glucose.
(b) Feed containing 5 g/100 cm³ each of fructose and glucose.
Data points for cycles 4 and 6 are almost coincident.

Table 2. Analysis of Raffinate and Extract Samples

	Run 1 (5% feed)				Run 2 (25% feed)			
	Extract		Raffinate		Extract		Raffinate	
Cycle	G	F	G	F	G	F	G	F
4	0.45	6.2	1.4	0.33	1.2	27	11.5	1.94
5	0.49	5.3	1.04	0.23	1.1	28	11.1	2.0
6	0.37	6.0	1.74	0.27	—	—	—	—

Concentration in g/100 cm³.

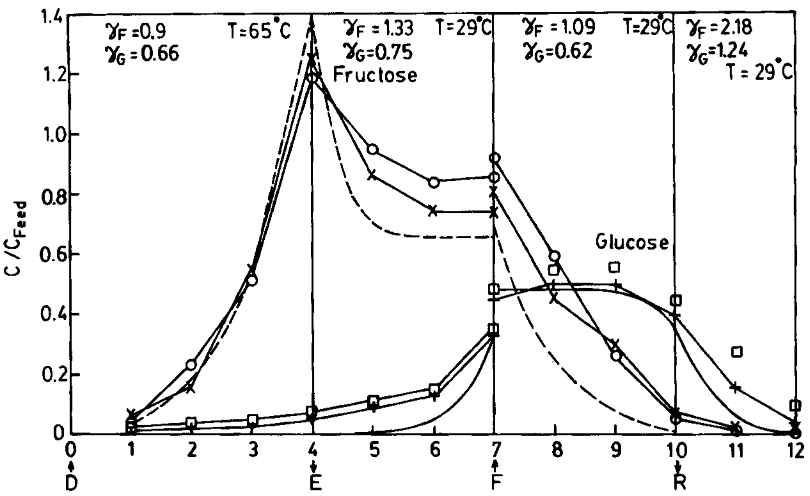

Figure 5. Experimental steady state concentration profiles for runs 1 and 2 plotted in terms of dimensionless concentration.

Fructose: x, 5% feed; O, 25% feed.
Glucose: +, 5% feed; □, 25% feed.
Also shown, approximate theoretical profile derived from linear model with $T = 65°C$ in section I and $T = 29°C$ in sections II–IV.
Fructose, ---; glucose, ___.

sionless concentration scale relative to the feed. When plotted in this way the profiles for 5 and 25% feed concentrations are seen to be essentially the same as is to be expected for a linear system. Also shown in Figure 5 is the theoretical profile calculated from the previously developed isothermal countercurrent dispersed plug flow model, with the distribution coefficients for fructose in section I and sections II–IV set at different values, i.e., section I is assumed isothermal at 65°C ($K_F = 0.68$) and sections II–IV are assumed isothermal at 29°C ($K_F = 0.88$); the temperature variation in columns 5 and 12 is neglected. The effective axial dispersion coefficient is taken to be independent of temperature and is given by $D_L = 5\ (u + v)$, as determined from the chromatographic measurements. Details of the model have been given by Ching and Ruthven (1985a, b). It is evident that this simplified model provides a reasonable approximate representation of the experimental profiles.

In order to demonstrate more directly that the enhanced performance of the system is indeed due to the temperature profile, after the nonisothermal steady state had been established run 1 was continued under the same flow conditions but with cooling water flowing through all columns to maintain a constant temperature of 29°C. The resulting steady state isothermal profile is shown in Figure 6. The glucose profile is the same as for nonisothermal operation, as is to be expected since K_G is essentially independent of temperature. However the fructose profile becomes very diffuse, since under nonisothermal conditions with the given flow rates the condition $\gamma_F < 1$ is not satisfied in section I.

The aim of this study was to demonstrate the potential advantages and practical feasibility of operating a process of this type in the nonisothermal mode. No attempt was made to optimize the operating conditions or to establish the maximum achievable

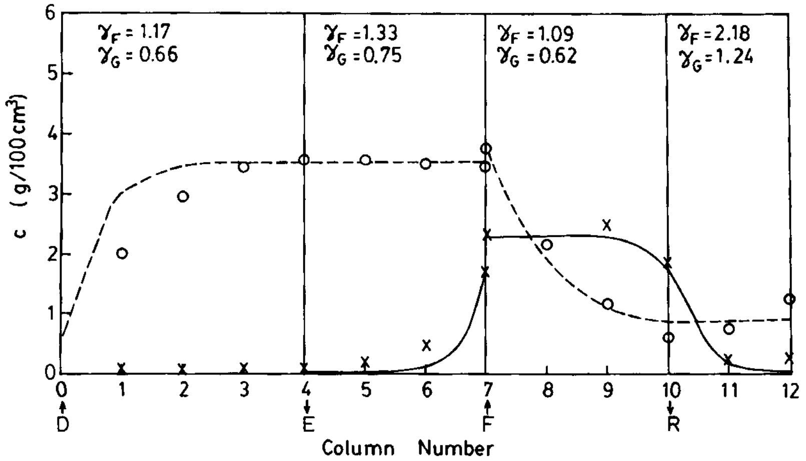

Figure 6. Experimental steady state concentration profiles for fructose and glucose obtained under isothermal conditions ($T = 29°C$) with the same flow rates as for the nonisothermal run (feed 5% glucose + 5% fructose).

Theoretical profiles derived from the model are shown for comparison.
Fructose, ---; glucose ___.

product concentration. It appears that significant benefit can be obtained from maintaining even a modest temperature difference in the system, and in any practical application of the process low-grade waste heat and relatively warm cooling water could therefore be used.

Before we started this study we anticipated that we might encounter problems at high concentrations due to the low viscosity of the sugar solutions at 29°C. In fact pressure drop did not prove problematic (although it was noticeably higher with the concentrated feed) since the region of highest concentration is at elevated temperatures.

Conclusions

It is shown that with a modest temperature difference between the hot and cold columns (~35°C) the more strongly adsorbed species (fructose) may be obtained at high purity and relatively high concentration in the extract product; e.g., with a feed containing 25% each of glucose and fructose an extract product containing 28–29% fructose and less than 1% glucose was easily obtained. No attempt was made to optimize the system and it is probable that further enhancement of product concentration could be achieved by small adjustments to the flow rates. With this type of system it may therefore be feasible to produce high-fructose syrup directly from the adsorption unit with little, if any, subsequent concentration by evaporation. Of course the enhanced performance relative to an isothermal system is not achieved without cost, as the additional capital and operating costs associated with the heat exchange system will not be insignificant. In the pilot unit adequate heat transfer was achieved through the column jacket exchangers, but a large-diameter unit would probably require fluid heat exchangers between the column elements. Since low-grade waste heat can be used, the operating cost of the proposed system will probably be lower than that of a conventional system with downstream evaporators. However, the capital cost of the heat exchangers and switching valves may well exceed the cost of the evaporator unit. The balance of economic advantage can therefore only be determined by detailed studies, taking account of the entire process and the local costs of the heating and cooling water.

Notation

A = cross-sectional area of column
c = fluid phase concentration of glucose or fructose
D = hypothetical eluent flow rate for countercurrent system
D_L = axial dispersion coefficient
E = extract flow rate
F = feed flow rate
K = adsorption equilibrium constant, defined by $q^* = Kc$
ℓ = column length
L = liquid flow rate
q = adsorbed phase concentration, based on total particle volume
R = raffinate flow rate
S = hypothetical solid flow rate for countercurrent system
t = time
u = hypothetical solid countercurrent velocity
v = hypothetical countercurrent interstitial velocity of liquid
μ = mean retention time
ϵ = bed voidage
$\gamma = = (1 - \epsilon)Ku/\epsilon v = KS/L$

Subscripts and superscript

F = fructose
G = glucose
$*$ = equilibrium value

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