Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Springfield, R. M. and Hester, R. D.(1999) 'Continuous Ion-Exclusion Chromatography System for Acid/Sugar Separation', Separation Science and Technology, 34: 6, 1217 — 1241
To link to this Article: DOI: 10.1080/01496399908951090
URL: http://dx.doi.org/10.1080/01496399908951090

SEPARATION SCIENCE AND TECHNOLOGY, 34(6&7), pp. 1217–1241, 1999

Continuous Ion-Exclusion Chromatography System for Acid / Sugar Separation

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ABSTRACT

A simulated moving bed ion exclusion chromatography system was constructed for the continuous separation of the components in an aqueous feed solution of sucrose and sulfuric acid. A system of 18 columns was arrayed about a central manifold system. Each column was packed with approximately 820 mL of porous cationic exchange resin. The system was designed for the flexibility to use fluid recycle loops and unrestricted placement of all inlet and outlet streams. Monitoring and control functions were performed using a Camile 2000 process controller integrated with a custom-built control computer. The aqueous feed solution, usually containing 10 wt.% sucrose and 10 wt.% sulfuric acid, was generally introduced into the system at a rate of roughly 2 L/hr. Approximately 4 L/hr of water was used to elute materials through the separation system. After optimization, the separation system allowed greater than 95% recovery of the feed sucrose in an exit stream containing 8.8 wt.% sucrose and 98% recovery of the feed acid in a second exit stream containing 5 wt.% acid.

INTRODUCTION

The work presented in this paper is part of an effort to develop a commercializable process for the conversion of lignocellulosic materials to fuel-grade ethanol. Candidate lignocellulosic materials include agricultural waste, energy crops, under-utilized and short rotation hard woods, and municipal waste. The process utilizes sulfuric acid to hydrolyze cellulose into simple sugars. The resulting acid/sugar mixture is then separated, after removal of lignin, to allow reuse of the acid and fermentation of the sugars to produce fuel-

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grade ethanol. Many benefits arise from the efficient conversion of lignocellulosic resources to ethanol and lignin for use as fuels. Among them are

- -A substantial reduction in the emission of carbon dioxide and an overall improvement in air quality through a reduction in vehicle exhaust emissions;
- -Recovery and utilization of waste materials;
- -Added value for agricultural and forestry crops; and
- -Improved market balance for individual crude oil refinery products

Process Overview

As shown in Figure 1, the major systems in this process for the conversion of lignocellulosic materials to ethanol and lignin are

1) Lignocellulosic solids feed and acid impregnation of the lignocellulosic material
2) Hemicellulose and cellulose hydrolysis to sugars and lignin separation
3) Acid recovery and sugar separation
4) Concentration acid and sugar solutions
5) Fermentation of the pentose and hexose sugars to ethanol
6) Ethanol recovery and effluent treatment

The impregnation system continuously exposes the lignocellulosics to sulfuric acid under high-shear conditions. After water dilution, the acid in the impregnated material serves as a catalyst in a continuous hydrolysis reactor. The high temperature hydrolysis reaction converts the acid impregnated cellulosic materials into an aqueous stream containing both sugars and acid called the hydrolyzate. The residual solids in the hydrolyzate are removed in the lignin separation system by a belt filter. The solids-free hydrolyzate, an aqueous solution of acid (~12 wt. %) and sugars (~5 wt. %), is then conveyed to the recovery system. The recovery system uses continuous ion exclusion to separate the hydrolyzate into an acid-rich aqueous stream and a sugar-rich aqueous stream. The acid-rich stream is concentrated to the initial acid concentration, 70 wt. %, by evaporation and then recycled to the impregnation system. The sugar-rich stream is concentrated by evaporation to 9.5 wt. % sugar and transported to the fermentation system for ethanol production.

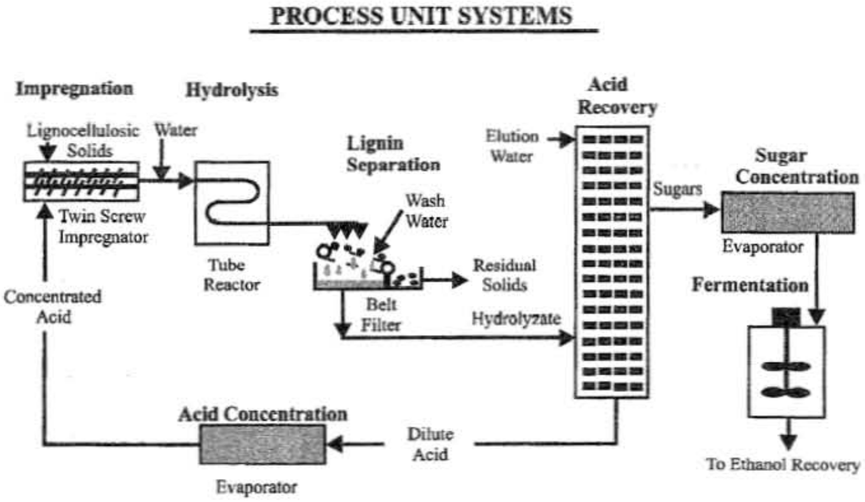


FIGURE 1. Ethanol from lignocellulosics process unit systems.

The focus of this paper is the acid recovery system: a continuous simulated moving bed (SMB) ion exclusion chromatography system used to separate the hydrolyzate into an acid-rich stream and a sugar-rich stream. The SMB system was studied at the University of Southern Mississippi (USM) using a laboratory scale continuous separation process consisting of several resin-packed columns connected by flow control valves. The following discussion details the design, fabrication, and experimental results of the laboratory scale work preformed at USM.

Ion Exclusion

Wheaton and Bauman first noted Ion Exclusion Chromatography (IEC) in 1953 (1). The foundational principle of this technique was recognized following the observation that the concentration of an electrolyte in a polar solvent is lower within the pores of a microporous ion exclusion resin than in the interstitial (hereafter referred to as macropore) volume. The resin used in these early experiments was a strong cationic exchange resin (sulfonated poly(styrene-co-divinylbenzene)) in the hydrogen form and is similar to the

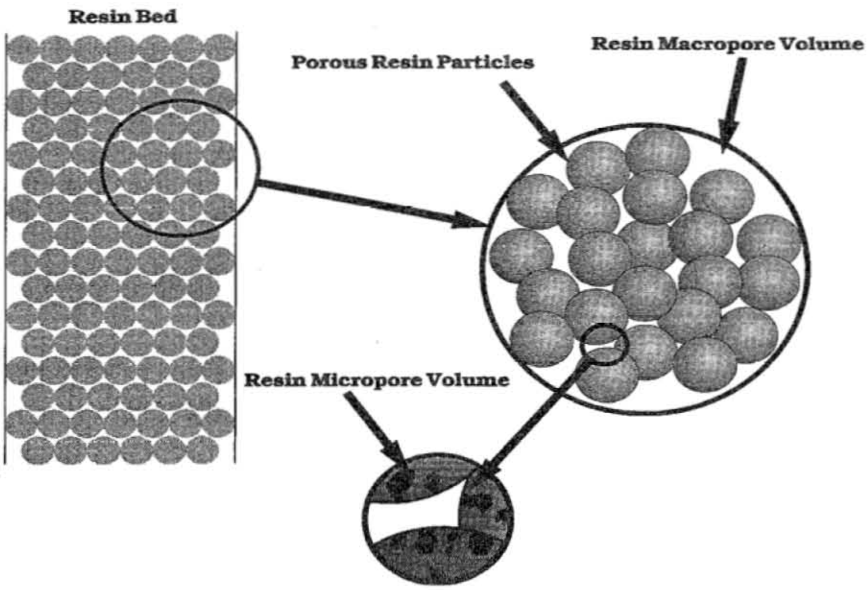


FIGURE 2. Schematic of resin.

resins used for this project. Wheaton and Bauman noted that the resin had to be of the same ionic charge as the ionic portion of the materials being separated (1). Figure 2 shows a schematic representation of the resin bed structure highlighting the micropores and macropores. Separation results from differences in the path the solute molecules travel, which is dependent upon the size and ionic nature of the solute. The mean path length for a charged solute through an ionic chromatographic system is greatly influenced by coulombic repulsive forces. Ionic separation of differing solutes is achieved if the solutes have sufficiently different ionic character. Conditions that contribute to good separation between ionic and non-ionic solutes include low ionic concentrations in the feed stream, small feed-to-solvent volume ratios, low feed rates, and elevated temperatures (2,3,4).

Simpson and Wheaton have shown that the most important descriptive parameter for separations using IEC is the difference in the distribution coefficient (5). Distribution coefficients describe the ratio of the concentrations of a solute in the micro- and macropores of the chromatography column. A polar solvent, used as the mobile phase in the chromatography system, typically swells the resin. Resin swelling is a response to an imbalance between osmotic pressure and the retractive forces acting on the polymeric chains of the resin. The swelling yields resin volume changes that reflect the new equilibrium of these forces. For example, an increase in the local ion concentration would reduce the electrostatic repulsive forces and result in micropore shrinkage. On the other hand, an increase in temperature allows the polymer to relax reducing the retractive forces and increasing the micropore volume. Ionic species are excluded from the micropores as explained by the Donnan exclusion principle, which states that the electric potential in the resin must remain balanced (6). Therefore, since the sulfonate group is physically attached to the polymer composing the resin, the ions are predominately excluded from the resin because their presence within the resin would disrupt the electric potential balance.

Some drawbacks are evident in the systems described above. These systems (known as fixed bed systems) suffer, according to Ernst and Hsu, from three basic problems: inefficient use of the resin, the requirement of a large amount of solvent (to prevent column saturation), and the need for large differences in the distribution coefficients (7). A minimization of these problems can be achieved by using a moving bed of resin. Physically moving a bed can damage the resin, therefore, most moving bed systems operate with the resin bed stationary and fluids routed to simulate bed movement.

Simulated Moving Bed Systems

The idea of simulated moving beds dates from the 1840's, according to Wankat (8), and has been used in many applications. The fixed resin bed system is simple in execution but inefficient, whereas a continuous countercurrent (or moving bed) method is rather complex in execution but more efficient. A simulated moving bed system is a simplification of the countercurrent flow system in which the solid phase (resin) movement with respect to the fluid is simulated by controlling the fluid flow with valves. Simulated Moving Bed (SMB) designs avoid the complexity of the countercurrent flow system, and both the total resin volume requirement and the volume of elution fluid needed are reduced. An additional benefit of the SMB system is obtaining product concentrations higher than in the feed when dilute materials are recycled in the SMB system (9). Simulated moving bed systems are found in many industries. For example, in purifying p-xylene to 99.5% purity an SMB system required only 804 cubic feet of resin compared with 20,600 cubic feet for a batch method (10). Advantages of SMB IEC systems are also well documented in the food industry where such systems are a standard tool in the purification of sugar (10).

SMB IEC systems are composed of a series of beds packed with a microporous ion exchange resin. The ionic species is excluded from the microporous interior volume because the resin walls repel the ionic species with like charge. In contrast, the non-ionic species have free passage into the micropore volume because they have no ionic charge. Because of this ionic exclusion, the interior volume of the resin becomes saturated with non-ionic species when it is exposed to the feed. Thereafter, simulated movement of the resin bed and the flow of fluid through the interstitial bed volume carry the non-ionic species away from the ionic species, which are principally located within the interstitial volume. The ionic species is removed from the SMB IEC system in an ionic species-rich stream. The non-ionic species are later forced out of the bed and removed from the SMB IEC system by a continuous flow of fresh elution fluid, in our case water, countercurrent to the resin movement. The resin, now free of non-ionic species, is recycled to be again exposed to the feed and thus continuously repeat the separation process.

A SMB IEC system for acid-sugar separation similar to that described by Hartfield (3) is shown in Figures 3 and 4. Figure 3 shows the conceptual arrangement of the different regions of the system. Indicated in the figure are the movement of the solid phase or resin and the flow of the fluid in the system. Resin flow is perhaps more readily seen in Figure 4 by following column three through a complete cycle. At specific times, flow valves may be set so that any column would correspond to the top of Zone I, in Figure 3. For example, in Time III of Figure 4, Column 3 is the top of Zone I.

Rationale for Acid / Sugar Separation SMB IEC System Configuration

Specifying the columns having the acid/sugar feed input stream, water input stream, sugar-rich takeoff stream, and acid-rich takeoff stream configures fluid movements

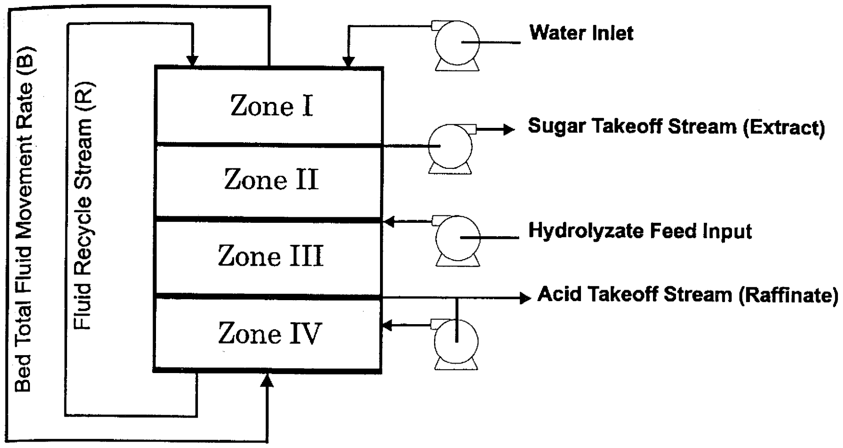


FIGURE 3. Typical SMB system configuration.

throughout the system. In addition, the input and output columns for internal system recycle must be defined. Also, the rate of bed fluid movement on a per column basis must be established by specifying the valve shift times. Each columnar bed contains approximately 650 ml of total fluid with 160 ml of resin. Thus the fluid movement rate is given by dividing the total column fluid by the shift time.

Although all columns are at the same elevation, for discussion purposes, we can consider the system to be stacked vertically with a continuous flow of fluid from top to bottom. The "top column" of the SMB IEC system is always considered the column having the elution water inlet stream as shown in Figure 3. The direction of column bed movement is always from the bottom of the system to the top of the system, thus the resin movement can be considered to go up the SMB IEC system.

SMB systems have been used with both three and four zones; however, the four-zone system offers a more economical use of elution fluid (11). The most familiar four-zone system is UOP's Sorbex family of separation processes (12,13). As shown in Figure 3, Zone I is from the water inlet through the sugar takeoff stream. Zone II is from the inlet below the sugar takeoff stream through the column preceding the acid/sugar feed stream

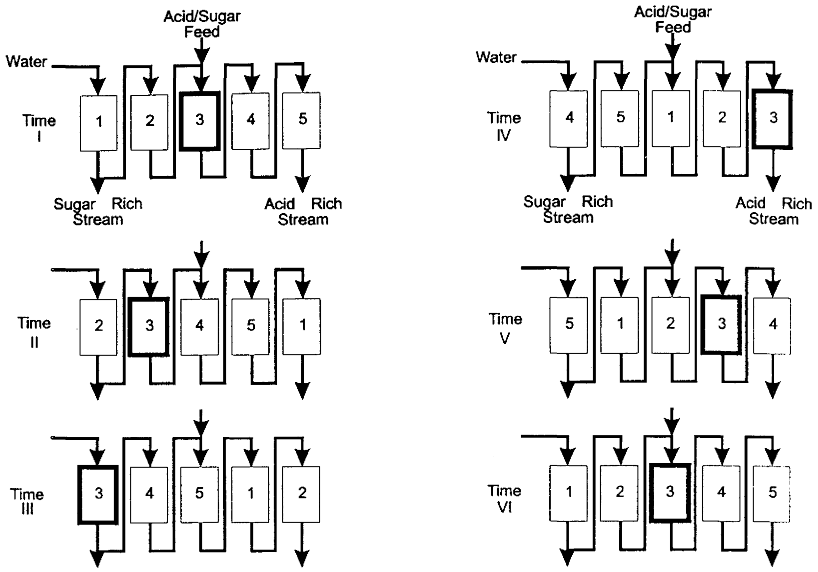


FIGURE 4. Continuous chromatography time based schematic.

inlet column. Zone III is from the acid/sugar feed stream inlet through the acid takeoff stream. Zone IV consists of all the columns remaining in the system from the inlet below the acid takeoff stream to the last column. The process is analogous to a distillation process in which Zones IV and I function as condenser and reboiler as noted by Ruthven and Ching (11).

Each zone of columns performs a specific function. The columns of Zone I function to purge sugar from the resin micropore volume and provide for its removal via the sugar takeoff stream. Zone II columns separate the acid from the sugar in the micropores. Zone III columns allow the resin micropore fluid to saturate with the sugar being introduced from the acid/sugar feed stream. In Zone III, sugar in the micropore fluid is carried up by the simulated upward flow of bed resin. Zone IV columns have labeled as a "solvent saver" zone by UOP writers, while Hotier recommends considering this as simply a buffer zone (13, 18). Regardless, due to the Zone flow rate requirements for correct system operation, only solvent passes from the last column in the system to the top and any acid entering Zone IV is carried upward for removal off the system (11).

Rationale for SMB IEC System Design

The process we have developed is similar to that of Broughton at UOP (12). While continuous annular chromatography and Advanced Separation Technologies' continuous ion exchange processes have been shown to be adequate for small and intermediate scale separations, it is believed that these systems would not provide, on an industrial scale, an economical solution to the separation requirements of this project (14,15,16).

Resin Selection

Based upon previous work and a literature review, eight different strongly acidic resins from three manufacturers were selected as candidate resins for the process. The resins were Dowex 50 WX4, Dowex Monosphere C-350, Dowex XUS 43435, Dowex XUS 40406, two different samples of Dowex XFS 43280 (the second sample was labeled as Monosphere 99), U.S. Filter SM 38, and Rohm and Haas Duolite CR1320.

The resins were evaluated using a statistically designed set of experiments to determine their separation performance on a fixed bed ion exclusion system. The fixed beds were assembled using commercially available stainless steel chromatography tubing (7.6 mm dia. x 460 mm length) and fittings. The assembled columns were placed in a temperature control jacket. The sugar concentration was set at a fixed value of 8 wt.%. A HP 1047 Refractive Index detector was used to monitor elution composition. A full factorial experimental design matrix consisting of two levels for four factors was carried out using factor levels based upon previous work. This yields 16 experiments per resin for evaluation of the materials. The factors evaluated on the fixed bed column included flux rate (0.66 and 0.98 cm/min), ionic species concentration (6 and 12 w% acid), temperature (25 and 75 °C), and column loading (50 and 200 ηl as the input pulse feed volume). The data was analyzed using standard statistical techniques, and model equations were developed that predicted resin separation performance as a function of the four factors.

Separating performance of the resins was evaluated based upon a separation parameter we defined as detailed below.

The response parameter, ^{x}, is dimensionless and expresses separation in a range from zero to one. This parameter is defined as shown in equation 1.

$$\xi \;=\; 1-\delta_h * \left(\frac{\dfrac{q_A}{\Delta_A}+\dfrac{q_S}{\Delta_S}}{q_A+q_S} \right) \qquad where \qquad q_i \;=\; \left(\frac{M_i * Q}{V_f} \right) \tag{1}$$

Here, q_A is the mass flow rate of the acid species, d_A is the height of the acid peak at the highest point and d_h is the height of the peak overlap. The quantities subscripted with an "s" refer to the sugar species. The mass flow rates are defined as the mass of the species injected, M_i, divided by the ratio of the final elution volume, V_f, to the volumetric flow rate, Q, through the bed. These quantities are depicted in Figure 5. Resin separation performance is improved when the ^{x} parameter value approaches one. The ^{x} function for the Monosphere 99 material is shown in Figure 6.

A particle size analysis was performed for the seven resins to quantify resin size influence on separation performance. There are generally two size groups of resins: those with a mean particle size distribution less than 500 microns and those with a mean particle size distribution greater than 500 microns. In this application, it was found that resins whose mean particle size distribution is generally less than 500 microns tended to outperform resins with a larger mean particle size distribution.

Using the above criteria, the best performing resins for this application were Dowex XFS 43280 and U.S. Filter SM 38. To ensure that the performance of a vendor's sample resin was comparable to that of the commercially available resin, the commercial materials were also tested prior to use in the SMB IEC system and found to perform the same as the laboratory samples.

As can be seen in Figures 7 and 8, the US Filter and Dow materials have similar separation performance. In general, the Dow resin separation performance was slightly

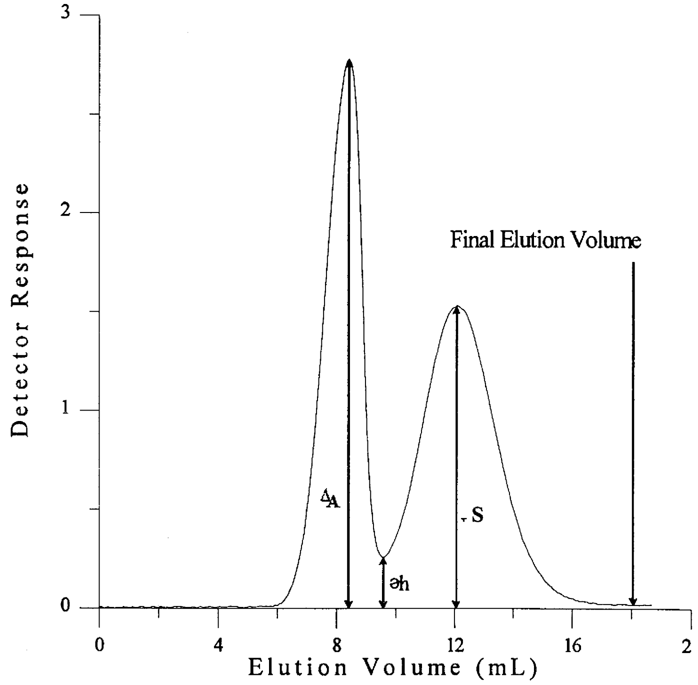


FIGURE 5. Definitions for analytical parameters.

better at lower temperatures and higher fluid throughput. The standard error of the mean, for the values reported in both Figures 7 and 8, is 0.009. Thus, a difference of approximately 0.020 or more in any values reported in both Figures 7 and 8 is considered statistically significant.

SMB IEC System Resin Packing

The columns were "overfilled" eight to ten percent with damp resin which was compressed upon capping. Compression packing was used to prevent the formation of "dead volume" (a volume of the column void of resin) within the resin bed. Dead volume, caused by resin shrinkage in the presence of acid, results in degradation of separation capacity because of increased dispersion or back-mixing of components (17). A study of

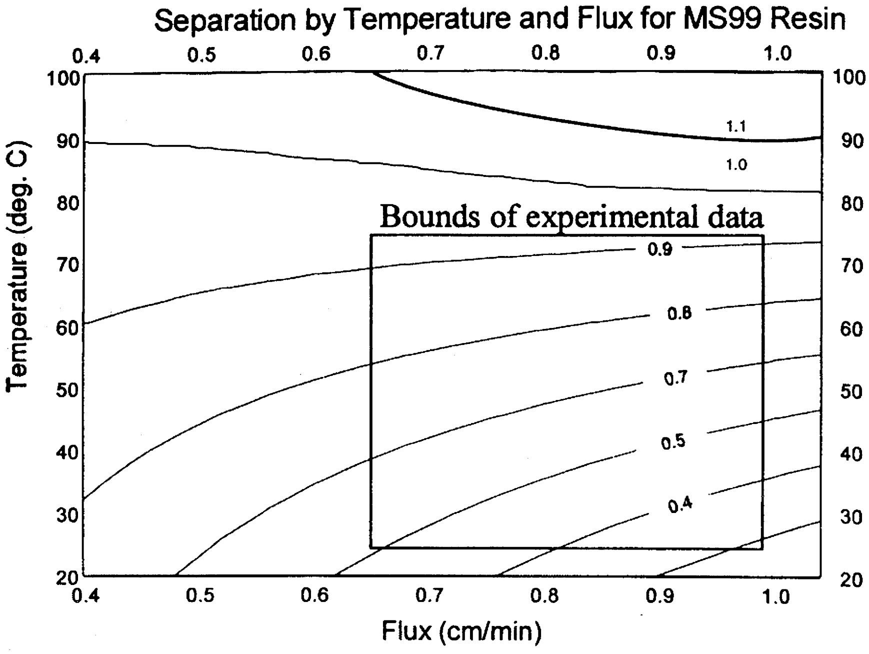


FIGURE 6. Model equation plot for Dow Monosphere 99.

resin shrinkage showed that resin volume shrinkage is approximately 5-10% at acid concentrations that correspond to the peak acid concentration in this SMB IEC process.

Mechanical Design and Fabrication

Knowledge gained from previous work with fixed-bed (batch) systems (3,4,8) was used in the design of the present SMB IEC system. The SMB IEC system was assembled on a steel frame with plywood flooring. A deionized water supply unit was used to supply process water. The 18 columns of the SMB IEC system were arranged in two banks of nine columns. Each bank was composed of two sets of columns, one with 4 columns and the other with 5. A passageway through the center was created to allow access to the columns while minimizing the distance between columns. All electrical connections to the

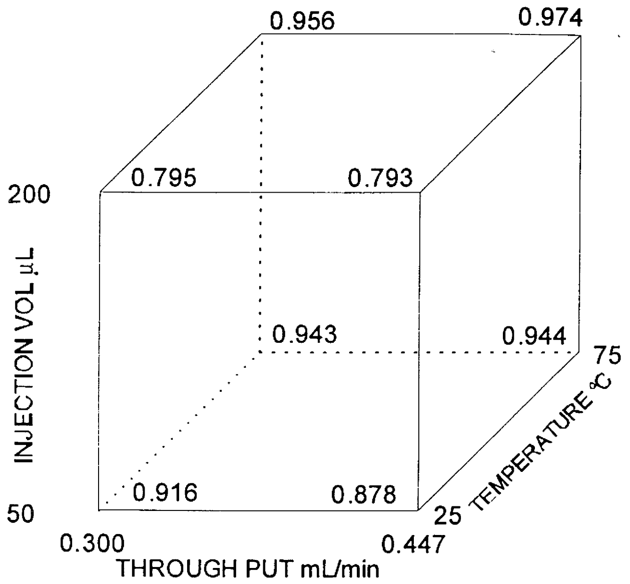


FIGURE 7. ι values for Dow Monosphere 99.

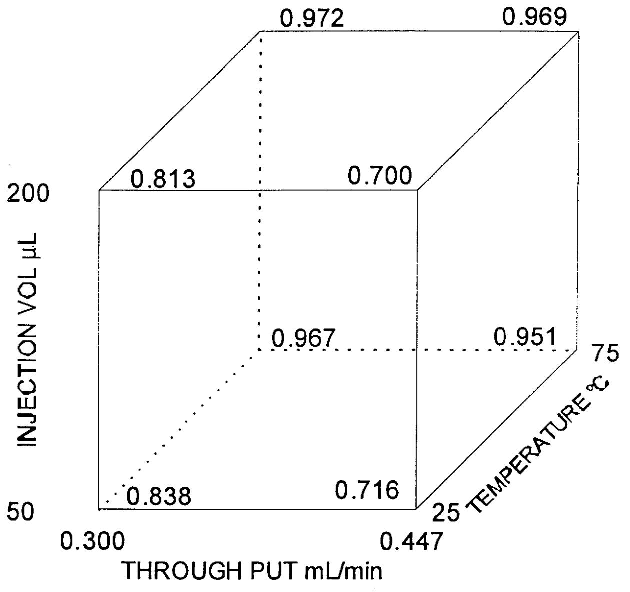


FIGURE 8. ι values for U.S. Filter SM-38.

126 fluid control valves were routed to the process controller. The system's five gear pumps were mounted on a dolly. Acid resistant rotameters with needle control valves were used for fine control of the process flow streams. Turbine and positive displacement flow detectors were also used. A heat exchanger was located near the columns to permit elevated temperature testing of the SMB IEC system. To explore as many flow-configurations as possible and maximize the potential of the system, two separate recycle streams were designed into the system. This system allowed for reconfiguration and flow reprogramming with relative ease and this capacity was used extensively in the system evaluation and optimization.

The packed beds were approximately 5.9 cm in diameter and 30 cm in length. Each column and heat exchanger jacket was fabricated from schedule 40 CPVC pipe and together they had 5 cm thick CPVC caps, top and bottom. Porous polyethylene or polypropylene material from Porex Technologies was used as a bed retainer and distribution plate. The porous material also assisted in achieving the bed compression necessary to prevent dead volume.

Two different cap manifolds, top and bottom, were used to connect the fluid control valves to the columns. Both manifolds were constructed of CPVC. The top cap manifold had three valve attachment ports since each column had three possible exit streams: to acid product collection, to sugar product collection, and to the next column in the array. The bottom cap manifold had six ports, including one for sampling. Sampling ports allowed for collection of process fluid samples from each column. These samples allowed the generation of concentration profile plots for monitoring the separation system. Two of the four solenoid-valve ports were used for recycle streams. The other two valves were used for the water and hydrolyzate input streams. A final port to receive fluid from the previous column in the array completes the list of ports in the bottom manifold.

A fluid distribution manifold stack was located at the center of the rectangular column array that collects or distributes process fluids. Each column inlet or outlet stream was connected to a manifold. Each manifold was connected to a rotameter. All the system components were leak tested to a pressure of 1 MPa.

Electronics Design and Fabrication

A crucial facet of this project was the design, fabrication and testing of the SMB IEC electronic control system. The control system for the SMB IEC system was composed of two parts: a Camile 2000 process controller and a custom designed and fabricated control unit. The custom controller consisted of three parts:

1) The control board, which was a Prologic® 8052 controller based on the Intel® 8052 processor
2) An interface board which received input from the control board and developed the signals necessary to control the solenoid valves
3) Three relay boards with relays that controlled the actuation of the individual solenoid valves

The custom controller was interfaced with a personal computer (PC) to facilitate programming changes without the need to reprogram the built-in read only memory. The PC was also interfaced with the Camile unit. The Camile unit, in turn, was directly tied to several of the devices needed to control or monitor the SMB IEC system, such as the level detectors in the 200 liter process tanks, and pump motors. Pressure transducers were also located in each pump discharge stream.

The Camile unit regulated the valve shift time. Once equilibrium was attained, small perturbations could be made to the separation process through changes to the shift time.

Initial Tests

The following is a brief description of the initial checkout effort. Note that due to the high cost of glucose, sucrose was used in all SMB IEC system tests. Laboratory fixed-bed chromatography tests showed that sucrose separation behavior was identical to glucose, within experimental error.

After ensuring that all components of the SMB IEC system functioned properly, it was decided to test the system with sucrose only in the feed stream. This allowed the opportunity to develop procedures and gain experience with the control system. Three runs were performed with a sugar-only aqueous feed stream. The shift times were two, three, and four minutes during the initial testing period. A refractometer, marked in Brix units, was used to monitor sugar concentrations in the system. Data from the Brix measurements indicated that the time required to reach SMB IEC system equilibrium was approximately 15 hours. Following the sugar-only tests, it was decided to run the system with an acid-only aqueous feed stream. The acid-only test also allowed the use of the refractometer to analyze the system's acid concentration profiles in the absence of sugar. The Brix scale was re-calibrated for acid concentration. Following these experiments we began our test program with the sulfuric acid and sucrose solution at concentrations simulating the hydrolyzate composition.

Since refractive index alone did not allow direct determination of acid and sugar content in a sample, a three level, two factor experimental design was performed to determine how the refractive index varied with solution composition. The refractive index (or Brix number) was found to be a linear function of both acid and sugar concentrations in weight percent. A technique was developed in which, after obtaining a sample Brix measurement, the acid concentration of the solution was determined by titration of a stream sample with sodium hydroxide solution. The sugar concentration was then calculated using the statistical calibration function. When a feed solution containing both acid and sugar was introduced into the SMB IEC system, monitoring the total refractive index of all streams present within the system allowed assessment of the separation process with respect to equilibrium. Upon reaching equilibrium, the Brix number and acid concentration of all streams in the system were measured; sugar concentrations were then calculated using the above procedure. Several of the streams were also measured in the analytical laboratory for acid and sugar concentrations using quantitative ion exclusion chromatography techniques. These concentration measurements confirmed stream composition analyses performed using the much faster titration and Brix refractive index calibration function technique.

SMB IEC SYSTEM PERFORMANCE

Three run configurations or processes are discussed below. All measurements assume a density of 1 gram / ml for all fluids. The first system configuration, Process I, was the process described in Figure 9. The second system configuration, Process II, shown in Figure 11, utilized the same control scheme; however, disabling the control valves on every other column effectively doubled the column length. Both of the first configurations used the Dow resin Monosphere 99. This second configuration was used to compare the performance of 9 columns of twice the length as studied in the first configuration. The third process made use of nine columns as in the second case, however, the US Filter material was used in the beds and the system temperature was lowered from 60 to 30 °C.

Figure 9 shows the arrangement of flow streams and the partitioning of the system into zones for Process I. Table 1 shows the equilibrium stream descriptions for Process I. The equilibrium concentration profile for the columns configured for Process I is shown in Figure 10. As evidenced in the mass balance given in Table 1, about 98% of the acid is present in the acid takeoff stream and only 2% of the acid is present in the sugar takeoff stream. About 96% of the sugar is present in the sugar takeoff stream and only 4% of the sugar is present in the acid takeoff stream. Also of interest is that while the time averaged sugar stream concentration is slightly less than the sugar concentration in the inlet stream (approximately 9 %), the instantaneous concentration measured in the column at the time of sampling is greater than 12 %. A series of samples was taken from the outlet stream and an oscillatory pattern was found. These fluctuations in concentration agree with those reported by Hotier and others (18,19,20). It was also noted that the temperature of the outlet stream fluctuates. The takeoff streams for Process I, as indicated in Figure 9, are located at columns 4 and 14. It can be seen in Figure 10 that the separations in the species at columns 4 (Sugar) and 14 (Acid) are reflected in both the instantaneous data (the curves) and in the time averaged data (as indicated by the text on the plot).

Figure 11 displays the column assignments when the SMB IEC system is configured to operate with 9 columns. In this case, Zone I has one fewer physical columns (120 cm total bed length versus 150 cm) and Zone IV has one more physical column (120 cm total bed length versus 90 cm). Table 2 shows that separation was achieved, even though the mass balance calculations indicate approximately a 1 ml/min imbalance in the flows at the time of data collection. This mass balance discrepancy is within experimental error.

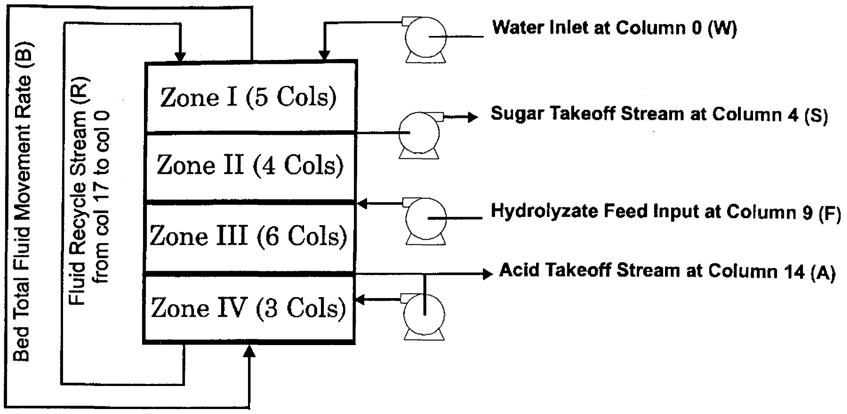


FIGURE 9. Continuous ion exclusion process with 18 columns (Process I).

TABLE 1. PROCESS I MASS BALANCE DATA

Stream Name		Bed Fluid Movement	Recycle	Hydrolysate Feed	Water Inlet	Sugar Takeoff	Acid Takeoff
Identification		B	R	F	W	S	A
Temperature	Deg. C	45	45	22	22	45	45
Water Flow Rate	g/hr	-	-	1728	3900	1589	4039
Acid Flow Rate	g/hr	-	-	216	0	4	212
Sugar Flow Rate	g/hr	-	-	216	0	207	9
Total Flow Rate	g/hr	12560	3600	2160	3900	1800	4260

Figure 12 shows the concentration profile from the system. Again there is a good degree of separation between the sugar and acid. An overlay of Process I and II is provided in Figure 13. It can be seen that the nine-column configuration (Process II) produces data that is not as smooth as that from the 18-column configuration (Process I). As anticipated; however, it is obvious from Figure 13 that the nine-column Process II is sufficient for separating the species.

Table 3 indicates the flow conditions for Process III and Figure 14 shows the concentration profiles. Process III differs from Process II due to the difference in the resin

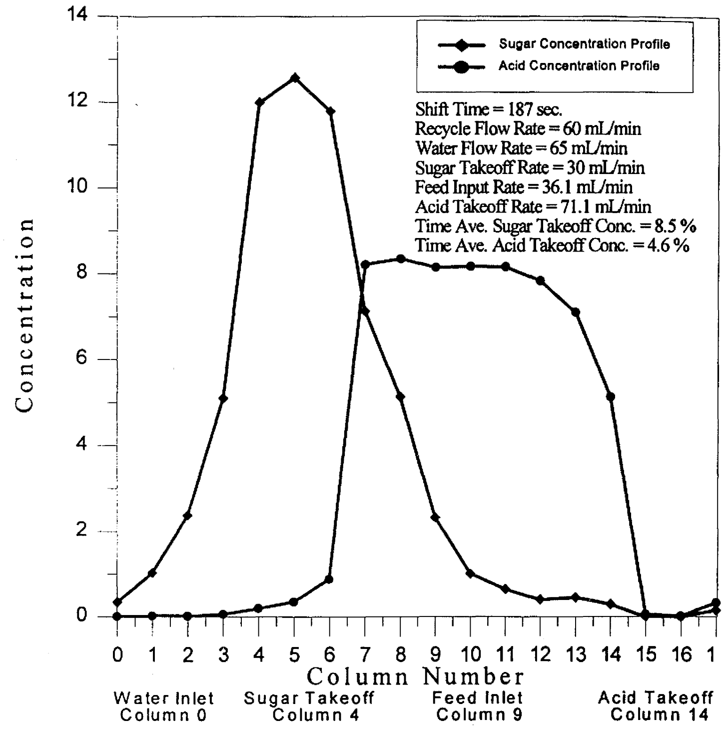


FIGURE 10. Process I system concentration profile.

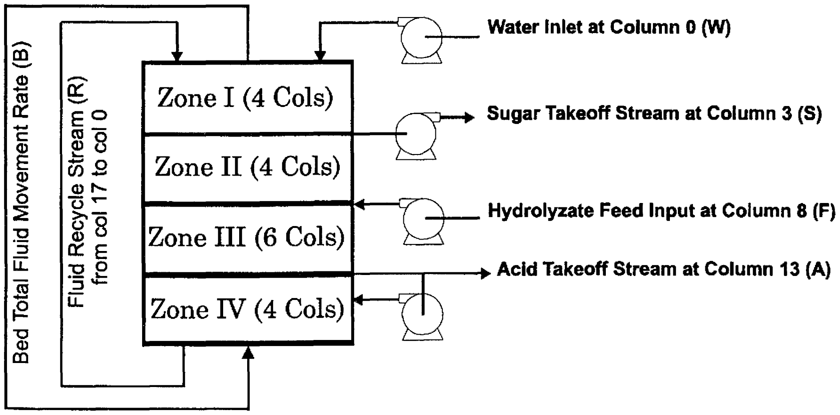
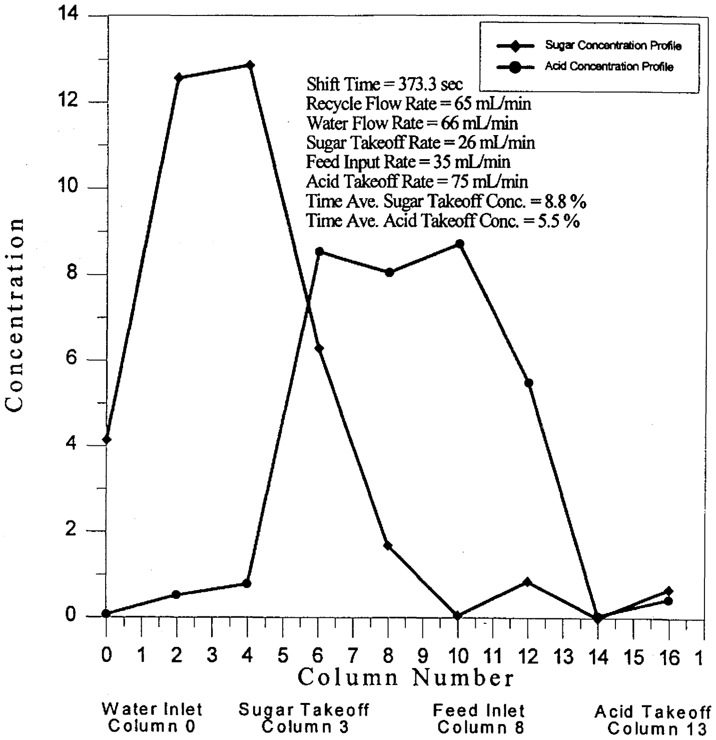


FIGURE 11. Continuous ion exclusion process with 9 columns (Processes II and III).

TABLE 2. PROCESS II MASS BALANCE

Stream Name		Bed Fluid Movement	Recycle	Hydrolyzate Feed	Water Inlet	Sugar Takeoff	Acid Takeoff	Mass Balance
Identification		B	R	F	W	S	A	-
Temperature	Deg. C	45	45	22	22	35	37	-
Water Flow Rate	g/hr	-	-	1666	4080	1479	4252	15
Acid Flow Rate	g/hr	-	-	198		5	248	-55
Sugar Flow Rate	g/hr	-	-	176		136	0	40
Total Flow Rate	g/hr	6294	3900	2040	4080	1620	4500	0



Shift Time = 373.3 sec
Recycle Flow Rate = 65 mL/min
Water Flow Rate = 66 mL/min
Sugar Takeoff Rate = 26 mL/min
Feed Input Rate = 35 mL/min
Acid Takeoff Rate = 75 mL/min
Time Ave. Sugar Takeoff Conc. = 8.8 %
Time Ave. Acid Takeoff Conc. = 5.5 %

FIGURE 12. Process II 9-column system concentration profile.

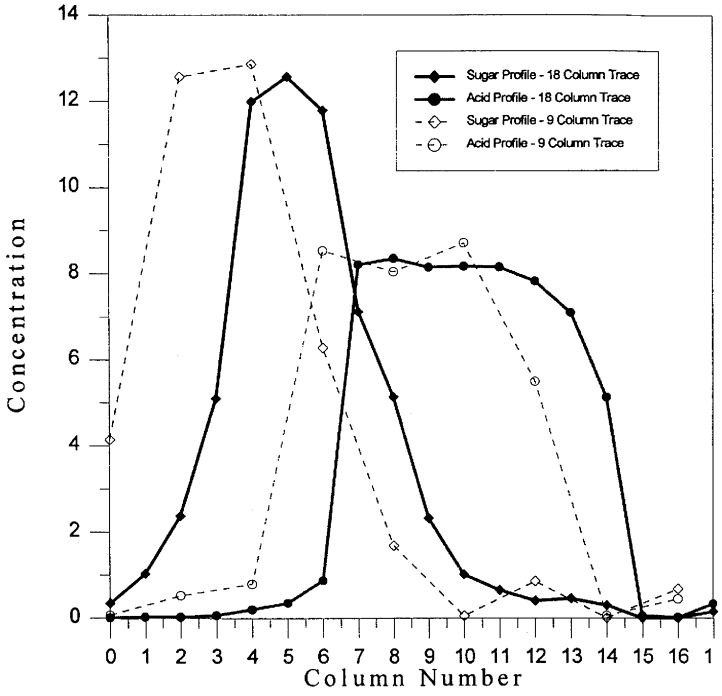


FIGURE 13. Comparison of Processes I and II.

TABLE 3. PROCESS THREE - US FILTER SM 38 RESIN

Stream Name		Bed Fluid Movement	Recycle	Hydrolysate Feed	Water Inlet	Sugar Takeoff	Acid Takeoff	Mass Balance
Identification		B	R	F	W	S	A	-
Temperature	Deg. C	31	31	22	22	31	31	
Water Flow Rate	mL/hr			1404	3420	1622	3230	-28
Acid Flow Rate	mL/hr			270		8	250	12
Sugar Flow Rate	mL/hr			126		110	0	16
Total Flow Rate	mL/hr	4460	4320	1800	3420	1740	3480	0

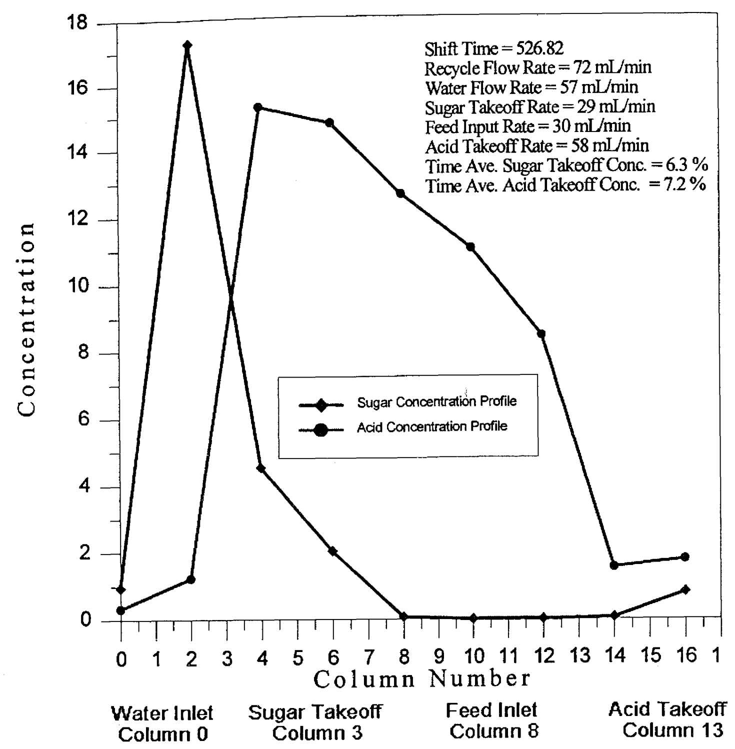


FIGURE 14. Process III system concentration profile with U.S. Filter resin.

used in the beds. The resin from US Filter performed well in the fixed-bed test described above, and was chosen for evaluation in the SMB IEC system as Process III. The most important difference in the two resins is that the US Filter material has a divinylbenzene (DVB) content of 4 wt.% where the Dow material (used in Processes I and II) has a 6 wt.% DVB content. The lower DVB content results in a resin with greater volume changes in the presence of the acid. It is believed that this is the significant difference between the materials, and that this accounts for the differences shown in Figures 7 and 8. The concentration profile obtained from Process III indicates that the columns may not have been packed well enough to prevent void formation in the column at high acid concentrations. Process III was not optimized. However, it did provide a separation condition in which no sugar was found in the acid stream and only 3 % of the acid was present in the sugar stream (which is desirable). Thus, it appears that this process offers considerable promise.

FUTURE WORK

There are several issues remaining unresolved. The foremost concern is that the lower DVB content may also cause a shorter resin life with prolonged usage or in a commercial environment. Therefore long-term resin performance testing is needed. Also, it is important to verify that sufficient compression was applied in the packing to prevent void formation for Process III. One final point of interest from Process III is that the time averaged sugar content is close to that of the feed stream (7 %) and the acid is roughly half of the feed (15 %). Further investigation is needed to clarify our findings regarding the concentration peaks within the system and optimize the potential of the outlet streams. Since the concentration profile leaving the system is oscillatory in nature, it is possible that the system could be configured so that only the high concentration material would be allowed to discharge and the remaining low concentration material recycled back into the system. This may provide an improvement in the process as it would reduce the amount of water required and yield higher concentrations in the takeoff streams.

CONCLUSIONS

A fully functional SMB IEC system has been constructed and found to provide excellent separation of sugar from sulfuric acid in an aqueous feed stream. The system preformed well in over 500 hours of operation. Our design has allowed for system reconfiguration to explore alternate system configurations. In the future this process is expected to provide excellent separations for ionic/nonionic mixtures.

ACKNOWLEDGEMENTS

Funding was provided by APACE Research Ltd., the Energy Research and Development Corporation of Australia, and the Tennessee Valley Authority. Portions of this work were performed for APACE and the ERDC under project number 2537. The authors also wish to thank Klenzoid Equipment Company's Jack Tobe for assistance in procuring resins.

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