Size-Exclusion Simulated Moving Bed for Separating Organophosphorous Flame Retardants from a Polymer

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Abstract: Over 500,000 tonnes of flame retardants in electronic wastes are consigned to landfills each year. A room-temperature, size-exclusion simulated moving bed (SEC-SMB) was developed to recover high purity (>99%) flame retardants with high yield (>99%). The SSWD method for ternary mixtures was developed for SEC-SMB. Fourteen decision variables were optimized to obtain the lowest separation cost within one minute. The estimated cost is less than 10% of the purchase cost of the flame retardants. The estimated cost of the optimized SEC-SMB is less than 3% of that of a conventional batch SEC processes. Fast startup methods were developed to reduce the SMB start-up time by more than 18 fold. SEC-SMB can be an economical method for separating small molecules from polymers.

Keywords: Simulated Moving Bed; Size-Exclusion; Electronic Waste; Phosphorous Flame Retardants; Polymer; Optimization

1.0 Introduction

Over 50 million tonnes of waste electrical and electronic equipment (WEEE) are generated worldwide each year and they are growing at a rate of 3–5% per year [1–5]. Polymeric materials make up about one third of that weight [6,7]. The United States Environmental Protection Agency estimated that less than 20% of the wastes, mostly metals and glass, are recycled [8,9]. The rest of the wastes are currently stored in landfills or scattered in the oceans around the world [10,11]. Slow degradation of the polymers releases toxic chemicals, which potentially endanger wildlife and affect our food supply [12,13]. Recovering polymers and valuable chemicals from the wastes can reduce these environmental hazards and the amount of raw materials and energy required for synthesis.

Recovery of high-purity polymers from a polymer waste is challenging because many polymers have similar physical properties and broad, overlapping molecular weight (MW) distributions. Single solvents do not have the selectivity to recover high-purity polymers with high yield. A room-temperature, mixed-solvent process, Sequential Extraction for Polymer Recovery (SEPoR), was developed to recover polymers from wastes [14,15]. The solvent compositions are designed using a combination of Hansen Solubility Parameter (HSP) theory, gradient polymer elution chromatography (GPEC), and solubility tests. SEPoR has already been developed for recovering high purity (>99%) polycarbonates (PCs) with high (>95%) yield from a computer waste. SEPoR uses 84% less energy than chemical synthesis and can reduce CO₂ emissions and reduce raw materials from petroleum used to synthesize virgin polymers [15]. poly(acrylonitrile-co-butadiene-co-styrene) (ABS) is removed as a separate, solid product. Flame retardants (FRs) and a polymer, poly(styrene-co-acrylonitrile) (SAN), are discharged in a side stream of 50/50 (vol %) acetone (ACE)/dichloromethane (DCM). Recovery of the FRs and SAN

from the side stream is economically desirable and beneficial to the environment, and it is the focus of this study.

Flame retardants, such as resorcinol bis-diphenylphosphate (RDP) and bisphenol A bis-diphenylphosphate (BPADP), are added to polymers in order to inhibit the spread of flames in case of fire [16,17]. Many flame retardants containing bromine or other halogens are being preplaced by organophosphorous FRs, which are safer and more environmentally benign [18,19]. This study focuses on the recovery of RDP (575–4,025 Da), BPADP (693 Da), and SAN (50,000–150,000 Da) from one of the side streams of the SEPoR process for PC recovery, Fig. 1. The molecular structures for the FRs and SAN are shown in Table 1.

The FRs are the most valuable components in the polymer wastes by weight. Polymers in WEEE have 10 wt % or more FRs. More than 500,000 tonnes of FRs potentially could be recovered annually from WEEE. Furthermore, FRs must be removed for recovering high-purity polymers from wastes.

The existing literature on organophosphorous FRs in polymer wastes focuses on analytical methods for detection [20–23]. Microwave-assisted extraction, combined with gel permeation chromatography and mass spectrometry, was used to detect organophosphorous FRs in biological samples from fish and birds [24]. Solid phase extraction, combined with reverse phase chromatography, was used to detect FRs in water samples [25]. Pressurized liquid extraction (acetonitrile and water), combined with gas chromatography, was used to analyze sediment samples [26]. No literature has been found for recovering organophosphorous FRs from polymer waste at large scale.

Since the MW of the FRs and SAN differ by two orders of magnitude, size-exclusion chromatography (SEC) is a potential separation technique. SEC has been widely used for

analyzing polymer mixtures [27,28]. SEC is a batch chromatography process, which is less efficient than simulated moving-bed (SMB) chromatography for large-scale production. SMB can achieve high product purity without sacrificing product yield. It also requires much less solvent and can have an order of magnitude higher adsorbent productivity. For this reason, this study focuses on developing an economical SMB process based on size exclusion principles (SEC-SMB) for separating the FRs from SAN.

SEC-SMB is a continuous chromatography process. The efficiency of SMB comes from a circular column configuration (a loop) and multiple inlet and outlet ports that divide this loop into various sections (or zones) with different flow rates. Figure 2 illustrates a typical 4-zone SMB with two columns per zone (2-2-2-2 configuration). A feed mixture is continuously input to the loop, while two products are drawn from two separate product ports. The ports move periodically along the loop to follow migrating solute bands. The time between port switches is called the switching time, or step time. Separation is achieved by controlling the flowrate in each zone such that the concentration waves of specific solutes are confined in specific zones. As seen in Fig. 2, the slow component is never present in Zone IV while the fast component is never present in Zone I. By confining the advancing and trailing concentration waves in their respective zones, pure slow and fast products can be continuously removed in the respective product ports. Only partial separation of the two solute bands in the loop is needed to recover two high-purity products with high yields. As a result, a large fraction of the stationary phase in the loop can be utilized and dilution of the bands can be reduced. For this reason, SMB can have an order of magnitude higher sorbent productivity and lower solvent consumption than conventional batch chromatography. SMB also requires fewer operators, takes up less floor space, and uses less costly equipment for large-scale production.

Although SMB has many advantages, it is not widely used for separation of complex mixtures. Design of a four-zone SMB requires specification of four zone flowrates, four zone lengths, and a step time. Dynamic concentration wave propagation in SMB is affected by multiple inlet and outlet streams and is not well understood. SMB experiments are also costly and time-consuming when developing a process.

The only large-scale SEC-SMB process is UOP's Molex^{TM} process, which separates n-paraffins from branched/cyclic hydrocarbons [29,30]. Lab-scale SEC-SMB studies have been reported for several important compounds. Some of these systems include influenza [31] and adenovirus [32] production for vaccines, recombinant protein purification [33], insulin purification [34–37], lactose removal from human milk [38], and polyethylene glycol fractionation by MW [39]. Only lab-scale operations have been performed for high MW molecules (MW >5 kDa). No studies on the separation of organophosphorous FRs from large polymers using SEC-SMB have been reported in the literature.

The five operating parameters (four zone velocities and one port velocity) can be designed by a number of methods, including the local equilibrium theory or “triangle” theory, which is widely used and works well for ideal systems (no mass transfer resistance) [40]. However, for non-ideal systems (with mass transfer resistance), this theory only gives the range of possible operating parameters where separation of the components will occur. It does not guarantee purity or yield and it does not give optimum operating parameters for non-ideal systems.

Another method for SMB design is the Standing Wave Design (SWD), which was first developed by Ma and Wang in 1997 for binary, linear adsorption systems with mass transfer resistances [41]. For fixed yields, material properties (size-exclusion factors, diffusivities,

particle porosity, bed void fraction, and particle size), and equipment parameters (column length, dead volume, column configuration, and pressure limit), the SWD determines the five optimum operating parameters to maximize productivity and minimize solvent consumption. It was extended to multicomponent linear systems [42] and nonlinear systems [43–45]. Pressure limit considerations were incorporated into the SWD [46] by checking that the resulting operating parameters did not violate the pressure constraint.

In a recent study, the SWD equations for SEC-SMB separations of binary mixtures were simplified using dimensionless groups. This new method was called the Speedy Standing Wave Design (SSWD) because it can quickly provide overviews of solvent consumption, sorbent productivity, and separation cost (with given cost functions) [47]. For given material properties, yields, and column configuration, the SSWD can be used to determine the operating parameters and column length from two key dimensionless groups: (1) the ratio of the step time to the intraparticle diffusion time and (2) the ratio of the dispersion time to the step time.

The objectives of this study are to: (1) extend the SSWD from binary to ternary mixtures; (2) estimate the material properties of a selected system (sorbent, solvent, solutes); (3) use the extended SSWD to design the operating parameters of SEC-SMBs for recovering both FRs and SAN with high purity and high yield; (4) experimentally test the design method and verify the estimated material properties; (5) develop and test fast startup methods to reduce the startup time of SEC-SMB; and (6) investigate the economic feasibility of the SEC-SMBs at large scale.

2.0 Theory

2.1 Standing Wave Design (SWD)

The SWD method was developed for steady state, continuous moving bed (CMB), systems with linear or nonlinear adsorption isotherms [41,46]. In an ideal CMB system (without mass transfer resistance), SWD works by matching the port velocity with the concentration wave velocity of a specific component in each zone. Those specific concentration waves are “standing” relative to the ports in CMB systems. In a non-ideal system (with mass transfer resistance), a difference between port velocity and concentration wave velocity is used to confine the waves by focusing them toward the zone boundaries. This concept is illustrated for a specific binary SEC system in Fig. 3a. Arrows in Fig. 3 indicate the confined wave in each zone. The trailing wave of the slow-moving component (RDP) is focused and confined in Zone I and that of the fast-moving component (SAN) is confined in Zone II. The advancing waves of RDP and SAN are confined in Zones III and IV, respectively.

The SWD equations for the non-ideal SMB separation of a binary feed mixture are shown in Eq. (1).

$$u_{w,2}^I = \frac{u_0^I}{1+\phi\delta_2} = v + \Delta_2^I \quad (1a)$$

$$u_{w,1}^{II} = \frac{u_0^{II}}{1+\phi\delta_1} = v + \Delta_1^{II} \quad (1b)$$

$$u_{w,2}^{III} = \frac{u_0^{III}}{1+\phi\delta_2} = v - \Delta_2^{III} \quad (1c)$$

$$u_{w,1}^{IV} = \frac{u_0^{IV}}{1+\phi\delta_1} = v - \Delta_1^{IV} \quad (1d)$$

$$u_F = u_0^{III} - u_0^{II} \quad (1e)$$

where $u_{w,i}^j$ is the wave velocity of component i in zone j ; u_0^j is the interstitial velocity of the fluid in zone j (zone velocity); ϕ is the phase ratio, $\phi = (1-\varepsilon_b)/\varepsilon_b$, with ε_b designating the interparticle void fraction; δ_i is the apparent retention factor for component i ; v is the port velocity, which is equal to the column length (L_c) divided by the step time (t_s); Δ_i^j is the mass transfer correction term for non-ideal systems, Eq. (A.1); and u_F is the feed velocity. If feed velocity (flowrate) and mass transfer parameters are given, Eq. (1) can be used to determine the port velocity and four zone velocities. Details are discussed in Appendix A.

2.2 Speedy Standing Wave Design (SSWD)

The SWD equations, Eq. (1), can be used to determine the operating parameters for given yields, material properties, and equipment parameters. In a recent study, these equations were simplified using dimensionless groups for SEC-SMB separation of a binary mixture. In this study, the SSWD equations are extended to ternary mixtures. Because there are three components and only two product ports, there are three splitting options (splits).

The first option is to recover the fastest solute (SAN) in the raffinate and to recover the slower solutes (BPADP and RDP) in the extract, Fig. 3b. The desired splitting can be achieved by confining the trailing wave of RDP in Zone I, the trailing wave of SAN in Zone II, the advancing wave of BPADP in Zone III, and the advancing wave of SAN in Zone IV. The trailing wave of BPADP is automatically confined (“pinched,” indicated by an asterisk in Fig. 3b) in Zone I since it moves faster than the trailing wave of RDP. Similarly, the advancing wave of RDP is pinched in Zone III since it moves slower than the advancing wave of BPADP.

The second option is to recover the slowest solute (RDP) in the extract and to recover SAN and BPADP in the raffinate, Fig. 3c. The desired splitting can be achieved by confining the trailing wave of RDP in Zone I, the trailing wave of BPADP in Zone II, the advancing wave of

RDP in Zone III, and the advancing wave of SAN in Zone IV. The trailing wave of SAN is automatically confined (“pinched,” indicated by an asterisk in Fig. 3c) in Zone II since it moves faster than the trailing wave of BPADP. Similarly, the advancing wave of BPADP is pinched in Zone IV since it moves slower than the advancing wave of SAN.

The third option is to allow one solute to be recovered in both product streams. The operating parameters for this option can be determined using the SSWD for a binary mixture of the two remaining components.

The key dimensionless groups used to simplify the SWD equations are shown in Table 2, where α_i is the selectivity of component i relative to the fast solute and is equal to the ratio of the apparent retention factor for component i over that of the fast solute; β_i^j is the natural logarithm of the ratio of the highest concentration to the lowest concentration of the standing wave of component i in zone j (the value of β_i^j is directly related to the yield of component i and the zone velocities), Eq. (A.3); N^j is the number of columns in zone j; λ_i is the ratio of the size-exclusion factor ($K_{se,i}$) for component i over that of the fast solute (SAN); γ_i is the ratio of the diffusivity of component i ($D_{p,i}$) over that of SAN; and I^j is the ratio of the axial dispersion coefficient of zone j over that of Zone IV ($E_{b,i}^j / E_{b,1}^{IV}$).

The dimensionless group which accounts for mass transfer effects due to intraparticle diffusion is N_D^* and is defined in Eq. (2) for splitting the fast solute from the slower solutes,

$$N_D^* = \frac{(\alpha_2-1) \phi \varepsilon_p K_{se,1} D_{p,1} L_c}{\phi \delta_1 R_p^2 \nu} = \frac{(\alpha_2-1) t_s}{\phi \delta_1 t_{D,1}} \quad (2)$$

where ε_p is the particle porosity; R_p is the particle radius; and $t_{D,1}$ is the characteristic diffusion time of solute 1, $t_{D,1} = R_p^2 / D_{p,1}$. A large N_D^* means that the solutes can diffuse into and out of the particles many times between port switches, which in turn means that the wave spreading due to

diffusion is small. A small N_D^* means that there is not enough time for the solute to diffuse through the particle within the step time, which in turn means wave spreading due to diffusion is significant.

The dimensionless group which accounts for mass transfer effects due to dispersion is the modified Peclet number (P_{eb}^*), which is defined in Eq. (3) for splitting the fast solute from two slower solutes,

$$P_{eb}^* = \phi(\delta_2 - \delta_1) \frac{\nu L_c}{E_{b,1}^{IV}} = \phi(\delta_2 - \delta_1) \frac{t_{Dax}}{t_s} \quad (3)$$

where t_{Dax} is a characteristic dispersion time, which is equal to L_c^2 divided by $E_{b,1}^{IV}$. A very large P_{eb}^* indicates that the dispersion time is much greater than the step time, meaning there is little effect of dispersion on the wave spreading. If P_{eb}^* is small, then the dispersion time is closer to the step time and the effects from dispersion are significant.

The detailed derivation of the SSWD equations for ternary mixtures is shown in Appendix A. The resulting equations for two different ternary splits are shown in Table 3, Eq. (4) and Eq. (5). Because Split 1 generates pure SAN in the raffinate and a mixture of FRs in the extract, both products are valuable. The SAN product is only valuable if it is pure, whereas the two FRs can be recycled as a mixture. The other splits do not produce two useful products. For this reason, only Split 1 is tested experimentally and verified with simulations. The theoretical results for the other splits are presented for completeness and can be used for other applications.

Pressure limitation can also be a major factor for some applications. For the separation of FRs from SAN to be economical, a concentrated feed solution is needed to reduce the overall separation cost, Eq. (B.1-B.4). A concentrated polymer solution can be very viscous, which in turn can lead to a high pressure drop. Systems can also be limited by pressure drop per unit packing length if the sorbent is very soft [34] or by the maximum pressure allowed by pumps,

valves, or column casings. The pressure drop for laminar flow across a uniformly packed bed of monodisperse, spherical particles can be estimated using the simplified Ergun equation, Eq. (6), [48].

$$\frac{\Delta P}{L^I} = \frac{150\mu u_0^I \phi^2}{4R_p^2} \quad (6)$$

The pressure drop across a zone is represented by ΔP and the viscosity of the fluid is represented by μ . Zone I always has the largest velocity and its value is limited by the maximum pressure allowed. The viscosity of the mobile phase in Zone I is assumed to have the same viscosity as the feed. Equation (4a) can be substituted into Eq. (6) and then rearranged to find a dimensionless group which represents the pressure limitations of the system. This group was derived by Weeden and Wang [47] and is defined for Splits 1 and 2 in Eq. (7) and Eq. (8), respectively. For fixed pressure limits, column configuration (N^j), and material properties (δ_i , R_p , μ , ϕ , λ_i , γ_i), the values of N_D^* and P_{eb}^* which will satisfy the pressure limit are bounded by Eq. (7) or Eq. (8).

2.3 Optimization of Decision Variables

The 15 decision variables that can be optimized are column configuration (4), column length, dead volume, three yields, particle size, and five operating parameters, Fig. 4. The SSWD equations in Table 2 determine the zone velocities and port velocity for given material properties, yields, and equipment parameters. Once the zone velocities are known, the solvent consumption, sorbent productivity, and total cost can be easily calculated (for given cost functions, Appendix B).

The dead volume has been shown to have little effect on SEC-SMB cost when it is less than 2% of the column volume [47], so it was kept at the experimental value of 1.9%. For the separation of FRs from SAN, DV is fixed and the remaining 14 are optimized, Section 4.7. The

algorithm used to optimize the 14 decision variables (column configuration, column length, yields, particle radius, zone velocities, and port velocity) to achieve minimum cost is shown in Appendix C, Fig. C.1.

2.4 Preloading Strategies for Fast Startup of SMB

The SWD method gives the operating parameters to achieve desired product purity or yield at steady state. However, it does not give the time for an SMB system to reach cyclic steady state (startup time), which can be determined using experiments or a simulation program, such as VERSE (description in Supplementary Materials, S.1). Generally, for an SMB starting from clean columns to reach cyclic steady state, the ports must move around the loop three or more times (cycles) [44]. Fast startup methods are needed to significantly reduce the time and materials required for startup.

A number of strategies for startup of SMB systems have been reported in the literature. One proposed method is for the operating parameters to be different from their cyclic steady-state values [49,50]. Xie et al. [36] proposed the following preloading strategy to reduce SMB startup time. Several columns were preloaded with feed solution. The columns were then connected and elution was used to obtain approximately the steady-state concentration profiles predicted by VERSE.

In this study, two strategies were developed and compared to the literature method of Xie et al. and startup from clean columns. To better approximate the steady-state column profiles, the first strategy involves preloading different columns with solutions of different concentrations, which were determined by VERSE simulations. The columns in Zone I were preloaded with a solution of the slow-moving solute at the steady-state concentration of the extract obtained from VERSE. Similarly, the columns in Zone III were preloaded with a solution of the fast-moving

solute at the steady-state concentration of the raffinate obtained from VERSE. The columns in Zone II were preloaded with a solution of both solutes at the same concentrations as the other two preloading solutions. The columns were then connected and elution was used to shift the solute bands into their steady-state positions. The second strategy uses the same method as the first, except the preloading concentrations were set to be the same as the product concentrations determined by mass balance using the zone velocities determined from SSWD.

3.0 Experimental

3.1 Materials

The polymer and the flame retardants were dissolved in a 50/50 (vol %) mixture of DCM and ACE. The solvents were obtained from Mallinckrodt and were more than 99% pure. Isopropanol (>99%) was used in column packing and was also purchased from Mallinckrodt. Blue dextran (average molecular weight = 2,000,000 Da) was obtained from Sigma-Aldrich. The mobile phase used for the HPLC analysis of the different components was a mixture of acetonitrile (ACN, >99.5% pure from Mallinckrodt) and tetrahydrofuran (THF, > 99.9% pure from Sigma-Aldrich) without stabilizer. The polymer, SAN, and the flame retardants, RDP and BPADP, were provided by SABIC Innovative Plastics. The packing material used for the SMB experiments was Amberlite XAD 1180N, which was purchased from DOW Water and Process Solutions. The average particle size was 450 μm with an average pore size of 450 Å.

3.2 Equipment

The SMB experiments were performed using a SEMBA Biosciences Octave 100 SMB unit with four pumps, all of which were compatible with dichloromethane. The pump

configuration is shown in Fig. 3. The 8 columns for the SMB experiments were obtained from ACE Glass, Inc. and were 65 cm in length with an inner diameter of 2.54 cm. HPLC analysis of samples from the SMB experiments was accomplished using an Agilent 1100 HPLC with a diode array detector and an auto-sampler. The column was an Inertsil ODS-2 HPLC column, which was 150 mm in length, had an inner diameter of 4.6 mm, and particle size of 5 microns. Batch SEC chromatography experiments were accomplished using a diode array detector (Agilent 1260 DAD VL), two Agilent PrepStar SD-1 pumps, a manual injection system, and an Agilent 440-LC fraction collector. SMB column packing that required recirculating solvent used an IsmaTec IP 65 pump.

3.3 Column Packing

The XAD 1180N resin was packed with sodium chloride and sodium carbonate salts in the pores to prevent bacterial growth. These salts must be removed to access all the pore space in the particles so the resin was washed with reverse-osmosis (RO) water using a resin to water ratio of 1:1.5 under stirring conditions for over 3 hours to remove the salts from the particles. The liquid was decanted, and the resin was washed two more times in the same manner to ensure that the salts were removed. After washing, the resin was dried overnight at room temperature in a fume hood and then weighed. Isopropanol (IPA) was added to the resin particles in a 1:1 volume mixture and sonicated for 30 minutes to removed bubbles from the porous particles. The low density of IPA ensured that all the resin particles were completely submerged and IPA can be easily displaced by the acetone/dichloromethane mixture which was used in later experiments. The mixture was allowed to settle overnight.

The dead volume for each column was determined by weighing the column caps dry and then reweighing the caps after pumping RO water through the caps until air bubbles were no longer produced.

Once the dry weights of all the parts of the column were obtained, a slurry, which consists of equal volumes of resin and IPA, was poured into the column with one end fitting attached at the column outlet without a plug, so the IPA was allowed to flow out of the column. When the top of the resin packing reached the top of the column, the bottom fitting was plugged and the other end fitting of the column was attached and plugged. IPA was recycled using downward flow at more than 30 mL/min. If the resin packing height was reduced, then more resin/IPA slurry was added to the top of the column and the IPA recycle was repeated. If the packing height did not change after more than 2 hours, the column was considered packed.

3.4 Column Characterization

To determine the interparticle bed void fraction (ϵ_b), 10 mL pulses of 0.5 g/L blue dextran in 50/50 IPA/water were detected at a wavelength of 500 nm. The flowrate was 5 mL/min with a downward flow direction. After the bed void fraction was determined, the solvent in the columns was exchanged for 50/50 (vol.%) DCM/ACE.

The total void fraction (ϵ_t) was determined from long pulses of RDP since it was small enough to completely penetrate all the pores of the particles. Long pulses were performed by feeding 1-1.3 column volumes (CV) of the polymer or flame retardant solution to the column, and then changing the feed to clean eluent to wash the column. The resulting breakthrough and wash curves were used to determine size exclusion factors of the different components. VERSE simulations of the experiments were used to determine apparent pore diffusivities for each component by fitting the simulations to the experimental data. Initial estimates for the pore

diffusivities were obtained from the Brownian diffusivities (D_{∞}) and the Mackie-Meares correlation [51] (Supplementary Materials, S.3). The flowrate was 5 mL/min in downward flow.

Since the mobile phase was 50% ACE by volume, SAN, RDP, and BPADP could not be monitored by the UV detector because of the large absorbance of ACE at all detectable wavelengths. To obtain breakthrough curves, effluent samples were collected periodically and analyzed by HPLC.

3.5 HPLC Analysis

A method to analyze SAN and the flame retardants (RDP, BPADP) was developed based on the principle of gradient polymer elution (GPEC) chromatography [28]. In GPEC, the sample was injected into a poor solvent for the components so that the components precipitated on the solid phase [52]. The mobile phase was then gradually changed to become a stronger solvent for the components, such that the components would redissolve at different mobile phase compositions. The different solubilities of the components in different mobile phase compositions provided the necessary separation for the components to be detected by a UV detector.

The poor solvent used was ACN and the strong solvent was THF. The main UV signal used for detection was 260 nm. The column was heated to 32°C and the injection volume was set to 10 μ L. The flowrates and solvent gradient are shown in Table S2.1 in the Supplementary Material.

3.6 SMB Fast Startup

The SEMBA system allowed for a feed solution to be pumped through specific columns and then sent to waste. For each preloading, a solution was pumped at 15 mL/min through a single column for 20 minutes. During this period, effluent samples were taken at 11, 13, 15, 17,

and 19 minutes after the start of the loading. If the solution contained SAN, sampling times were added at 7 and 9 minutes. The samples were analyzed using HPLC to obtain breakthrough curves, which can be compared with VERSE simulations to verify the parameters.

After the 20 minutes had elapsed, the SEMBA unit added the next column in series to the original column. The same solution was again pumped at 15 mL/min for 20 minutes with the same sampling schedule. After two columns had been loaded, the solution was changed and the process was repeated for the next set of columns.

This procedure was performed for Runs 1, 4, and 6. For Runs 4 and 6, an elution step was added after the three sets of columns were loaded. Clean eluent was pumped through all 8 columns connected in series at 5 mL/min for 20 minutes. This elution step shifted the concentration profiles into the same positions as the steady-state concentration profiles, which reduced the amount of time for the SMB experiments to reach cyclic steady state.

3.7 SMB Operation

The feed solutions were made by dissolving SAN, RDP, or BPADP in 50/50 DCM/ACE by volume. The eluent was clean 50/50 ACE/DCM by volume. The pump flowrates and switching time were determined from the Speedy Standing Wave Design (SSWD) method and set in the SEMBA program.

Glass bottles (~100 mL) were used to collect the extract and raffinate product streams for HPLC analysis. Immediately after a switch, a set of bottles (Set 1) was substituted with a new set of bottles (Set 2) while the currently full set was weighed. Samples of roughly 20 mL were taken from the bottles for archival purposes. Small (~1 mL) samples were taken and analyzed by HPLC to determine the polymer concentrations in each product stream. Extract samples were diluted to 50% of the original concentration to keep RDP concentrations within the linear region

of the established calibration curve. The bottles of Set 1 were then emptied, rinsed with DCM, and dried before replacing the bottles of Set 2 after the next switch.

4.0 Results

4.1 Intrinsic Parameters for SSWD and VERSE Simulations

HPLC calibration results are shown in Fig. S2.1 in the Supplementary Material. Column packing and characterization results are presented in Table 4, along with numerical parameters used in VERSE simulations. Average particle size was provided by the manufacturer. Bed void (ε_b) and total void (ε_t) fractions were determined using blue dextran pulses and RDP frontals, respectively. Particle porosity (ε_p) was determined from the other two void fractions. The dead volume (DV), in terms of percent of one column volume (CV), includes the system dead volume per CV and the dead volume in the caps of a column.

Apparent pore diffusivities (D_p) and size-exclusion factors (K_{se}) listed under the Batch column were estimated from column frontal data. The K_{se} values of SAN and BPADP were fine-tuned using SMB data and are listed under the SMB column.

4.2 Column Characterization

Chromatograms of the component frontals and blue dextran pulses are shown in Fig. 5. The mass center of the blue dextran pulse gives the bed void fraction (0.37). The component frontals were fit with VERSE simulations to determine their size-exclusion factors and diffusivities, which are reported in Table 4. The estimated intraparticle diffusivities are less than 10% of the Brownian diffusivities. These ratios are similar to those of other polymeric resins reported in the literature [44].

4.3 Experimental Testing of SSWD and Fast Startup Methods

The intrinsic parameters obtained from batch chromatography in Table 4 were used to design the SMB flowrates and switching times for Runs 1-3. After these runs, the parameters were fine-tuned by comparing the VERSE column profiles with experimental profiles near cyclic steady-state to fit the experimental data. The SMB design for Run 4 was obtained using the new parameters. Fast startup methods based on the design of Run 4 were compared to the literature fast startup method and to startup from clean columns. Run 5 was designed to separate a ternary mixture. The results were used to fine-tune the size-exclusion factor for BPADP, which was overestimated from batch SEC experiments. The fine-tuned size-exclusion factor was used to design Run 6. Summaries of the SMB designs (operating parameters) and experimental results are presented in Tables 5 and 6, respectively.

4.4 SMBs for Separating SAN from RDP (Runs 1–4)

4.4.1 SMB Run 1

The first SMB run was designed for 95% yield of each component and to verify the estimated intrinsic parameters. To quickly reach cyclic-steady-state, the feed flowrate was set at 0.6 mL/min so that the switching time would be relatively short (~37 min).

To quickly reach steady-state, the columns were preloaded with SAN/RDP solutions to approximate the final steady state column profile predicted from the VERSE chromatography simulation software. The feed solutions were 3 wt.% RDP for columns 1 and 2, 3 wt.% RDP with 2 wt.% SAN for columns 3 and 4, and 2 wt.% SAN for columns 5 and 6. The preloaded column profiles obtained from a rate-model based simulation program (VERSE) are shown in Fig. 6a.

The column profiles and effluent histories for Run 1 at the end of step 33 are shown in Fig. 6. The simulated SAN profile lagged behind the experimentally obtained profile, Fig. 6b. The $K_{se,SAN}$ was reduced from 0.63 to 0.61 to better fit the simulated SAN profile to the experimental results, Fig. 6c. The raffinate history of Run 1 shows periodic fluctuations, which resulted from the recycle flowrate being set to zero on the fifth step of every cycle. The error was corrected after the 24th step (886 minutes) and the raffinate concentration stabilized very quickly to the value predicted by VERSE simulation.

The experimental RDP concentrations on the plateau are lower than the simulation results, which is most likely due to some dilution of the profile samples because of the dead volume in the sampling tubing. There also may have been some errors in diluting the profile samples for HPLC measurement.

4.4.2 SMB Run 2

The second SMB experiment did not have a cleaning step between experiments, so the column profile in Fig. 6b was used as the initial column profile for Run 2 in simulations. The feed for Run 2 was also 5 wt.% of each component, but the desired yield was increased to 97%. The effluent histories and column profiles at the end of 51 steps are shown in Fig. 7.

The simulated column profiles values lagged behind the experimental profiles when the column length was assumed to be 65 cm, Fig. 7a. When the packing length was changed to 63 cm, the simulation results fit the experimental data much better, Fig. 7b. The error in packing length appears more prominently in Run 2 because it was run for a larger number of steps (~84, in total) compared to Run 1 (33 steps). The small error (~3%) in packing length could be from a small error in estimating the bed void fraction or column dead volume, such that the effective packing length was 2 cm shorter than the nominal length. It could also be due to small errors in

the length or inner diameter of the glass columns. The rest of the simulations were based on a packing length of 63 cm. The RDP wave was more affected by the column length change than the SAN wave because the size-exclusion factor of RDP is larger than that of SAN. Reducing the column length from 65 cm to 63 cm (3% difference) advances the edge of the RDP trailing wave in Zone I by the difference in retention (i.e. $0.03 * L_c * \text{retention factor} (0.69) * 51 \text{ steps} \approx 1 L_c$). The same reasoning predicts that the SAN waves should differ by $\sim 0.6 L_c$ (retention factor = 0.42). However, the differences for edges of the advancing waves in Zone IV are reduced because the SWD focuses them toward the raffinate port.

The initial column profile of Run 2 was the final profile of Run 1 and the desorbent port was located at the inlet of Column 1 (in SEMBA notation). As the operating conditions changed to Run 2, the default location of the desorbent port in SEMBA was the inlet of Column 1. Instead of entering Column 2 as intended, the desorbent again entered Column 1 at the beginning of Run 2. This resulted in low RDP concentration in the extract at the start of the experiment. As SMB operation continued, the concentration waves recovered to their cyclic-steady-state positions. The column profiles at the end of Run 2 agreed with the predicted values from simulation. The effluent histories were well predicted by VERSE, which took into account the port location at the beginning of Run 2.

4.4.3 SMB Run 3

Run 3 also did not have a cleaning step, so the initial column profile for Run 3 was the final profile of Run 2 in the simulation. Run 3 was a repeat of the designed operating conditions for Run 1, which were determined from SSWD based on the nominal column length of 65 cm.

The effluent histories and column profiles at the end of step 56 are shown in Fig. 8. The sharp rise in the RDP concentration around step 17 was most likely due to a flowrate problem

caused by the desorbent pump, which produced a lower flowrate than desired. This problem persisted for 3 steps before it could be corrected. After correction, RDP concentrations slowly approached the steady-state value.

From the data obtained from Runs 1-3, the average column length was determined to be 63 cm instead of 65 cm and the size exclusion factor for SAN was reduced to 0.61 from 0.63. The designs of Runs 4 and 6 were based on these new parameters.

4.4.4 SMB Run 4

Run 4 was designed to separate RDP from SAN with higher feed concentrations (7 wt.% each) and a higher yield requirement (99%) compared to the previous runs. The columns were washed with pure solvent after Run 3. The first preloading strategy (VERSE) was used to approximate the steady-state column profile. The preloading solutions were 6.5 wt % RDP for columns 1 and 2 (Zone I), 6.5 wt % RDP with 5.7 wt % SAN for columns 3 and 4 (Zone II), and 5.7 wt % SAN for columns 5 and 6 (Zone III). All eight columns were then connected in series and eluent was pumped at 5 mL/min for 20 minutes. This elution step shifted the concentration waves into their steady-state positions. The preloaded column profiles obtained from VERSE are shown in Fig. 9a. Dips in concentrations on the plateaus are due to incomplete saturation of the columns before elution.

The column profiles and effluent histories of Run 4 at the end of step 27 are shown in Fig. 9b. The extract flowrate in the first two steps was lower than the set flowrate. After the flowrate was corrected, the effluent data agreed with simulation results. The purities for both streams were greater than 99%. The experimental product concentrations, purities (>99%), and yields (>99%) agreed closely with those of SWD. This preloading strategy effectively shortened

the time required for the product concentrations to reach 95% of their cyclic steady-state values to 3 steps.

4.5 Comparison of Fast Startup Methods

Once the first fast startup method was verified with experiments, it was compared to other fast startup methods and startup from clean columns. Run 4 was used as the base case and VERSE simulations were used to determine the startup time for each method. The results of the VERSE simulations of SMB Run 4 are shown in Fig. 10. A clean startup of Run 4 was simulated for 80 steps. The product concentrations after 80 steps were determined to be the cyclic steady-state values. All the preloading strategies achieved cyclic steady state in fewer steps than the regular startup from clean columns, which took over 36 steps (>4 cycles).

The literature method of preloading four columns with the feed solution was the easiest to implement, but has a longer startup time than the two proposed methods. The extract product had very low purity until after 15 steps and the raffinate product did not reach 95% of the cyclic steady-state value until after 29 steps. However, this strategy does not require already pure solutions for preloading and can be beneficial when first starting up a process.

Within one step, the product concentrations of the first (VERSE) preloading strategy reached 95% of their cyclic steady-state values and the product purities were greater than 99%. This preloading strategy allows for continuous product withdrawal from the first step, unlike the literature method.

The second (SWD) strategy can be used when simulation software, such as VERSE, is unavailable. This strategy uses the SWD to determine the four zone flowrates for a given feed flowrate and specified yield. Once the zone flowrates are specified, the product flowrates can be calculated and an overall mass balance can be performed to determine the product

concentrations. These concentrations are used for the preloading solutions. However, the first strategy is more general and can take into account components which are allowed to distribute between the product ports. The two preloading strategies give similar effluent histories and reduce the startup time by more than 31 fold.

4.6 SMBs for Separating SAN from RDP/BPADP (Runs 5–6)

4.6.1 SMB Run 5

A second flame retardant (BPADP) was added to the feed mixture for Run 5. Because the two flame retardants (FRs) can be recovered together, the separation is pseudo-binary. The two flame retardants were expected to migrate at the same speed in SMB, based on the batch experiments. Thus the operating parameters for Run 5 were the same as Run 2. The effluent histories are presented in Fig. 11.

Some BPADP was found in the raffinate and its concentration in the Extract was lower than that of RDP, most likely due to the overestimation of the size-exclusion factor of BPADP. Column profiles were not taken because raffinate flowrate was found to be lower than the set value and leaks were also observed near the end of the experiment. The results indicated that BPADP migrated faster than predicted and the $K_{se,BPADP}$ was overestimated from batch tests. By reducing $K_{se,BPADP}$ from 1.0 to 0.96, the simulated raffinate and extract histories of all components agreed closely with the experimental histories over 50 steps, Fig. 11.

4.6.2 SMB Run 6

The revised parameters for BPADP were used in the SSWD to obtain the operating conditions of Run 6. The columns were washed with pure solvent, then preloaded using the first preloading method to approximate the steady-state column profiles.

The preloading solutions were 4.5 wt % RDP and 4 wt % BPADP for Zone I, 4.5 wt % RDP and 4 wt % BPADP with 4 wt % SAN for Zone II, and 4 wt % SAN for Zone III. All eight columns were then connected in series and eluent was pumped through at 5 mL/min for 20 minutes. This elution step shifted the solute bands into their steady-state positions, Fig. 12a. The transient column profiles from the preloaded columns to the start of step 40 are shown in Fig. 12a-f. The simulated effluent histories and column profiles at the end of step 40 are compared with experimental data in Fig. 12g.

The extract and raffinate histories agree with simulations and reach 95% of their steady-state values within 2 steps (37 steps if starting from clean columns). The preloading strategy reduced the startup time by more than 18 fold. The purities of both streams are also very high (~100% for the extract, 98% for the raffinate) and agree closely with those from SSWD.

4.7 SSWD Optimization of a Large-Scale SEC-SMB

After the intrinsic parameters were fine-tuned and verified with pilot SMB experiments, SSWD was used to optimize a large scale SEC-SMB for the lowest unit separation cost while satisfying an imposed pressure limitation. The production was scaled to 10,000 tonnes of FR/year and the maximum pressure drop was set at 100 psi per zone. The feed concentration was fixed at 10 wt % FR and 10 wt % SAN and the viscosity was estimated to be 100 cP [53]. The 15 decision variables that can be optimized are column configuration (4), column length (1), dead volume (1), yields (3), particle size (1), and operating parameters (5). As discussed in Section 2.3, *DV* was fixed at 1.9% of the total column volume. The total number of columns was varied from eight to twelve. In order for the true moving bed assumption to apply to SMBs, a constraint of two or more columns per zone was placed on the column configuration [41]. Because of the high feed viscosity, the column length allowed by the pressure limit is relatively short. In order

to obtain a practical column length, the minimum column length was set to be 0.5 m. Because the FRs must be recovered with high purity, the yields were set to be 99% or higher for each component. The particle size was allowed to vary from 0.5–2.0 times the experimental particle radius.

The SSWD equations for the ternary separation of FRs from SAN were used to determine solvent consumption and sorbent productivity for a given SEC-SMB design. These performance criteria combined with cost functions (see Appendix B) can generate total separation costs for a large number of SEC-SMB designs by systematically varying the decision variables. The values of the decision variables which result in the lowest total separation cost were found by the algorithm shown in Fig. C.1.

The optimal particle size was found to be 112 μm , which was the smallest particle size examined. Assuming the resin cost is independent of particle size, smaller particles result in higher productivity and lower cost. Because of the high feed viscosity, the column length is already relatively short (0.56 m). Decreasing the particle size further would shorten the column length to below 0.5 m.

The column configuration did not have a large effect on the overall separation cost. Adding more columns further reduces the column length. In order to obtain a column length larger than 0.5 m, the optimum column configuration was found to be 2-2-2-2.

The optimal yields were found to be 99% for each component. Increasing the yields of the components increases the total cost of the separation, with a very sharp increase in cost when yields approach 99.9%.

When particle size, column configuration, and yields are fixed at the optimal values, the total cost can be plotted against two key dimensionless groups, P_{eb}^* and N_D^* . This surface gives

an overview of how total cost varies with column length (P_{eb}^*) and step time (N_D^* , Eq. (2)) and how a pressure limit constrains column length and step time. Because the total cost surface is concave up, the inverse of total cost is plotted for convenience in Fig. 13a. The highest point in Fig. 13a corresponds to the design with the lowest separation cost.

The dark grey surface represents the system's pressure limit. This surface was produced using Eq. (6). Particle size, pressure limit, phase ratio, and viscosity are fixed. The column length in the denominator of the left hand side of Eq. (6) can be replaced with the Peclet number, Eq. (A.13b), and the port velocity can be replaced by N_D^* , Eq. (2). Since the material properties are fixed, Eq. (6) is only a function of P_{eb}^* and N_D^* . Equation (6) can be rearranged to have the left hand side be a constant and the right hand side be a function of P_{eb}^* and N_D^* , which results in a pressure limit line, Fig. 13b. To visualize the designs which will satisfy the pressure limit, this pressure limit line is extended in the cost dimension as a surface, Fig. 13a. The intersection of the pressure surface and the cost surface represents the combinations of $L_c (P_{eb}^*)$ and zone velocities (N_D^*) that give the pressure drop in Zone I equal to ΔP_{max} . Designs to the left of the surface, smaller P_{eb}^* (shorter L_c) or larger N_D^* (slower zone velocities), will satisfy the pressure requirement. Lines of constant total cost are plotted in Fig. 13b along with the pressure limit curve. The minimum cost design which satisfies the pressure limitation is marked with an "x."

Figure 14 shows the equipment, solvent, sorbent, and total costs plotted against N_D^* at the optimum P_{eb}^* (~353). The vertical black line represents the pressure limit and designs to the left of the line do not satisfy the pressure requirement. Because the material properties are fixed, the column length can be calculated from P_{eb}^* and the port velocity can be calculated from N_D^* .

Estimated costs for separating FRs from SAN at a scale of 10,000 tonnes of FRs/year for the optimized SEC-SMB and batch SEC elution are shown in Table 7. Given the same feed and

product requirements, the unit separation cost of SEC-SMB is only 2.6% of that of conventional batch elution SEC. Since the separation cost is less than 10% of the purchase cost of these FRs, this technology is economically attractive at this scale.

5.0 Conclusions

The SSWD theory has been extended to ternary mixtures and was verified by SEC-SMB experiments. SEC-SMB can produce high purity FRs and SAN with high yield from one of the side streams of the SEPoR process. The results of this study show that intrinsic parameters estimated from single column experiments can have a small (a few %) errors. The operating flow rates and step time based on the estimated parameters can result in significant deviations of column profiles or product purities in long SMB operations. Pilot SMB experiments with 10 or more cycles are needed to detect any small errors. Comparison of VERSE simulated column profiles and effluent histories with the pilot SMB data can help obtain accurate parameters, which are needed for designing reliable SMBs for large-scale production. Fast startup methods based on SWD and VERSE effectively reduced the startup time for the SMB by more than 18 fold. The estimated separation cost for FR recovery by SEC-SMB is less than 3% of that for batch SEC and is less than 10% of the FR purchase price. The results of this study may help develop other SEC-SMB processes for recycling applications, which require high-purity products.

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786 Appendices

787 Appendix A – SSWD Derivation

788 The mass transfer correction term in Eq. (1) is given by Eq. (A.1),

$$789 \quad \Delta_i^j = \frac{\beta_i^j}{L^j(1+\phi\delta_i)} \left[E_{b,i}^j + \frac{\phi(\delta_i v)^2}{K_i^j} \right] \quad (\text{A.1})$$

790 where L^j is the length of zone j, which is equal to L_c times the number of columns in zone j (N^j);

791 and K_i^j is the overall mass transfer coefficient of component i in zone j. Equation (A.1) can be

792 substituted into Eq. (1) and the result can be solved for the zone velocities, Eq. (A.2).

$$793 \quad u_0^I = (1 + \phi\delta_2)v + \frac{\beta_2^I}{L^I} \left[E_{b,2}^I + \frac{\phi(\delta_2 v)^2}{K_2^I} \right] \quad (\text{A.2a})$$

$$794 \quad u_0^{II} = (1 + \phi\delta_1)v + \frac{\beta_1^{II}}{L^{II}} \left[E_{b,1}^{II} + \frac{\phi(\delta_1 v)^2}{K_1^{II}} \right] \quad (\text{A.2b})$$

$$795 \quad u_0^{III} = (1 + \phi\delta_2)v - \frac{\beta_2^{III}}{L^{III}} \left[E_{b,2}^{III} + \frac{\phi(\delta_2 v)^2}{K_2^{III}} \right] \quad (\text{A.2c})$$

$$796 \quad u_0^{IV} = (1 + \phi\delta_1)v - \frac{\beta_1^{IV}}{L^{IV}} \left[E_{b,1}^{IV} + \frac{\phi(\delta_1 v)^2}{K_1^{IV}} \right] \quad (\text{A.2d})$$

$$797 \quad u_F = u_0^{III} - u_0^{II} \quad (\text{A.2e})$$

798 The feed velocity (u_F) is determined by a mass balance at the feed port. The equations for

799 the β terms are given by Eq. (A.3), which were derived from equations presented in Hritzko et al.

800 [42].

$$801 \quad \beta_2^I = \ln \left[\frac{Y_2}{(1-Y_2)} \frac{\left(\frac{u_0^{III}}{u_0^{IV}} - 1 \right)}{\left(1 - \frac{u_0^{II}}{u_0^I} \right)} \right] \quad (\text{A.3a})$$

$$\beta_1^{II} = \ln \left\{ \frac{\left(\frac{u_0^I}{u_0^{II}} - 1 \right)}{(1-Y_1)} \left[\frac{Y_1}{\left(1 - \frac{u_0^{IV}}{u_0^{III}} \right)} - 1 \right] \right\} \quad (\text{A.3b})$$

$$\beta_2^{III} = \ln \left\{ \frac{\left(1 - \frac{u_0^{IV}}{u_0^{III}} \right)}{(1-Y_2)} \left[\frac{Y_2}{\left(\frac{u_0^I}{u_0^{II}} - 1 \right)} + 1 \right] \right\} \quad (\text{A.3c})$$

$$\beta_1^{IV} = \ln \left[\frac{Y_1}{(1-Y_1)} \frac{\left(1 - \frac{u_0^{II}}{u_0^I} \right)}{\left(\frac{u_0^{III}}{u_0^{IV}} - 1 \right)} \right] \quad (\text{A.3d})$$

The Chung and Wen correlation for low Reynolds numbers ($\text{Re} < 10$) (Eq. A.4) was used to evaluate the axial dispersion coefficients.

$$E_b^j = 10 \varepsilon_b R_p u_0^j \quad (\text{A.4})$$

The ratios of the axial dispersion coefficients (Γ^j) were determined by substituting Eq. (A.4) into the definition of Γ^j in Table 2 and the resulting equations were rearranged to solve for Γ^j , Eq. (A.5).

$$\Gamma^I = \frac{1 + \phi \delta_2}{1 + \phi \delta_1 - \frac{\phi(\delta_2 - \delta_1)}{P_{eb}^*} \left(\frac{\beta_1^{IV}}{N^{IV}} + \frac{\beta_2^I}{N^I} \right)} \quad (\text{A.5a})$$

$$\Gamma^{II} = \frac{1 + \phi \delta_1}{1 + \phi \delta_1 - \frac{\phi(\delta_2 - \delta_1)}{P_{eb}^*} \left(\frac{\beta_1^{IV}}{N^{IV}} + \frac{\beta_1^{II}}{N^{II}} \right)} \quad (\text{A.5b})$$

$$\Gamma^{III} = \frac{1 + \phi \delta_2}{1 + \phi \delta_1 - \frac{\phi(\delta_2 - \delta_1)}{P_{eb}^*} \left(\frac{\beta_1^{IV}}{N^{IV}} - \frac{\beta_2^{III}}{N^{III}} \right)} \quad (\text{A.5c})$$

The overall mass transfer resistance, $\frac{1}{K_i^j}$, can be written explicitly as mass transfer

resistances in series for linear systems, as shown in Eq. (A.6),

$$\frac{1}{K_i^j} = \frac{R_p^2}{15K_{se,i}\varepsilon_p D_{p,i}} + \frac{R_p}{3k_{f,i}} \quad (\text{A.6})$$

where $k_{f,i}$ is the film mass transfer coefficient. The last term on the right hand side of Eq. (A.6) is negligible compared to intraparticle diffusion, or axial dispersion, for most low pressure systems. The simplified Eq. (A.6) can be substituted into Eq. (A.2). The resulting equations can then be simplified using the dimensionless groups in Table 2, Eq. (A.7).

$$u_0^I = v \left(1 + \phi\delta_2 + \frac{\beta_2^I \Gamma^I}{P_{eb}^{IV} N^I} + \frac{\phi^2 \beta_2^I \delta_2^2}{15N_{D,1} \lambda_2 \gamma_2 N^I} \right) \quad (\text{A.7a})$$

$$u_0^{II} = v \left(1 + \phi\delta_1 + \frac{\beta_1^{II} \Gamma^{II}}{P_{eb}^{IV} N^{II}} + \frac{\phi^2 \beta_1^{II} \delta_1^2}{15N_{D,1} N^{II}} \right) \quad (\text{A.7b})$$

$$u_0^{III} = v \left(1 + \phi\delta_2 - \frac{\beta_2^{III} \Gamma^{III}}{P_{eb}^{IV} N^{III}} - \frac{\phi^2 \beta_2^{III} \delta_2^2}{15N_{D,1} \lambda_2 \gamma_2 N^{III}} \right) \quad (\text{A.7c})$$

$$u_0^{IV} = v \left(1 + \phi\delta_1 - \frac{\beta_1^{IV}}{P_{eb}^{IV} N^{IV}} - \frac{\phi^2 \beta_1^{IV} \delta_1^2}{15N_{D,1} N^{IV}} \right) \quad (\text{A.7d})$$

An even more detailed derivation of the SSWD equations for separations of binary mixtures can be found in Weeden and Wang [47].

Equations (A.3), (A.5), and (A.7) can be extended to separations of ternary mixtures. The only differences are the component subscripts, which denote which component is confined in that zone. If the fast solute (solute 1) is split from the other two (Fig. 3b), then the slowest solute (solute 3) is controlled in Zone I, solute 1 is controlled in Zone II, solute 2 is controlled in Zone III (and solute 3 is pinched), and solute 1 is controlled in Zone IV. The resulting zone velocity equations are shown in Table 3, Eq. (4).

If solute 3 is split from the other two (Fig. 3c), then solute 3 is controlled in Zone I, solute 2 is controlled in Zone II (and solute 1 is pinched), solute 3 is controlled in Zone III, and solute 1 is controlled in Zone IV. The resulting zone velocity equations are shown in Table 3, Eq. (5).

Once the zone velocities are known, the inlet flowrates can be determined using mass balances. The desorbent and feed flowrates are given by Eq. (A.8) and Eq. (A.9), respectively,

$$D = \varepsilon_b S(u_0^I - u_0^{IV}) \quad (\text{A.8})$$

$$F = \varepsilon_b S(u_0^{III} - u_0^{II}) \quad (\text{A.9})$$

where S is the column cross-sectional area.

One important factor in calculating the overall cost for SEC-SMB systems is the amount of solvent used by the process. The solvent cost is related to the ratio of the desorbent flowrate over the feed flowrate (D/F), which is also an indicator of the dilution of the products. The equation for D/F for splitting solute 1 from solutes 2 and 3 is shown in Eq. (A.10a). The equation for D/F when splitting solute 3 from solutes 1 and 2 is shown in Eq. (A.10b).

$$\frac{D}{F} = \frac{u_0^I - u_0^{IV}}{u_0^{III} - u_0^{II}} = \frac{\frac{(\alpha_3 - 1)}{(\alpha_2 - 1)} + \frac{1}{P_{eb}^*} \left(\frac{\beta_3^I \Gamma^I}{N^I} + \frac{\beta_1^{IV}}{N^{IV}} \right) + \frac{1}{15N_D^*} \left(\frac{\beta_3^I \alpha_3^2}{\lambda_3 \gamma_3 N^I} + \frac{\beta_1^{IV}}{N^{IV}} \right)}{1 - \frac{1}{P_{eb}^*} \left(\frac{\beta_2^{III} \Gamma^{III}}{N^{III}} + \frac{\beta_1^{II} \Gamma^{II}}{N^{II}} \right) - \frac{1}{15N_D^*} \left(\frac{\beta_2^{III} \alpha_2^2}{\lambda_2 \gamma_2 N^{III}} + \frac{\beta_1^{II}}{N^{II}} \right)} \quad (\text{A.10a})$$

$$\frac{D}{F} = \frac{\frac{(\alpha_3 - 1)}{(\alpha_3 - \alpha_2)} + \frac{1}{P_{eb}^*} \left(\frac{\beta_3^I \Gamma^I}{N^I} + \frac{\beta_1^{IV}}{N^{IV}} \right) + \frac{1}{15N_D^*} \left(\frac{\beta_4^I \alpha_3^2}{\lambda_3 \gamma_3 \alpha_2^2 N^I} + \frac{\beta_1^{IV}}{\alpha_2^2 N^{IV}} \right)}{1 - \frac{1}{P_{eb}^*} \left(\frac{\beta_3^{III} \Gamma^{III}}{N^{III}} + \frac{\beta_2^{II} \Gamma^{II}}{N^{II}} \right) - \frac{1}{15N_D^*} \left(\frac{\beta_3^{III} \alpha_3^2}{\lambda_3 \gamma_3 \alpha_2^2 N^{III}} + \frac{\beta_2^{II}}{\lambda_2 \gamma_2 N^{II}} \right)} \quad (\text{A.10b})$$

Another important factor for calculating costs is the cost of the stationary phase (resin cost). This cost is mainly affected by the system productivity ($P_{R,i}$), which can be calculated using Eq. (A.11),

$$P_{R,i} = \frac{S(u_0^{III} - u_0^{II}) C_{F,i} Y_i}{SL_c N \phi \rho_p} \quad (\text{A.11})$$

where ρ_p is the particle density (mass of stationary phase per particle volume).

The zone velocities in Eq. (A.11) can be replaced with Eq. (4) or Eq. (5), depending on which type of split is required, to give Eq. (A.12a) or Eq. (A.12b), respectively.

$$P_{R,i} = \frac{Y_i C_{F,i} (\delta_2 - \delta_1)}{N t_s \rho_p} \left[1 - \frac{1}{P_{eb}^*} \left(\frac{\beta_2^{III} \Gamma^{III}}{N^{III}} + \frac{\beta_1^{II} \Gamma^{II}}{N^{II}} \right) - \frac{1}{15 N_D^*} \left(\frac{\beta_2^{III} \alpha_2^2}{\lambda_2 \gamma_2 N^{III}} + \frac{\beta_1^{II}}{N^{II}} \right) \right] \quad (A.12a)$$

$$P_{R,i} = \frac{Y_i C_{F,i} (\delta_3 - \delta_2)}{N t_s \rho_p} \left[1 - \frac{1}{P_{eb}^*} \left(\frac{\beta_3^{III} \Gamma^{III}}{N^{III}} + \frac{\beta_2^{II} \Gamma^{II}}{N^{II}} \right) - \frac{1}{15 N_D^*} \left(\frac{\beta_3^{III} \alpha_3^2}{\lambda_3 \gamma_3 \alpha_2^2 N^{III}} + \frac{\beta_2^{II}}{\lambda_2 \gamma_2 N^{II}} \right) \right] \quad (A.12b)$$

Since the Chung and Wen correlation is used to evaluate the axial dispersion coefficients, the Peclet numbers can be simplified by substituting Eq. (A.4) into Eq. (3) and rearranged to solve for P_{eb}^* , resulting in Eq. (A.13a).

$$P_{eb}^* = \frac{\phi(\delta_2 - \delta_1)}{(1 + \phi\delta_1)} \left[\frac{L_c}{10 \varepsilon_b R_p} + \frac{\beta_1^{IV}}{N^{IV}} \right] \quad (A.13a)$$

Equation (A.13a) can be rearranged to solve for L_c , Eq. (A.13b).

$$L_c = 10 \varepsilon_b R_p \left[\frac{P_{eb}^* (1 + \phi\delta_1)}{\phi(\delta_2 - \delta_1)} - \frac{\beta_1^{IV}}{N^{IV}} \right] \quad (A.13b)$$

Appendix B – Cost Functions

The total cost function used in this work to estimate the separation cost for SEC-SMB is shown in Eq. (B.1).

$$Total\ Cost\ (TC) = Resin\ Cost\ (RC) + Solvent\ Cost\ (SC) + Equipment\ Cost\ (EC) \quad (B.1)$$

where all the costs have the units of \$/kg FR.

The resin cost was calculated according to Eq. (B.2),

$$RC \left[\frac{\$}{kg_{FR}} \right] = \frac{(Vol.\ of\ resin)(Resin\ price)}{(Resin\ Life)(Production)} = \frac{\left(\frac{N L_c \pi (ID)^2}{4} [L\ CV] \right) \left(19 \left[\frac{\$}{L\ CV} \right] \right)}{(10\ [years]) (10,000,000 \left[\frac{kg_{FR}}{year} \right])} \quad (B.2)$$

where N is the total number of columns and ID is the column inner diameter.

The solvent cost was calculated according to Eq. (B.3),

$$SC \left[\frac{\$}{kg_{FR}} \right] = \frac{\left(\frac{D}{F} \right) [RR * recycle\ cost + (1 - RR) * Solvent\ price]}{(Feed\ Conc.)(Yield)} = \frac{\left(\frac{D}{F} \right) (.99 * .002 + .01 * 1) [\$/L] \left(1,000 \left[\frac{g_{FR}}{kg_{FR}} \right] \right)}{\left(C_F \left[\frac{g_{FR}}{L} \right] \right) (Yield)} \quad (B.3)$$

where RR is the recycle ratio of solvent.

The equipment cost was calculated according to Eq. (B.4).

$$EC \left[\frac{\$}{kg_{FR}} \right] = \frac{(SMB \text{ price})}{(Depreciation \text{ Time})(Utilization \text{ Factor})(Production)} = \frac{(3,000,000[\$])}{(7 [\text{years}])(.96)(10,000,000 \left[\frac{kg_{FR}}{\text{year}} \right])} \quad (B.4)$$

Appendix C – Cost Optimization Algorithm

The cost optimization algorithm that was used to determine the optimum yields, particle radius, column configuration, column length, zone velocities, and port velocity is shown in Fig. C.1. Material properties (other than particle radius), dead volume, pressure limit, feed concentration, packing density, fluid viscosity, and production scale were held constant. The total number of columns was varied from eight to twelve and each zone was constrained to have at least two columns. The number of columns in Zone IV was calculated from the column balance of the other zones and the total number of columns. N_D^* ranged from 0.1 to 20, P_{eb}^* ranged from 5 to 1,000, R_p ranged from 112 μm to 450 μm , and yields ranged from 0.990 to 0.999. The initial values of the variables were passed to the SSWD algorithm, Fig. C.1b, which used an initial guess for β_i^j and Γ^j and then evaluated u_{ϕ}^j/ν . The SSWD algorithm then calculated β_i^j (Eq. (A.3)), and Γ^j (Eq. (A.5)) from u_{ϕ}^j/ν . If the calculated values were not within 0.001 of the guessed values, then the u_{ϕ}^j/ν calculations were repeated with the calculated values of β_i^j and Γ^j . Once the values were within the tolerance, L_c was calculated from P_{eb}^* using Eq. (A.13) and ν was calculated from N_D^* using Eq. (2). Once ν was calculated, the zone velocities were calculated using Eq. (4). The solvent consumption and sorbent productivity were then calculated using Eq. (A.10a) and Eq. (A.12a), respectively. The overall separation cost (total cost) was then calculated using Eqs. (B.1-B.4). The pressure drop of the system was calculated using Eq. (4) and compared to the set pressure limit of 100 psi per zone. If the calculated pressure exceeded the pressure limit, then the design was not considered feasible. After the pressure check, the Peclet number was increased and the process repeated until $P_{eb}^* = 1,000$. Then, N_D^* was

897 increased and the P_{eb}^* cycle repeated. Once N_D^* reached a value of 20, the particle size increased
898 and the N_D^* and P_{eb}^* cycles repeated. In similar fashions, all the cycles were repeated for varying
899 column configuration and yield of each component. After all the cycles were completed, the
900 minimum cost was found from all the stored values and the associated cost, Y_i , R_p , L_c , N^j , u_0^j , and
901 ν were determined. This algorithm was implemented using MATLAB R2014a on a laptop
902 computer with a total run time of less than one minute.
903

Figure Captions

Figure 1. Overview of Purdue process to recover high-purity polycarbonates and FRs from an electronic waste stream. ^{*}SEPoR process and cost estimate described in Weeden et al. [15]. [†]Cost estimate for 10,000 tonnes FR/year, Table 7.

Figure 2. Diagram of a four-zone SMB. (a) Step N; (b) step N + 1. Large red spheres represent the fast component; small green spheres represent the slow component.

Figure 3. Standing Wave Design end-step concentration profiles for (a) binary, (b) ternary – Split 1, and (c) ternary, Split 2 non-ideal separations. Pump configuration for the SMB experiments is also shown. The feed, desorbent, extract, and Zone IV recycle flowrates were controlled by individual pumps while the rest of the streams were determined by mass balance. The black arrows indicate the standing waves in each of the four zones. Asterisks indicate pinched waves.

Figure 4. SSWD overview for ternary SEC-SMB.

Figure 5. (a) Blue dextran pulse to determine bed void fraction, and (b) component frontals to determine size-exclusion factors and diffusivities of each component. BPADP frontal not shown as it overlaps with the RDP data.

Figure 6. (a) SMB Run 1 preloaded column profiles predicted by VERSE, (b) column profiles for $K_{se,SAN} = 0.63$ (c) column profiles for $K_{se,SAN} = 0.61$ (top), extract history (bottom left), and raffinate history (bottom right) for SMB Run 1, end of step 33. Lines are from VERSE simulations while squares and diamonds are HPLC data points. Design in Tables 5, 6.

Figure 7. (a) column profiles for Run 2 at the end of the 51st step. VERSE simulations used a column length of 65 cm. (b) column profiles (top), extract history (bottom left), and raffinate history (bottom right) for SMB Run 2 using a column length of 63 cm, end of step 51. Lines are from VERSE simulations while squares and diamonds are HPLC data points. Design in Tables 5, 6.

Figure 8. Column profiles (top), extract history (bottom left), and raffinate history (bottom right) for SMB Run 3, end of step 56. Lines are from VERSE simulations while squares and diamonds are HPLC data points. Design in Tables 5, 6.

Figure 9. (a) Preloaded column profiles obtained from VERSE simulations, (b) column profiles (top), extract history (bottom left), and raffinate history (bottom right) for SMB Run 4, end of step 27. Lines are from VERSE simulations while squares and diamonds are HPLC data points. Design in Tables 5, 6.

Figure 10. Comparison of pre-loading strategies and regular startup for binary SEC-SMB. SMB design is the same as Run 4. Effluent histories: (a) raffinate and (b) extract. RDP concentrations not shown in (a) since all strategies resulted in very low concentrations of RDP throughout the simulations. Likewise the SAN concentrations are not shown in (b) except for the feed loading strategy which has significant SAN contamination.

Figure 11. (a) Extract and (b) raffinate histories from SMB Run 5. No column profiles were taken for Run 5. Design in Tables 5, 6.

Figure 12. (a) SMB Run 6 preloaded column profiles predicted by VERSE, prior to start of SMB operation; (b) SMB column profile at start of step 8; (c) start of step 16; (d) start of step 24; (e) start of step 32; (f) start of step 40; (g) column profiles (top), extract history (bottom left), and raffinate history (bottom right) for SMB Run 6, end of step 40. Lines are from VERSE simulations while squares, triangles, and diamonds are HPLC data points. Design in Tables 5, 6.

Figure 13. (a) Inverse of total cost surface for ternary separation with pressure limit surface and (b) contour plot of (a) with pressure limit (black line) and minimum cost point (x). $N^j = 2-2-2-2$, $DV = 1.9\%$, $\Delta P_{max} = 100$ psi per zone, $Y_i = 99\%$, $R_p = 112$ μm .

Figure 14. Total, sorbent, solvent, and equipment costs versus N_D^* at P_{eb}^* for minimum cost. Vertical black line represents the pressure limit – operating at N_D^* values to the right of the line will satisfy the pressure requirement.

Figure C.1. (a) algorithm for optimizing 14 decision variables (yields, particle size, column configuration, column length, zone velocities, and port velocity) for minimum cost and (b) algorithm used by SSWD to determine column length, β_i^j , Γ^j , zone velocities, and port velocity from given dimensionless groups.

Figureg

Figure 1

Figure 2

(a)

(b)

Figure 3

Figure 4

Figure 5

Figure 6

(a)

(b)

(c)

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

(a)

(b)

Figure 14

Figure C.1

Table 1
Main components of one of the side streams from the SEPoR process.

Component	Molecular Structure	MW Range (g/mol)	Bulk Retail Price (\$/kg) ^a
RDP ^b		575 – 4,025	4.00
BPADP ^c		693	3.00
SAN ^d		50,000 – 150,000	1.00

^a Obtained from alibaba.com, May 2014

^b Resorcinol bis-diphenylphosphate

^c Bisphenol A bis-diphenylphosphate

^d Poly(styrene-co-acrylonitrile)

Table 2
Dimensionless variables and groups for ternary, SEC-SMB

Symbol	Name	Definition	Description
δ_i	Retention factor	$\delta_i = \varepsilon_p K_{se,i} + \frac{DV}{(1 - \varepsilon_b)}$	Measure of how much each component is retained by the sorbent
α_i	Selectivity	$\alpha_i = \frac{\delta_i}{\delta_1}$	Ratio of retention factors: greater than one for separation
β_i^j	-	$\beta_i^j = \ln \left(\frac{C_{max,i}^j}{C_{min,i}^j} \right)$	Natural log of ratio of max. conc. to min. conc. of standing component in zone j
γ_i	Diffusivity ratio	$\gamma_i = \frac{D_{p,i}}{D_{p,1}}$	Ratio of intraparticle diffusivities
λ_i	Size-exclusion ratio	$\lambda_i = \frac{K_{se,i}}{K_{se,1}}$	Ratio of size-exclusion factors; equal to α if there is no dead volume
ϕ	Phase ratio	$\phi = \frac{1 - \varepsilon_b}{\varepsilon_b}$	Particle phase relative to bed void
$N_{D,i}$	-	$N_{D,i} = \frac{\phi \varepsilon_p K_{se,i} D_{p,i} L_c}{R_p^2} = \frac{t_s}{t_{D,i}}$	Step time relative to diffusion time
N_D^*	-	$N_D^* = \frac{N_{D,1}(\alpha_2 - 1)}{\phi \delta_1} = \frac{N_{D,i}(\alpha_2 - 1)}{\lambda_i \gamma_i \phi \delta_1}$	Component-independent N_D ; $N_{D,1}$ as base Split 1 from 2 and 3
		$N_D^* = \frac{N_{D,1} \left(\frac{\alpha_3}{\alpha_2} - 1 \right)}{\phi \delta_2}$	Split 1 and 2 from 3
$N_{\Delta P}$	-	$N_{\Delta P} = \frac{\Delta P_{max} R_p^2}{37.5 \phi \mu L_c \nu} = \frac{t_s}{t_c^I}$	Step time relative to pressure-limited convection time
P_{eb}^j	Peclet number	$P_{eb}^j = \frac{\nu L_c}{E_b^j} = \frac{t_{Dax}}{t_s}$	Axial dispersion time relative to step time
Γ^j	Axial dispersion ratio	$\Gamma^j = \frac{E_b^j}{E_b^{IV}}$	Ratio of axial dispersion coefficients of zone j and zone IV
P_{eb}^*	-	$P_{eb}^* = \phi(\delta_2 - \delta_1) P_{eb}^j \Gamma^j$ $P_{eb}^* = \phi(\delta_3 - \delta_2) P_{eb}^j \Gamma^j$	Zone-independent Peclet number, Zone IV as base Split 1 from 2 and 3 Split 1 and 2 from 3

Table 3
SSWD equations for ternary SEC-SMB.

Split 1 (solute 1 from solutes 2 and 3)		Split 2 (solutes 1 and 2 from solute 3)	
$u_0^I = v \left(1 + \phi\delta_3 + \frac{\beta_3^I \Gamma^I \phi(\delta_2 - \delta_1)}{P_{eb}^* N^I} + \frac{\phi\beta_3^I \alpha_3^2 (\delta_2 - \delta_1)}{15N_D^* \lambda_3 \gamma_3 N^I} \right)$	(4a)	$u_0^I = v \left(1 + \phi\delta_3 + \frac{\beta_3^I \Gamma^I \phi(\delta_3 - \delta_2)}{P_{eb}^* N^I} + \frac{\phi\beta_3^I \alpha_3^2 (\delta_3 - \delta_2)}{15\alpha_2^2 N_D^* \lambda_3 \gamma_3 N^I} \right)$	(5a)
$u_0^{II} = v \left(1 + \phi\delta_1 + \frac{\beta_1^{II} \Gamma^{II} \phi(\delta_2 - \delta_1)}{P_{eb}^* N^{II}} + \frac{\phi\beta_1^{II} (\delta_2 - \delta_1)}{15N_D^* N^{II}} \right)$	(4b)	$u_0^{II} = v \left(1 + \phi\delta_2 + \frac{\beta_2^{II} \Gamma^{II} \phi(\delta_3 - \delta_2)}{P_{eb}^* N^{II}} + \frac{\phi\beta_2^{II} (\delta_3 - \delta_2)}{15N_D^* \lambda_2 \gamma_2 N^{II}} \right)$	(5b)
$u_0^{III} = v \left(1 + \phi\delta_2 - \frac{\beta_2^{III} \Gamma^{III} \phi(\delta_2 - \delta_1)}{P_{eb}^* N^{III}} - \frac{\phi\beta_2^{III} \alpha_2^2 (\delta_2 - \delta_1)}{15N_D^* \lambda_2 \gamma_2 N^{III}} \right)$	(4c)	$u_0^{III} = v \left(1 + \phi\delta_3 - \frac{\beta_3^{III} \Gamma^{III} \phi(\delta_3 - \delta_2)}{P_{eb}^* N^{III}} - \frac{\phi\beta_3^{III} \alpha_3^2 (\delta_3 - \delta_2)}{15\alpha_2^2 N_D^* \lambda_3 \gamma_3 N^{III}} \right)$	(5c)
$u_0^{IV} = v \left(1 + \phi\delta_1 - \frac{\beta_1^{IV} \phi(\delta_2 - \delta_1)}{P_{eb}^* N^{IV}} - \frac{\phi\beta_1^{IV} (\delta_2 - \delta_1)}{15N_D^* N^{IV}} \right)$	(4d)	$u_0^{IV} = v \left(1 + \phi\delta_1 - \frac{\beta_1^{IV} \phi(\delta_3 - \delta_2)}{P_{eb}^* N^{IV}} - \frac{\phi\beta_1^{IV} (\delta_3 - \delta_2)}{15\alpha_2^2 N_D^* N^{IV}} \right)$	(5d)
$\frac{\Delta P}{L^I} = \frac{150\mu u_0^I \phi^2}{4R_p^2}$	(6)		
$N_{\Delta P} = \frac{\Delta P_{max} R_p^2}{37.5\phi\mu L_c v} = \phi \left(1 + \phi\delta_3 + \frac{\beta_3^I \Gamma^I \phi(\delta_2 - \delta_1)}{P_{eb}^* N^I} + \frac{\phi\beta_3^I \alpha_3^2 (\delta_2 - \delta_1)}{15N_D^* \lambda_3 \gamma_3 N^I} \right)$	(7)	$N_{\Delta P} = \frac{\Delta P_{max} R_p^2}{37.5\phi\mu L_c v} = \phi \left(1 + \phi\delta_3 + \frac{\beta_3^I \Gamma^I \phi(\delta_3 - \delta_2)}{P_{eb}^* N^I} + \frac{\phi\beta_3^I \alpha_3^2 (\delta_3 - \delta_2)}{15\alpha_2^2 N_D^* \lambda_3 \gamma_3 N^I} \right)$	(8)

Table 4

Summary of material properties, system parameters, and numerical parameters for VERSE simulations.

Column Packing Parameters								
R_p (μm)	L_c (cm)		ID (cm)	ε_b	ε_p	ϕ	DV (% CV)	
	Batch	SMB						
XAD-1180N								
225	65	63	2.54	0.37	0.69	1.70	1.9	
Mass Transfer Parameters								
Component	D_∞^e (cm ² /min)	D_p (cm ² /min)	K_{se}		δ		E_b (cm ² /min)	k_f (cm/min)
			Batch	SMB	Batch	SMB		
SAN	1.0 x 10 ⁻⁴	0.7 x 10 ⁻⁵	0.63	0.61	0.43	0.42	Chung and Wen correlation	Wilson and Geankoplis correlation
BPADP	1.0 x 10 ⁻²	40.0 x 10 ⁻⁵	1.00	0.96	0.69	0.66		
RDP	1.0 x 10 ⁻³	10.0 x 10 ⁻⁵	1.00	1.00	0.69	0.69		
Numerical Parameters								
No. of axial elements	Collocation Points				Tolerance			
	Axial		Particle		Absolute		Relative	
100	4		1		0.001		0.001	

^e Brownian diffusivities (see Supplementary Materials, S.3).

Table 5
Summary of designs for SMB runs.

Design		Flowrates (mL/min)								Switching Time (min)
Run	L_c^f (cm)	Feed	Desorbent	Extract	Raffinate	Zone I	Zone II	Zone III	Zone IV	
1	65	0.59	1.97	0.79	1.77	7.45	6.66	7.25	5.48	36.9
2	65	0.4	1.18	0.49	1.09	4.59	4.1	4.5	3.41	59.7
3	65	0.59	1.97	0.79	1.77	7.45	6.66	7.25	5.48	36.9
4	63	0.36	0.54	0.39	0.51	2.21	1.82	2.18	1.67	119.6
5	65	0.4	1.18	0.49	1.09	4.59	4.1	4.5	3.41	59.7
6	63	0.36	0.65	0.45	0.56	2.59	2.14	2.5	1.94	102.5

^r L_c is the packing length used in the SWD

Table 6
Summary of results for SMB experiments.

Run	Feed Conc. (wt.%)			SWD Purity		Exp. Purity		End step	Comments
	SAN	RDP	BPADP	Extract (FR)	Raffinate (SAN)	Extract (FR)	Raffinate (SAN)		
1	5	5	0	95	95	100	98 ^g	33	Verify fast startup, quickly verify intrinsic parameters
2	5	5	0	97	97	100	92 ^h	51	Longer run time, fast start from end of Run 1, packing length inaccurate
3	5	5	0	95	95	100	87 ^h	56	Repeat of Run 1 design, fast start from end of Run 2, new simulated length
4	7	7	0	99	99	100	99.8	27	Cleaned, then fast start, designed for 63 cm length
5	5	5	5	99.5	98.0	100	65 ⁱ	50	3-component, clean start, verify BPADP parameters – inaccurate
6	5	5	5	99.5	98.0	100	97.6	40	Tuned BPADP parameters, fast start

^g The high raffinate purity of Run 1 was a result of the recycle flowrate being 0 every 8 steps. The run had not yet reached steady state.

^h The raffinate purity of Runs 1-3 should be ~ 88-93% because the SMB designs were based on a column packing length of 65 cm, when the effective packing length was 63 cm.

ⁱ The low raffinate purity was due to the overestimated size-exclusion factor of BPADP.

Table 7

Comparison of estimated costs^j of SEC SMB and batch SEC for separating FRs from SAN.

Parameter (10,000 tonnes FR/year)	Optimized SEC-SMB	Batch SEC^k
Feed Concentration (wt.%)		
RDP	5	5
BPADP	5	5
SAN	10	10
Product conc./Feed conc.	0.83	0.10
Yield of each component	99	99
Column configuration	2-2-2-2	100 units
Column length (cm)	55.2	126
Inner diameter (m)	9.65	8.19
Feed flowrate (L/min)	175	210 (per unit)
Equipment cost (\$/kg FR)	0.04	0.82
Solvent cost (\$/kg FR)	0.18	6.05
Sorbent cost (\$/kg FR)	0.07	4.40
Total cost (\$/kg FR)	0.29	11.27

^j Cost calculated for product coming from PC extraction technology. Thus, the feed cost and cost of solvent for the feed are considered part of the PC extraction cost and not part of the SMB separation cost. The particle radius used for cost calculations was 112 micron. The estimates do not include cost of concentrating feed.

^k The batch SEC elution design can be found in the Supplementary Materials, S.4.