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Separation of Fructose and Glucose from Cashew Apple Juice by SMB Chromatography

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Abstract: The simulated moving bed (SMB) technology has been applied to a number of carbohydrate separations. The cashew apple is the pseudo-fruit of the cashew tree; it contains approximately equal amounts of fructose and glucose and is presently an agricultural waste largely found in Northeastern Brazil. This work shows experimental results for the separation of fructose from glucose, found in cashew apple juice, using a conventional four-section SMB. The two sugars were successfully separated with product purities around 90%. The operating conditions were chosen from the equilibrium theory applied to a multicomponent system with linear uncoupled isotherms. The performance at cyclic steady state was well predicted with both TMB- (true moving bed) and SMB-based models. However, during startup, there was a buildup of sugar concentration in the unit, which was not observed for synthetic mixtures. Fixed-bed adsorption and desorption runs were performed with dilute cashew apple juice. They provided experimental evidence that high molecular weight molecules might have been adsorbed onto the resin, which could be a probable explanation for the anomalous behavior previously observed. Clarified cashew apple juice (free of tannins) was also used as the SMB feed and no anomalous transient behavior was observed. On the contrary, process performance perfectly matched that obtained

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from simulation assuming a synthetic glucose-fructose mixture. The results presented herein are the first record of sugar separation in SMB from cashew apple juice and should provide scientific support for economic alternatives to the industrial processing of the cashew crop.

Keywords: SMB chromatography, fructose, cashew juice

INTRODUCTION

The simulated moving bed (SMB) technology was first patented by UOP (Universal Oil Products) as the Sorbex process (1), which was first applied to the petrochemical and then to the sugar industry. The key of the Sorbex technology is a rotary valve, which periodically advances the inlet and outlet streams along a sectioned column in the direction of fluid flow. An identical configuration may be achieved by using multibed units (2) made commercially available by such companies as Novasep (Champignelles, France) and Knauer (Berlin, Germany). With the expiration of key patents on SMB in the last few years, the SMB technology has found significantly broader applications, largely for separating fine chemicals (3). Recently, more sophisticated modes of operation have been proposed, such as the Varicol (4), ModiCom (5), and Powerfeed (6), which essentially derive from the conventional SMB providing higher resolution and general superior performance.

For the past 30 years, SMB processes have been applied on a massive scale in the carbohydrate industry, from the former SAREX process (7) to the recent isolation of betaine from sugar industry molasses (8). The SAREX process is the SORBEX version to separate fructose-glucose solutions, resulting from the enzymatic conversion of cornstarch, in order to produce high fructose corn syrups (HFCS). Since fructose index of sweetness is about twice as much as that of glucose, the separation of fructose from this mixture and recycling of glucose for enzymatic isomerization is of great commercial importance. Figures from the Corn Refiners Association (9) show that, in 2000/2001, around 20% of all corn consumed in the U.S.A. was used in the production of corn sweeteners, which in turn accounted for nearly 53% of the market of nutritive sweeteners. The first patent issued by UOP for glucose-fructose separation (10) used zeolite Y as the adsorbent, ion-exchanged with cations of metals K, Cs, Mg, Co, Sr, Ba + K, and Ba + Sr. The adsorbent selectivity for fructose ranged from 1.4 to 6.2. Subsequent patents introduced the use of ion-exchange resins (11) and X zeolite exchanged for potassium (12). In the latter, selectivity was greater than one for glucose, rather than fructose.

The cashew tree (*Anacardium Occidentale, L.*) is a Brazilian tropical native crop that is cultivated in sandy fields on the northeastern coast of the country, the state of Ceará being its major producer (13). It was originally found in Brazil by the Europeans in the sixteenth century and further taken to India and East Africa. Botanically speaking, the nut is the fruit of the tree, which is topped by a fleshy and juicy peduncle, whose colour varies from yellow to intense red. This peduncle, also called the pseudo-fruit, apple or pear, may be consumed "in natura" or it may be processed industrially to produce a wide range of products from concentrated juice to sweets. The world production of cashew apples in 2003, as estimated by FAO (14), was around 1,671 billion tons from which Brazil's production accounted for 95%. Although India, Nigeria, Tanzania, and Viet Nam are great world producers of the cashew tree, the economic exploitation of the crop is restricted to the cashew nut. The cashew agroindustry has an outstanding role in the economic and social context of these countries since it is a highly labor intensive activity which offers one of the few, if not only, job opportunities in such under-developed areas. Out of the 30–35 products from the cashew tree, the nut is the most valuable one. In Brazil alone cashew production generates 16,000 jobs in nut processing, 43,000 jobs in farm management, and 280,000 temporary jobs during the harvest period (15). At present, the cashew nut is the most largely exported agroproduct in the state of Ceará (16).

Regarding the cashew apples, it is the internal market that basically consumes the industrially processed products derived from it, and such industry does not play an important role to the economy of the state. Unfortunately, most of the cashew apple production spoils in the soil. In the state of Ceará, for instance, the industrial exploration of the cashew apple ranges from 2 to 6% according to Lopes Neto (17). In such context, the use of the cashew apple as a source of high added-value sugars may represent an attractive economic alternative to the Northeast region. In a previous publication (18), the chromatographic analysis of the solid-free juice aqueous phase revealed that glucose and fructose are present in approximately equal amounts (around 50 g/l each). The present work investigates the technical feasibility of obtaining high-fructose solutions from cashew apple juice by showing experimental results for the separation of fructose and glucose. Industrialized "bottle" juice and clarified juice (tannins removed) were fed into a SMB adsorber operated under conditions for fructose-glucose separation. Experimental steady-state performance for SMB operation at 55°C followed closely the predictions from simulation packages. Purity around 90% was obtained for the fructose-enriched extract. However, the transient history of product concentrations and internal band profiles showed an unexpected behavior for the first time the resin was contacted with the bottle juice. Concentrations of carbohydrates went beyond the values of the periodic steady state temporarily. Fixed-bed experiments seem to suggest that the phenomenon is caused by irreversible adsorption of larger molecules such as tannins. This behavior was not observed for the operation with clarified cashew apple juice, which is free of tannins. These experimental evidences indicate that SMB chromatography may be used to produce high-fructose solutions from a subutilized feedstock with simple pretreatment operations.

Design of SMB Operating Conditions

A conventional SMB unit configuration is composed of at least four columns connected in closed circuit under continuous flow. The inlet flow rates (feed and eluent) and outlet flow rates (extract and raffinate) are constant and located between two adjacent columns at a given time. Then, after some time (switching time), they are simultaneously shifted one bed ahead in the direction of fluid flow. This configuration is depicted in Fig. 1(a). Very

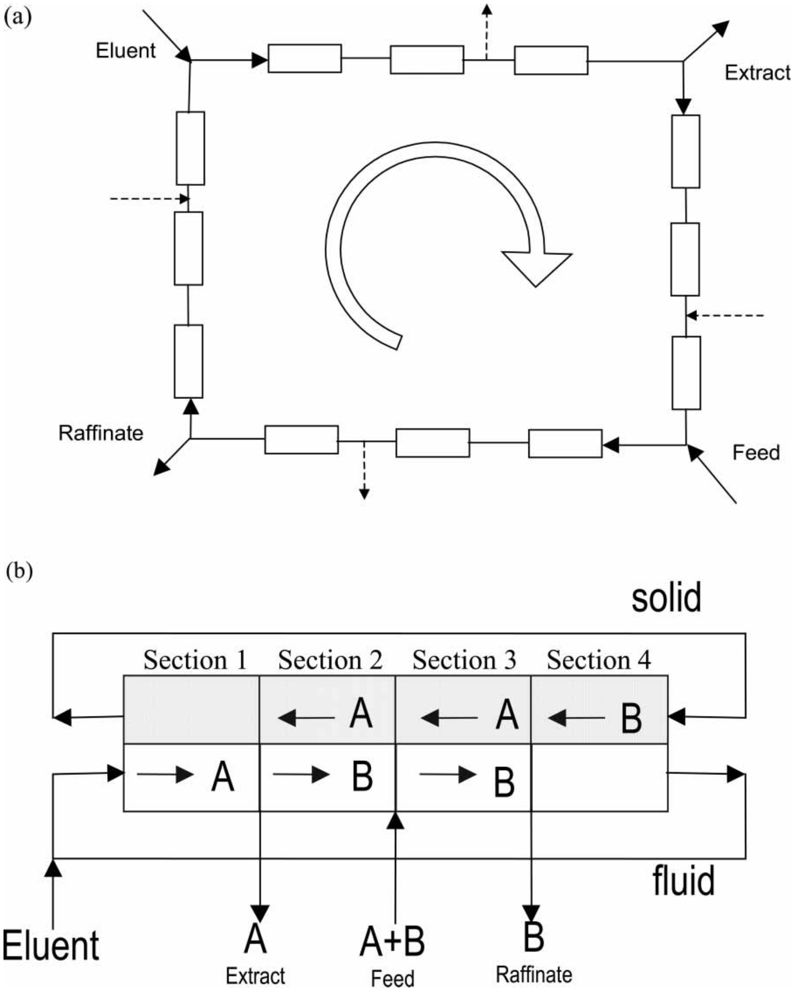


Figure 1. Conventional configuration of a four-section SMB with three columns per section (a) and the equivalent true moving bed (TMB) unit (b) showing the relative movement of two chemical species A and B to be separated.

frequently, the design of SMB conditions is based on the concept of the analogous true moving bed (TMB), which is depicted in Fig. 1(b). The relative motion of chemical species A and B to be separated in the SMB/TMB is shown.

Under equilibrium isotherms, for separation of a mixture A and B to occur, A being the strongest adsorbed species, the following velocity ratio constraints must be met:

$$\nu K'_A < \gamma_1 < \infty \tag{1}$$

$$\nu K'_B < \gamma_2 < \gamma_3 < \nu K'_A \tag{2}$$

$$0 < \gamma_4 < \nu K'_B \tag{3}$$

It has been shown before (18) that the aqueous phase of cashew apple juice is essentially a carbohydrate multicomponent mixture. The design of operating conditions under which an SMB adsorber will separate fructose from this mixture must take into account the adsorption and kinetic data of the individual chemical species present in the mixture. The aqueous phase of the juice is a multicomponent mixture composed of fructose, glucose, citric acid, malic acid, ascorbic acid, unknown higher weight sugars, and tannins. Since all species, other than fructose and glucose, are present in much lower concentrations, linear uncoupled equilibria onto the SMB packing (cation-exchange resin) were assumed. The linear adsorption constants of individual cashew apple constituents were determined according to the following procedure:

- Standard solutions of the following chemical species were prepared: sucrose, citric acid, glucose, fructose, and malic acid. The concentrations were nearly those present in the juice and shown in a previous publication (18). Ascorbic acid was neglected since it decays quite fast after being exposed to oxygen and light.
- Samples of the solutions were injected into a SMB column (29 cm length, 2.6 cm i.d.) with the aid of an injecting loop (500 μl) and the column response was monitored by a RI detector.
- The linear equilibrium constant (K_i') of each of the chemical species investigated was calculated from the stoichiometric time of the respective experimental curve according to equation (4):

$$t_{st_i} = \frac{V_c}{Q}\left(\varepsilon + (1-\varepsilon)K_i'\right) \tag{4}$$

where V_c is the column volume, Q is the volumetric flow rate and ε is the void fraction of the packing. The linear adsorption constants (K_i') obtained at 55°C were 0.12; 0.26; 0.27; 0.42; 0.51 for sucrose, citric acid, glucose, malic acid, and fructose, respectively. The same pulse chromatography experiment was performed for a tracer component (blue dextran) in order to measure the void fraction of each of the columns used in the SMB setup. The mean value obtained for the void fraction ε was 0.40 ± 0.01. Note that we have chosen to increase operating temperature to 55°C in order to inhibit bacterial growth and not to reach the limiting temperature of the equipment (60°C). The equilibrium theory has been successfully applied to multicomponent mixtures (19, 20) in order to predict the distribution pattern in the extract and raffinate of the chemical species involved. For linear systems, the theory is readily applicable and easily understood by the usual triangle representation, which defines the flow rate ratios in sections 2 and 3 for different separations. In the case of cashew apple juice, the different separation zones, found in the frame of equilibrium theory, are shown in Fig. 2.

The points F, M, G, C, and S are located on the diagonal line ($\gamma_2 = \gamma_3$) and their coordinates are ($\nu K_i'$, $\nu K_i'$), which refer to the equilibrium data obtained for fructose ($i = F$), malic acid ($i = M$), glucose ($i = G$), citric acid ($i = C$) and sucrose ($i = S$), respectively. Four distinct triangles may be observed in Fig. 2, which define operating points under which the SMB adsorber may be operated in order to achieve different distributions of the mixture components in the extract and raffinate products. For, instance, if one chooses to use a (γ_2, γ_3) point located inside triangle 2, the extract will collect glucose, malic acid, and fructose, whereas the raffinate will contain sucrose and citric acid. If the SMB is operated within the (γ_2, γ_3) parameter space just above triangle 4, nearly pure fructose may be obtained in the extract and all other species, plus some traces of fructose, will be obtained in the raffinate. Table 1 summarizes the implications of operating a SMB adsorber under (γ_2, γ_3) pairs located in triangles depicted in Fig. 2. Inside all of them, within the frame of equilibrium theory, there is no cross-contamination and the products collected in each product are 100% pure.

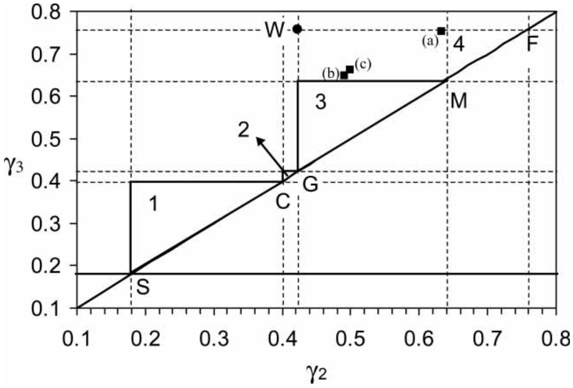


Figure 2. Separation regions for a multicomponent mixture according to the equilibrium theory applied to linear adsorption isotherms. The black squares indicate the operating points of run 1 (a), runs 2/3 (b), and run 4 (c).

Table 1. Species collected in the extract and raffinate products of a SMB operated under different section flow conditions

Triangle	Conditions on γ_2 and γ_3	Species in extract	Species in raffinate
1	$\gamma_1 > \nu K'_F$ and $\gamma_4 < \nu K'_S$ $\nu K'_S < \gamma_2 < \gamma_3 < \nu K'_C$	*C, G, M, F*	*S*
2	$\gamma_1 > \nu K'_F$ and $\gamma_4 < \nu K'_S$ $\nu K'_C < \gamma_2 < \gamma_3 < \nu K'_G$	*G, M, F*	*S,C*
3	$\gamma_1 > \nu K'_F$ and $\gamma_4 < \nu K'_S$ $\nu K'_G < \gamma_2 < \gamma_3 < \nu K'_M$	*M, F*	*S, C, G*
4	$\gamma_1 > \nu K'_F$ and $\gamma_4 < \nu K'_S$ $\nu K'_M < \gamma_2 < \gamma_3 < \nu K'_F$	*F*	*S, C, G, M*

Note that these statements are strictly valid only if mass-transfer effects are neglected, which is an applicable assumption if column HETP is low enough. Experience has shown that this is not the case of the columns used in this work (21). Furthermore, it is desirable to obtain a fructose-enriched extract with high recovery of this sugar from the feed. Therefore, we have chosen to operate inside the triangle GWF, which includes triangles 3 and 4. If we were to obtain "malic-free fructose," very low throughputs would be processed and mass-transfer effects would eventually forbid the operation of our present equipment to reach this purity requirement. This decision also implies that some contamination of malic acid in both extract and raffinate may be tolerated.

EXPERIMENTAL

Experimental results were obtained in fixed bed and in simulated moving bed using as feed synthetic sugar solutions, cashew apple juice as obtained industrially (whole and dilute) and after a clarification procedure. All experiments in SMB mode were performed in a pilot scale plant LICOSEP 12-26, by Novasep (Champignelles, France). Twelve Superformance columns (by Gotec Labortechnik, Muhltal, Germany) were used, with dimensions of 29 cm length and 2.6 cm internal diameter. The distribution of columns in the sections was 3-3-3-3 for the run with a synthetic mixture and 3-3-4-2 for the other runs. The choice for a longer section 3 and a shorter section 4 for some runs was based on simulation studies (22), which showed that, for the SMB pilot plant under study, this subdivision improved adsorbent productivity as compared to the usual 3-3-3-3 subdivision. The packing was a strongly acid cation-exchange resin of gel type, Dowex Monosphere, in Ca form with particle diameter of 320 μm. Three different kinds of feed were used, in chronological order: (1) a synthetic solution of glucose, fructose, and malic acid, (2) “bottle” cashew apple juice, and (3) clarified cashew apple juice, all of which were filtered (0.5 μm filter cloth) and degassed prior to each experiment. Table 2 summarizes the experimental conditions for each of these three experiments. The experiment with bottle juice was performed twice (runs 2 and 3). Before conducting the experiment with clarified cashew apple juice (run 4), the SMB columns were washed with a dilute NaOH solution followed by rinsing with deionized distilled water in order to remove organic matter eventually accumulated in the resin. Afterward, the columns were ion-exchanged with $CaCl_2$ so as to restore the calcium form of the resin and finally rinsed with plenty of distilled deionized water. Additionally, three fixed-bed experiments were performed with dilute cashew apple (bottle) juice followed by leaching with NaOH. The experimental conditions under which the fixed-bed runs were carried out are summarized in Table 3. Sugar assay, in all samples collected in the seven experiments reported, was measured by HPLC, as described elsewhere (18). Hydrodynamic parameters as well as those for adsorption equilibrium and kinetics (used in the dynamic simulation packages) were mostly measured in our laboratory and are presented in Table 4. Further experimental details may be found in previous publications (21, 22).

RESULTS AND DISCUSSION

SMB Fructose-Glucose Separation from a Synthetic Mixture

Before using the actual juice as feed, a SMB experiment was performed using a synthetic mixture of glucose, fructose, and malic acid. Besides glucose and fructose, citric acid and malic acid are the two organic acids in larger

Table 2. Operating conditions for SMB fructose-glucose separation experiments

Experiments	Run 1	Run 2^a	Run 3^a	Run 4^a
Switching time, min	3.3	3.3		3.3
Flowrates, mL/min:				
Eluent	11.00	10.91		11.00
Extract	4.59	7.04		7.00
Feed	2.43	2.90		2.90
Raffinate	8.84	6.77		6.77
Recycle (Q_4)	24	24		24.09
$\gamma_1, \gamma_2, \gamma_3, \gamma_4$	0.88, 0.63, 0.76, 0.29	0.87, 0.49, 0.65, 0.29		0.88; 0.50; 0.66; 0.29
Type of feed	Synthetic soln.	Bottle juice		Clarified juice

^{a}Configuration of 3, 3, 4, and 2 columns in sections 1, 2, 3, and 4, respectively.

Table 3. Experimental conditions for fixed-bed experiments

	Run 5	Run 6	Run 7
Temperature (°C)		55	
Fructose concentration in feed (g/l)	10	0	27.5
Glucose concentration in the feed (g/l)	10	0	27.5
Volumetric flow rate (mL/min)		5	
Column length (cm)		8.5	
Column internal diameter (cm)		2.6	

quantities that would potentially pose any problem concerning the change of the resin ionic form. Note that citric acid is an antioxidant added to the industrial juice and would not be present in freshly expressed juice. Hence, we decided to verify fructose-glucose SMB separation in the presence of malic acid. The operating conditions used in this experiment are shown in Table 2. We assigned values to γ_2 and γ_3 nearly equal to the coordinates of the vertex of triangle 4 (see Fig. 2), which is the equilibrium triangle for complete separation of fructose (collected in the extract) from the other cashew juice components (collected in the raffinate). At this point, the equipment could be operated at the maximum throughput that allowed complete separation under equilibrium conditions. Nonetheless, some contamination of malic acid in the extract was to be expected due to the equilibrium theory requirements. Figure 3 shows the internal concentration

Table 4. Model parameters used in the process simulations reported in this work

	T = 55°C		
Parameter	Glucose	Malic Acid	Fructose
Pe/column		500	
ε		0.4	
ε_p		0.1	
K'	0.27	0.42	0.51
$\frac{(1-\varepsilon)}{\varepsilon}K'$	0.41	0.63	0.77
k_p, min^{-1a}	2.5	2.5	2.5
k_μ, min^{-1a}	1.5	1.5	1.5
k_{LDF}, min^{-1b}	1.89	1.48	1.33

[a] Kinetic parameters used in the true moving-bed model (bi-LDF approximation).

[b] Kinetic parameters used in the dynamic simulated moving-bed model (LDF approximation), correlation found in Azevedo and Rodrigues (23).

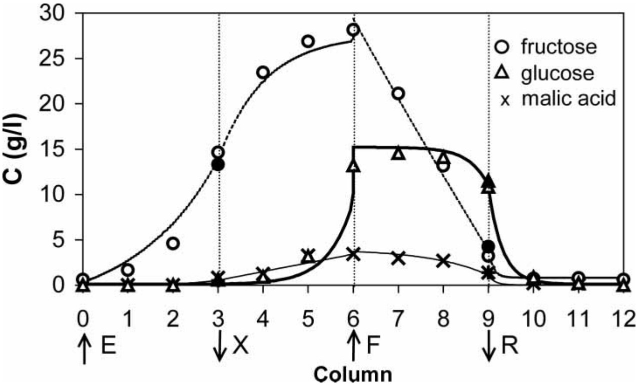


Figure 3. Concentration profiles at cyclic steady state for the separation of synthetic fructose and glucose in the presence of malic acid. Symbols are experimental data and curves are simulated using a TMB model.

profiles of fructose, glucose, and malic acid at cyclic steady state. The points were collected at 50% of each period of cycle 15. The dark points are the average extract and raffinate concentrations measured from the products collected for a whole cycle. The curves are simulated data from a TMB-based model, described elsewhere (21), assuming uncoupled linear equilibrium isotherms for the three chemical species. A good agreement may be observed and the presence of malic acid does not seem to have altered the resin adsorption and mass transfer characteristics. As expected, malic acid contaminates the extract since it is not completely desorbed in section 2 due to the slow mass transfer.

SMB Fructose-Glucose Separation from Commercial Cashew Apple Juice

In the following experiments (runs 2 and 3), real cashew apple juice was used. The cashew apple juice, as found in commercial brands, had to undergo a filtration step before being fed into the SMB. The eluent was distilled deionized water, which was filtered and degassed prior to SMB operation. Both feed and eluent pumps made use of online filters before and after the pump heads. Eluent and feed reservoirs were kept in a thermostat bath at 55°C throughout the experiment. The operating conditions under which the SMB was operated in order to separate fructose from cashew apple juice are summarized in Table 2. Note that the restriction of the equilibrium theory on the velocity ratio for section 4 was intentionally violated ($\gamma_4 = 0.29$, which is larger than the maximum value 0.18, according to Fig. 2). The equilibrium restriction for this section is based on the equilibrium constant of sucrose, which is present in very small amounts. The little sucrose present in the feed is readily inverted when it contacts the separation resin, which is highly acid. This is verified by the absence of sucrose peaks in the chromatographic analysis of both the products and internal profile samples. Besides, operating the SMB under the restriction on section 4, the other ratios held constant, would require very large eluent flow rates and cause undesired dilution.

The extract and raffinate streams were collected for a complete cycle at the second, third, fifth, sixth, eighth, tenth, and fifteenth cycles. Their average cycle concentration was determined by HPLC analysis. By decreasing the mobile phase flow rate in the conditions of analysis, it was possible to resolve the peak of malic acid and calculate its concentration in the sample. However, for the sake of clarity, only fructose and glucose concentrations will be shown in some plots since they are present in a much higher content. Figure 4 shows the experimental histories of the average extract and raffinate concentrations. The curves represent simulated results, assuming linear uncoupled isotherms as measured previously for the individual sugars. An unexpected behavior is observed. The product concentrations surpass those values eventually reached at steady state. The internal profiles were also sampled at 50% of each of the periods of the fifth, tenth, and fifteenth cycles. Figure 5 shows the profiles obtained at the fifth and tenth cycles, as compared with the predictions from a model using a real SMB strategy (21). The same anomalous behavior is observed, being more pronounced at the fifth cycle. In sections 2 and 3, fructose and glucose concentrations go far beyond those expected assuming linear uncoupled isotherms and mass transfer described by the LDF expression.

This behavior is not usual in systems with linear equilibria. No such phenomenon was observed for the fructose-glucose experiments using synthetic solutions. Therefore, it may be due to other chemical species present in the feed (and not identified by the previous HPLC analysis).

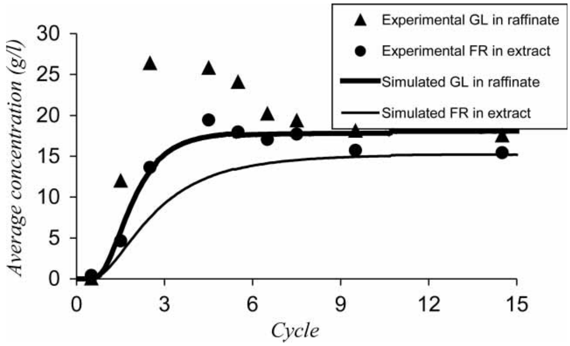


Figure 4. Histories of average extract and raffinate concentrations for SMB experiment (run 2) with cashew apple juice. Curves were obtained from simulations of a SMB model.

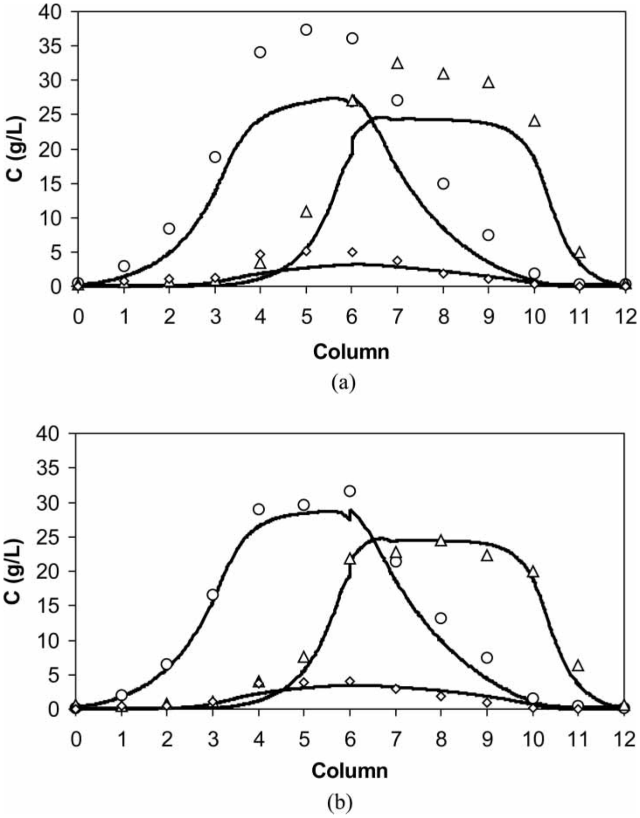


Figure 5. Experimental concentration profiles for fructose (circles), glucose (triangles), and malic acid (diamonds), sampled at 50% of each of the periods of the fifth (a) and tenth (b) cycles. Lines are simulations for a real SMB model. The thick lines are results from a dynamic SMB model and the thin ones are results from a true moving-bed model.

These species may have nonlinear equilibrium isotherms, which are probably much more favorable (irreversible) than the sugar isotherms in the low concentration range. However, as the steady state was reached, the resin capacity for glucose and fructose seems to be unchanged. The periodic steady state was assumed to have been achieved in the fifteenth cycle. This was confirmed by measuring unchanging average product concentrations and by checking glucose and fructose global mass balances. The profile obtained at a half period of the fifteenth cycle is illustrated in Fig. 6. The curves stand for simulations: the thick ones were obtained from an SMB strategy and the thin ones, from a TMB strategy. There is very good agreement among simulation results obtained at the periodic steady state. The performance criteria obtained experimentally agree reasonably well

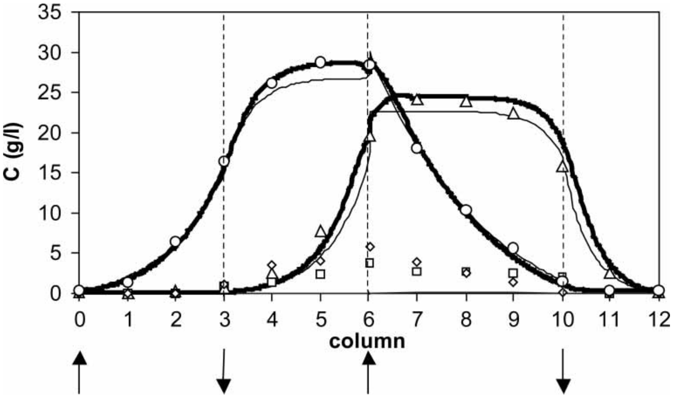


Figure 6. Experimental concentration profiles for fructose (circles), glucose (triangles), malic acid (diamonds), and citric acid (squares) obtained at half period in the fifteenth cycle. Curves stand for simulation results.

with those predicted from simulation using both TMB and SMB strategies, as may be verified in Table 5. Even though experimental purities are below the predicted ones, the concentration of the key products (fructose and glucose) obtained in the extract and raffinate follow closely those calculated from numerical simulation.

A second experiment in the simulated moving bed was performed using cashew apple juice as feed (run 3). The operating conditions were the same as in run 2. Between the two runs, no special procedure was employed to "clean" the columns. The equipment was run for several cycles with only water (about 10 L) as both feed and eluent in order to rinse the resin and elute all sugars. In run 3, the raffinate and extract were collected for a whole cycle in the second, fourth, fifth, eighth, tenth, twelfth and fifteenth cycles. The surpassing of steady-state product concentrations previously reported for run 2 was not observed. Figure 7 shows the concentrations of fructose in the extract and glucose in the raffinate as compared to the

Table 5. Comparison of performance criteria obtained experimentally and through simulations using TMB and SMB strategies (run 2)

Performance criteria	Experimental	Simulated from TMB strategy	Simulated from SMB strategy
PU_X (%)	90.2	92.3	94.5
PU_R (%)	88.4	91.8	93.6
Average PR_i (kg/hr/m^3)	6.4	6.2	6.5
Fructose in extract (g/l)	15.5	14.8	15.9
Glucose in raffinate (g/l)	18.0	17.0	18.0

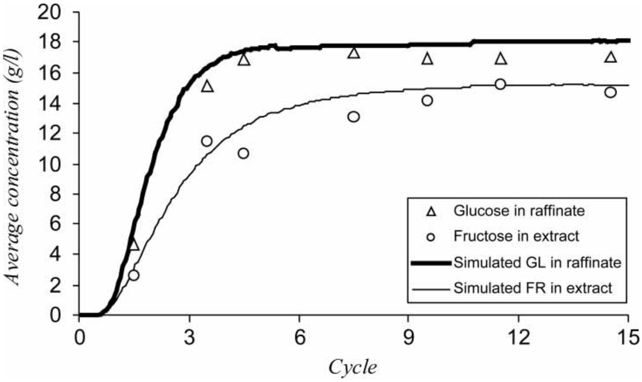


Figure 7. Concentration histories of fructose in the extract and glucose in the raffinate, run 3. The curves are simulated (SMB model) and represent the average concentrations at each period. The symbols are concentrations measured from the products collected for a whole cycle.

simulated curves. The internal concentration profiles were also sampled at 50% of each of the switching times of the fifth and the tenth cycles. The results are shown in Fig. 8. For the sake of clarity, the profiles of the other species are omitted. The black symbols stand for the concentrations obtained in run 2 whereas the white symbols are those obtained in run 3. It is clear that, in run 3, the transient behavior of sugar concentrations follows the fashion predicted by the process simulator for a synthetic mixture. Both mass-transfer phenomena and equilibrium parameters seem to have been preserved despite the anomalous behavior detected in run 2.

Breakthrough and Elution Experiments from Dilute Cashew Apple Juice

Additional experiments were carried out in fixed bed using dilute cashew apple juice as feed in order to search for reasonable hypothesis to explain the observed transient behavior in SMB separation. Since the steady-state performance in the simulated moving bed did not seem to be affected, the possible cause of the observed anomalous behavior in the initial cycles in run 2 is likely to be related to diffusion barriers caused by larger molecules present in the juice such as polyphenols, oligosaccharides, or proteins. In order to test this hypothesis, a column was packed with resin Dowex Monosphere and a set of breakthrough and regeneration curves were obtained. Figure 9 shows the breakthrough (a) and elution curves (b) obtained for the fresh resin. Figure 9c shows another breakthrough curve obtained right after the elution curve. The first breakthrough curve (Fig. 9a) shows a small overshoot of both sugar concentrations beyond the feed concentration. This behavior

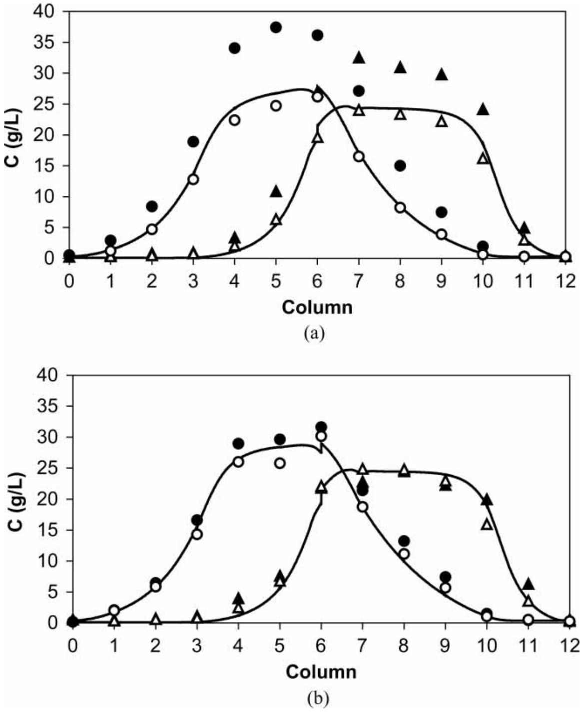
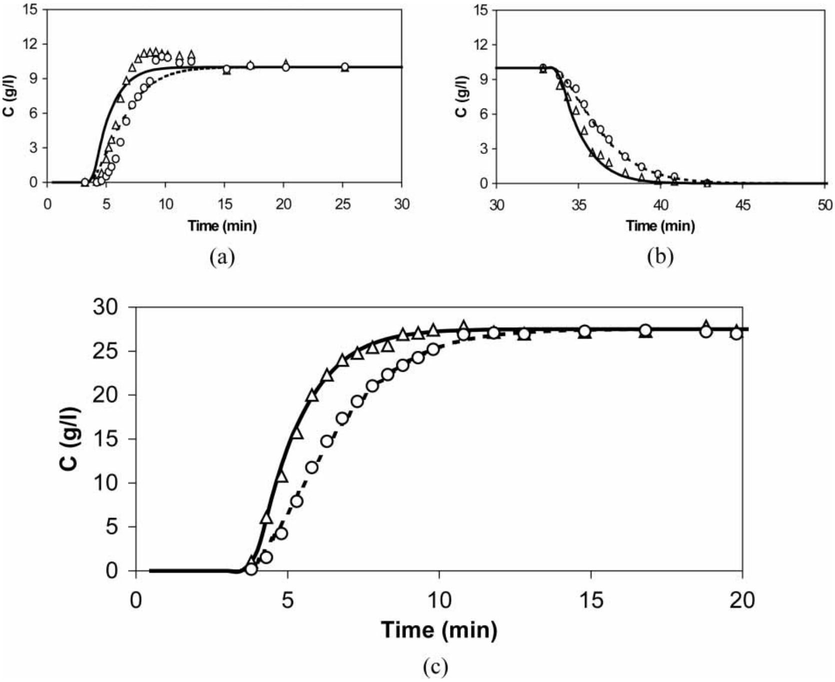


Figure 8. Internal concentration profiles for glucose (triangles) and fructose (circles) sampled at the fifth (a) and tenth (b) cycles. Black symbols refer to run 2 and white ones refer to run 3. Curves are simulated (SMB model).

resembles that observed for run 2 in the initial cycles of SMB operation (see Fig. 4). However, the adsorbent capacity seems to remain unchanged, which is evidenced by the experimental regeneration curve. The adsorbed phase concentrations for fructose and glucose, as calculated from the regeneration curve, are 5.47 and 2.95 g/l, respectively. These figures would be 5.10 and 2.80 g/l, respectively, as calculated from the equilibrium isotherm, which means an experimental deviation of 7% and 5%, respectively. Therefore, this behavior might confirm the previously stated hypothesis: unknown chemical species are irreversibly adsorbed (very favorable isotherm) on the resin and cause the “rollup” behavior of the sugars. Such behavior is not observed in the second experiment since the resin has already reached the equilibrium capacity of the unknown chemical species, which were irreversibly adsorbed in the first experiment. Nevertheless, adsorption capacity of both sugars (fructose and glucose) on the resin remains the same, which is confirmed by the second breakthrough experiment, shown in Fig. 9c.

In order to check whether any chemical species had been irreversibly adsorbed on the resin, the same column used in runs 5, 6, and 7 was



(a) (b) (c)

Figure 9. Breakthrough curve obtained for dilute cashew apple juice, run 5 (a), followed by elution with water, run 6 (b), and a second breakthrough curve with a more concentrated juice, run 7 (c). Triangles represent glucose concentration, and circles represent fructose concentration.

washed with NaOH. Two liters of a 1N solution were pumped into the column at 4 mL/min so as to completely exchange cations Ca^{++} for Na^{+} and desorb any organic matter that might have been accumulated in the resin. A sample was taken from the collected wash, neutralized with HCl, and injected into an HPLC column under the same analytical conditions for sugar assay. Figure 10 shows the chromatogram obtained for the NaOH eluate as compared to that for the whole juice. The peaks at 10 and 17.5 min were identified as having been retained in the column. These peaks are presently unidentified but probably correspond to polyphenols. They may have an effect on the behavior observed both for SMB and fixed bed with fresh resin contacted with whole juice.

SMB Fructose-Glucose Separation from Clarified Cashew Apple Juice

The SMB columns, previously used to perform runs 1, 2, and 3, were washed with NaOH (10 L of 1 N solution), rinsed with water (about 20 L) and

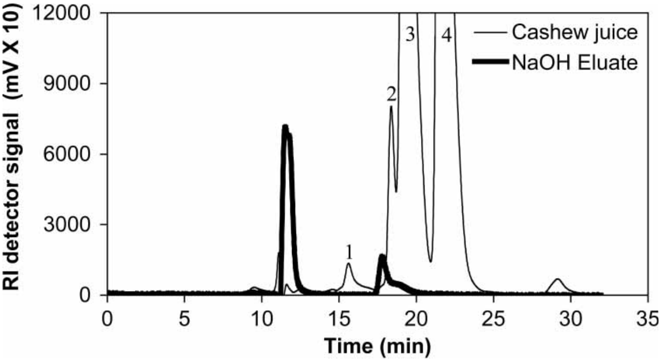


Figure 10. Chromatograms of cashew apple juice (thin lines) and NaOH eluate (thick lines). Peaks 1 to 4 have been identified for the juice (18) as sucrose, citric acid, glucose and fructose (+ malic acid), respectively. The other peaks are unknown substances.

ion-exchanged back with $CaCl_2$ (10 L of 1 N solution). After all organic matter had been removed, and the Ca^{2+} ionic form was restored, run 4 was carried out under the conditions referred in Table 2. This time, clarified cashew apple juice was used, which is obtained by precipitation and removal of tannins using gelatin. Figure 11 shows the internal profiles obtained after the steady state was reached (fifteenth cycle). Experimental results follow closely those predicted by simulation and, during the transient period, no anomalous behavior was observed. This confirms that the cause of the overshoot pattern observed for the first time that fresh resin was contacted with whole juice must have been caused by the presence of polyphenols, which were removed from the juice in the clarification procedure.

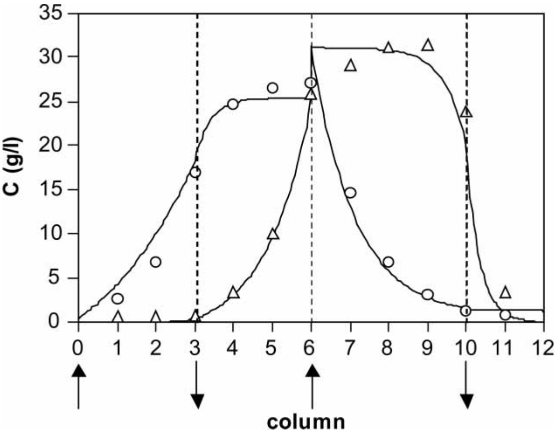


Figure 11. SMB internal concentration profile of glucose (triangles) and fructose (circles) as compared to TMB-model simulated curves (run 4).

CONCLUSIONS

This paper examined the potential use of cashew apple juice as a source of fructose and glucose to be separated by SMB chromatography. Since these sugars naturally occur in cashew apple juice in approximately equal amounts ($50\,\mathrm{kg/m^3}$) and this is a presently low-cost agricultural waste, the results of the present investigation may indicate alternatives to industrial exploitation of the crop. The steady-state performance of an SMB pilot plant using commercial cashew apple juice as feed (with no special pretreatment) agreed quite well with the theoretical predictions, as obtained from process models described in previous publications for synthetic fructose-glucose mixtures (21). Interesting anomalous behavior was obtained at the transient state for the first time that the adsorbent resin was contacted with the juice both in SMB and fixed-bed modes. Larger molecules present in the juice, such as polyphenols, might have been strongly and irreversibly adsorbed on the resin. During the transient period, the more favorable adsorption of larger molecules may have caused the overshoot pattern observed for the sugars. Experimental work carried out in fixed-bed mode support this theory. Moreover, results obtained with clarified cashew apple juice (free of tannins) confirm that polyphenols should be the cause of the overshoot pattern observed. Further investigation into the long-term life of the resin and combination of SMB separation with vacuum evaporation (for syrup production) are strongly recommended for future research.

NOTATION

K'	linear adsorption constant assuming homogeneous solid
K_{LDF}	rate constant for LDF approximation to intraparticle mass transfer, min^{-1}
k_{μ}	mass-transfer rate coefficient in adsorbent solid phase, min^{-1} (bi-LDF approximation)
k_p	mass-transfer coefficient in adsorbent pore phase, min^{-1} (bi-LDF approximation)
Pe	Peclet (axial) number
Q	SMB volumetric flow-rate ($\mathrm{cm^3/min}$)
t_{st}	stoichiometric time (min)
V_c	column volume ($\mathrm{cm^3}$)

Greek Letters

ε	packing void fraction
ε_p	resin particle void fraction
ν	Phase ratio $= (1 - \varepsilon)/\varepsilon$
γ	ratio between velocity of the liquid and solid phase

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REFERENCES

1. Broughton, D.B., and Gerhold, C.G. Continuous Sorption Process Employing Fixed Bed of Sorbent and Moving Inlets and Outlets. U.S. Patent No. 2,985,589, 23 May 1961.
2. Keller II, G.E. (1995) Adsorption: building upon a solid foundation. *Chem. Eng. Prog.*, 91 (10): 56–67.
3. LeVan, M.D. (1998) Adsorption Processes and Modeling. In: Fundamentals of Adsorption 6, Proceedings of the Sixth International Conference of Fundamentals of Adsorption, Gien, France, May 24–28; Meunier, F. (Ed.); Elsevier: Amsterdam, 19–29.
4. Subramani, H.J., Hidajat, K., and Ray, A.K. (2003) Optimization of simulated moving bed and varicol processes for glucose-fructose separation. *Trans IchemE*, 81 (partA): 549–567.
5. Schramm, H., Kaspareit, M., Kienle, A., and Seidel-Morgenstern, A. (2002) Improving SMB process by cyclic modulation of the feed concentration. *Chem. Eng. Technol.*, 25 (12): 1151–1155.
6. Zhang, Z.Y., Mazzotti, M., and Morbidelli, M. (2003) Powerfeed operation of simulated moving bed units: changing flow-rates during the switching interval. *J. Chromatography A*, 1006 (1–2): 87–99.
7. De Rosset, A.J., Neuzil, R.W., and Korous, D.J. (1976) Liquid column chromatography as a predictive tool for continuous counter adsorptive separations. *Ind. Eng. Chem. Proc. Des. Dev.*, 15 (2): 261–266.
8. Giacobello, S., Storti, G., and Tola, G. (2000) Design of a simulated moving bed unit for sucrose-betaine separations. *J. Chromatography A*, 872 (1–2): 23–35.
9. http://www.corn.org/web/suppdisp.htm (accessed Oct 2004).
10. Neuzil, R.W., and Priegnitz, J.W. Process for separating a ketose from an aldose by selective adsorption. US Patent No. 4,226,977, 7 Oct 1980.
11. Fickel, R.G. Simulated countercurrent sorption process employing ion exchange resins with periodic backflushing. US Patent No. 4,319,929, 16 March 1982.
12. Neuzil, R.W., and Priegnitz, J.W. Process for separating glucose from fructose by selective adsorption. US Patent No. 4,442,285, date (1984).
13. Lima, V.P.M.S. (1988) *The Cashew Crop in Northeastern Brazil (in Portuguese)*; BNB-ETENE: Fortaleza, 486 pp.
14. http://www.fao.org (accessed Oct 2004).
15. Pessoa, P.F.A.P., Leite, L.C.S., and Pimentel, C.R.M. (1995) Present situation and perspectives in tropical agroindustry (in Portuguese). In: *Cashew Culture, Modern Production Techniques*, 1st Ed.; Araújo, J.P.P. and Silva, V.V., eds.; EMBRAPA/CNPAT: Fortaleza, Brazil, 23–42.
16. Leite, L.A.S. (1994) *The Cashew Agroindustry in Brazil* (in Portuguese). 1st Ed.; EMBRAPA-CNPAT: Fortaleza, Brazil, 195 pp.
17. Lopes-Neto, A. (1981) *Cashew Agroindustry in the Northeast and other World Producers*. (in Portuguese), 1st Ed.; Banco do Nordeste do Brasil: Fortaleza, Brazil, 472 pp.

18. Azevedo, D.C.S. and Rodrigues, A.E. (2000) Obtainment of high-fructose solutions from cashew (Anacardium occidentale, L.) apple juice by simulated moving-bed chromatography. *Sep. Sci. Technol.*, 35 (16): 2561–2581.
19. Chiang, A.S.T. (1998) Equilibrium theory for simulated moving bed adsorption processes. *AIChE J.*, 44 (11): 2431–2441.
20. Migliorini, C., Mazzotti, M., and Morbidelli, M. (2000) Design of simulated moving bed multicomponent separations: langmuir systems. *Sep. Pur. Technol.*, 20 (1): 79–96.
21. Azevedo, D.C.S. and Rodrigues, A.E. (2001) Fructose-glucose separation in a SMB pilot unit: modeling, simulation, design and operation. *AIChE J.*, 47 (9): 2042–2051.
22. Azevedo, D.C.S. (2001) *Separation/Reaction in Simulated Moving Bed: Application to the Production of Industrial Sugars*; PhD Dissertation, University of Porto: Porto, 206 pp.
23. Azevedo, D.C.S. and Rodrigues, A.E. (1999) Bilinear driving force approximation in the modeling of a simulated moving bed using bidisperse adsorbents. *Ind. Eng. Chem. Res.*, 38 (9): 3519–3529. Please check in reference 8, “(2000)” was given after page range.