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Modified simulated moving bed chromatography with two pumps for sugar separation

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Abstract−A modified SMB system composed of two pumps was developed for the separation of L-ribose and L-arabinose from its binary mixture. In two-pump SMB operation, the flow rates required for separation in every column zones and product ports are identical to those in conventional SMB equipped with four pumps and are controlled by appropriate operation of valves during a cycle of switching time. The purity, yield and enrichment of sugars obtained by two-pump SMB separation were comparable to that of conventional SMB. The two-pump SMB system is therefore considered to be more economically efficient than conventional SMB by reducing the cost for SMB installation and pump operation.

Keywords: Two-pump, SMB, Chromatography, Sugar Separation, Energy Efficient

INTRODUCTION

Simulated moving bed (SMB) chromatography is a robust continuous separation technique with higher productivity than conventional batch liquid chromatography. Introduced in the early 1960s SMB has been mainly applied for the large scale production in petrochemical and sugar industries. However, it also has been applied for the separation of various materials such as pharmaceutical compounds, fine chemicals, amino acids and proteins.

SMB is considered as practical implementation of the true moving bed (TMB) chromatography concept where the physical movement of a solid bed (i.e., circular column) is impractical [1]. In SMB, the circular column is replaced by a finite number of conventional columns, and the movement of solid bed is implemented by periodically shifting the position of the columns in the network. The physical movement of the columns is avoided by switching the network connectivity through a complex system of pumps, valves and tubes. The typical 4 zone SMB configuration has four ports (i.e., feed, desorbent, extract and raffinate), 4-24 columns allocated in 4 zones and 4-5 pumps. The valves that periodically control the flow direction of fluid are located at the column junctions (Fig. 1). The suitable operating conditions of SMB (e.g., switching time and zone flow rates) are determined based on the triangle theory [2].

During the last decade, many studies have investigated improv-

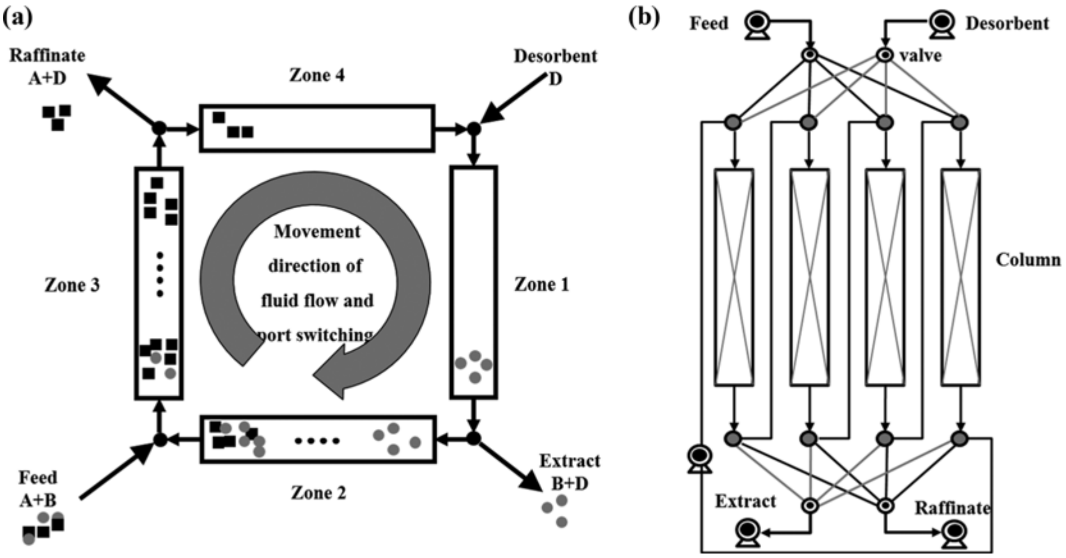

Fig. 1. Schematic diagram and configuration of conventional SMB.

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ing the purity and productivity of the SMB process (e.g., Varicol [3], ModiCon [4], Partial discard [5]) as well as applying SMB for ternary or multicomponent separations (e.g., SMB cascades, five zone SMB, etc.) [6-15]. However, few studies have addressed the separation cost of the SMB process [16-20]. The major costs of SMB separation have been identified as resin, column, pump, the cost for pumping, heating and evaporation to obtain dry product [20]. For processes that use water as eluent (e.g., sugar purification), elution cost does not significantly contribute to the cost of SMB, but for processes using organic solvents, the eluent plays a major role in SMB separation cost [19].

In this study, a modified 4 zone SMB system with two pumps was investigated for binary separation. In comparison to conventional 4 zone SMB equipped with 4 to 5 pumps, a two pump SMB can reduce the cost of SMB installation and operation.

TWO PUMP SMB CONCEPT

The conventional 4 zone SMB configuration is generally composed of four or five 4 or 5 pumps which independently control the flow rates of feed, desorbent, the stream into the column or product ports (i.e., raffinate and extract) and recycle stream. The pumps were operated at constant flow rates during the SMB process (Fig. 1(b)).

The configuration of a 4 zone SMB system composed of two pumps proposed in this study is shown in Fig. 2. In the two-pump SMB system, one pump controls the flow rate of feed and the other controls the flow rate of desorbent stream, respectively. These two pumps are preceded by the rotary valves which can periodically control the direction of flow streams into column zones or product ports. The pumps are also operated at constant flow rates during the SMB separation, but the ratio of stream flows into the column and product ports is controlled by the opening or closing of the valves placed between each column zone and product ports. Thus, the pumps required to control the flow rate of raffinate, extract and recycle streams in conventional SMB are replaced by the valves that can control the direction of corresponding streams in two-pump SMB system. Consequently, all the parameters required for the operation of two-pump SMB, such as the flow rate ratio in each column zone, raffinate, extract and recycle stream are identical to that of conventional SMB system. The operation details of two-pump SMB are explained in the Materials and methods section.

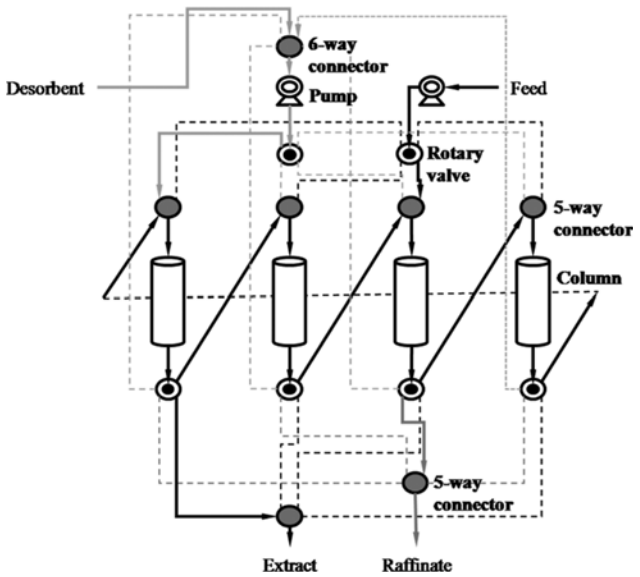

Fig. 2. Schematic configuration of the two-pump SMB.

MATERIALS AND METHODS

1. Materials

L-ribose and L-arabinose were purchased from the Danisco Cultor (Kotka, Finland). Dow 50WX4 (Ca^{2+} form) resins were purchased from Dow Chemical Co. (Midland, MI, USA). The resins were washed with several bed volumes of deionized water before use. The deionized water (DIW) obtained from Milli-Q system (Bedford, MA, USA) and filtered through 0.22 μm filters was used as eluent throughout the study. The jacketed glass column (19.7× 2.5 cm ID) purchased from Diba industries (Danbury, CT, USA) was used as column for sugar adsorption isotherm determination and SMB experiments. Solution of Dow 50WX4 (Ca^{2+} form) resins with DIW was packed in a jacketed glass column by slurry method.

2. Single-step Frontal Analysis

The adsorption isotherm of L-ribose and L-arabinose was determined by single-step frontal analysis [21]. At first, single component of sugar with various concentration (30-120 g/L) applied in column at 50 °CDIW was used as the mobile phase with a flow rate of 1.5 mL/min. Every 1.5 mL of effluent was fractioned and their concentration was determined by HPLC analysis to establish breakthrough curves (Fig. S1, supplementary information). Subsequently, the breakthrough curves of the binary mixture of sugars with various concentration (30-120 g/L) were also determined (Fig. S2, supplementary information). From the breakthrough results, it was shown that the adsorption isotherms of the L-arabinose and L-ribose follow the competitive Langmuir isotherm. The competitive parameters are as follows:

$$q_{L\text{-}ribose} = \frac{1.504 \times C_{L\text{-}ribose}}{1 + C_{L\text{-}arabinose} + 0.00212 \times C_{L\text{-}ribose}} \quad (1)$$

$$q_{L\text{-}arabinose} = \frac{0.563 \times C_{L\text{-}arabinose}}{1 + C_{L\text{-}arabinose} + 0.00212 \times C_{L\text{-}ribose}} \quad (2)$$

where q_i and C_i are concentrations of solute in the solid (resin) and mobile phase, respectively. The isotherms were confirmed by simulation using Aspen Chromatography Ver 7.1. The simulation results agreed well with experimental data (Fig. S3, supplementary information).

The adsorption isotherm constant of L-ribose and L-arabinose was 1.504 and 0.563 L/g, respectively. As a result, in SMB separation L-ribose and L-arabinose will be collected at extract and raffinate port, respectively.

3. Two Pump SMB Design, Simulations and Experiments

Fig. 2 shows the configuration of a 4 zone SMB system composed of two pumps in this study. The SMB system basically consists of four columns, two Valco M Series syringe pumps (CP-DSM2, Valco Instruments Co., Inc.), three rotary valves (EMTMA-CE,

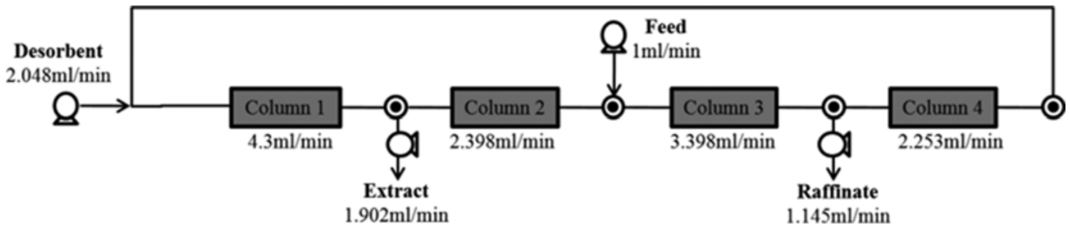

Fig. 3. Zone flow rates in conventional SMB.

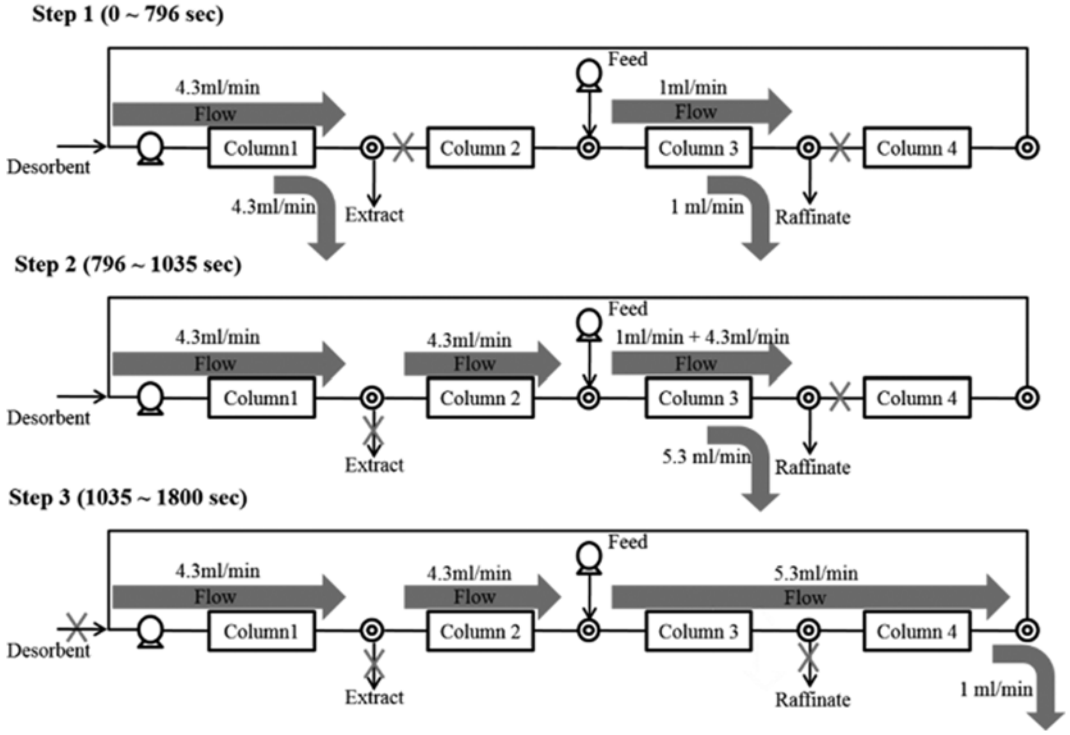

Fig. 4. Zone flow rates and time interval of valve operation in two-pump SMB.

Valco Instruments Co. Inc.) and seven connectors. The samples at extract and raffinate port were collected by two fraction collectors (Foxy 200, Teledyne Isco). The rotary valves have two independent inlet streams and 24 corresponding outlet streams for each inlet; therefore three rotary valves work as six independent valves. Note that the installation cost of the two-pump SMB system used in this study was about 80% of the conventional SMB system consisting of four pumps and two valves.

To set up the operating conditions for a two-pump SMB system, the operating conditions to separate L-ribose and L-arabinose by conventional 4 zone SMB with four pumps were first determined based on the triangle theory. For instance, the flow rates of each zone of conventional SMB during one cycle of switching time (i.e., 30 min) are shown in Fig. 3. Consequently, identical flow rate of column zones and product ports from conventional SMB were applied into two-pump SMB process. The flows were controlled by the opening/closing time of corresponding valves during the SMB operation. Fig. 4 shows the time interval operation of valves in three time steps within one cycle of switching time. In one cycle of switching time, the total flow rate of each column zone and product port is identical to that of conventional SMB process with four pumps. All the simulation of the SMB process was executed with Aspen Chromatography. The parameters used for simulation are shown in Table 1. The total dead volume (less than 3 mL) of a conventional and two-pump SMB was neglected since it is very

Table 1. Process parameters for conventional SMB and two-pump SMB

Process parameters	
Column length (cm)	19.7
Column internal diameter (cm)	2.5
Particle radius (μm)	38
Interparticle porosity (ε_i)	0.47
Mass transfer coefficients (min^{-1})	
L-arabinose	5
L-ribose	10
Liquid viscosity (cP)	0.547
Mass density of eluent (g/cm^3)	0.998

Table 2. Time interval of valve operation in two-pump SMB

Step	Time interval (seconds)					Extract flow	Raffinate flow
	Case 1 (1 time)	Case 2 (2 times)	Case 3 (3 times)	Case 4 (6 times)	Case 5 (30 times)		
1	0-796	0-398, 900-1298	0-265.3, …, 1200-1465.3	0-132.7, …, 1500-1632.7	0-26.5, …, 1740-1766.5	Open 4.3 mL/min	Open 1 mL/min
2	796-1035	398-517.5, 1298-1417.5	265.3-345, …, 1465.3-1545	132.7-172.5, …, 1632.7-1672.5	26.5-34.5, …, 1766.5-1774.5	Close 0 mL/min	Open 1 mL/min
3	1035-1800	517.5-900, 1417.5-1800	345-600, …, 1545-1800	172.5-300, …, 1672.5-1800	34.5-60, …, 1774.5-1800	Close 0 mL/min	Close 0 mL/min
Average flow-rate						1.902 mL/min	1.145 mL/min

small compared to that of the column volume (ca. 400 mL).

4. Analytical Methods

The concentrations of L-ribose and L-arabinose were analyzed by HPLC system (LC-10AD, Shimadzu, Japan) equipped with Shodex SUGAR SP0810 (8.0×300 mm) column and refractive index detector (RID-10A, Shimadzu, Japan). DIW was used as mobile phase at flow rate of 1.5 mL/min. The analysis was performed at 85 °C.

RESULTS AND DISCUSSION

1. Simulation Studies

For the operation of two-pump SMB, it is required to maintain identical flow rate in column zones and product ports as in conventional SMB. This can be done by the appropriate operation of the valves placed between column zones and ports within a cycle of switching time. Table 2 shows several cases where different time intervals for valve operation to maintain the flow rates in extract and raffinate port were investigated. In case 1, for example, the valve at extract port was opened for the first 796 seconds and closed for the rest of the 1,004 seconds, while the valve at raffinate port was opened for the first 1,035 seconds and closed for the rest of the 765 seconds during one cycle of switching time of 30 min (Fig. 4). The effective valve operation frequency was investigated by reducing the time interval of valve operation to one-half, one-third, one-sixth, and one-thirtieth of that in case 1 during one cycle of switching time as shown in case 2 to case 5, respectively (Table 2).

The simulation results regarding the column internal profiles and purity, yields and enrichment of L-ribose and L-arabinose obtained by two-pump SMB at different time intervals of valve operation were compared with those produced by conventional SMB as shown in Fig. 5 and Table 3. In conventional SMB, clear separation of L-ribose and L-arabinose in the extract and raffinate zone was observed. However, in two-pump SMB, a tailing of L-ribose was observed in the raffinate (L-arabinose) zone. In addition, the peak tailing increased as the time interval of valve operation decreased. As a result, the purity and yield of L-arabinose decreased with decreasing time interval of valve operation accordingly. Moreover, a fronting peak of L-arabinose in the extract (L-ribose) zone was also observed (Fig. 5). Therefore, the performance of two pump SMB was slightly decreased as compared with conventional SMB. This can be explained by the different flow rates in the column zone of a two pump SMB compared to that of conventional SMB, which affects the performance of columns due to mass transfer and axial dispersion as depicted by the van Deemter equation [22]. The results

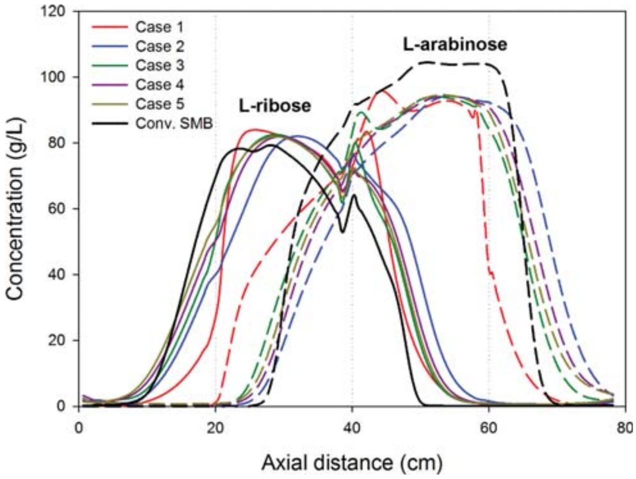

Fig. 5. Internal profile of L-ribose and L-arabinose in two-pump SMB.

Table 3. Simulation results of conventional SMB and two-pump SMB

Parameters	Extract (L-ribose)						Raffinate (L-arabinose)					
	Conventional SMB	Two-pump SMB					Conventional SMB	Two-pump SMB				
		Case 1	Case 2	Case 3	Case 4	Case 5		Case 1	Case 2	Case 3	Case 4	Case 5
Purity (%)	99.99	95.10	94.76	94.04	93.79	94.16	99.93	99.18	97.42	96.52	95.78	94.99
Yield (%)	99.89	99.52	97.66	96.73	95.97	95.06	99.99	93.60	94.25	93.63	93.51	94.34
Enrichment (%)	53.30	54.82	53.29	52.55	52.44	50.73	88.29	71.38	77.94	79.49	81.34	83.34

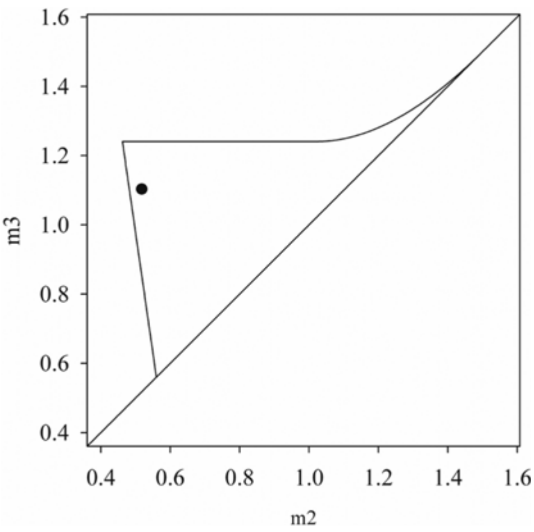

Fig. 6. Operating point of two-pump SMB in triangle theory separation region.

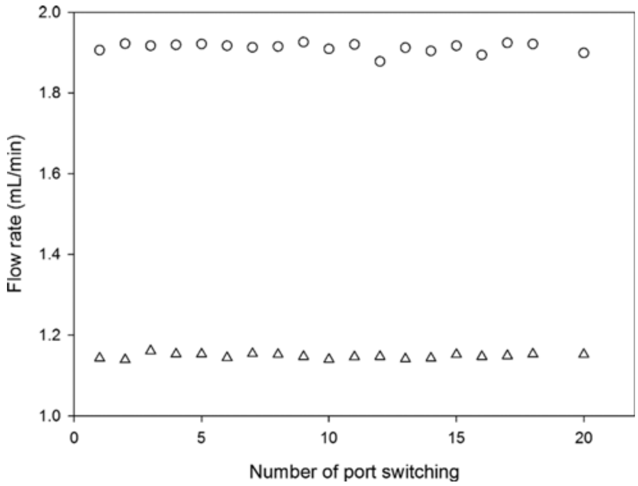

Fig. 7. Flow rate history of extract and raffinate in two-pump SMB.

indicated that a constant stream flow through column zones and product ports is favorable for SMB separation. Among the different case operations in two-pump SMB, case 1 where the valves in extract and raffinate port were switched only one time within one cycle of switching time was similar to that of conventional SMB. Therefore, operation condition in case 1 was selected to carry out a two-pump SMB experiment.

2. SMB Experiments

SMB experiments were carried out to validate the performance of two-pump SMB system. The SMB experiments were carried out for five cycles including 20 switching steps with the feed solution containing 95.03 and 95.66 g/L of L-arabinose and L-ribose, respectively.

In SMB operation, the optimal operating condition is at the vertex point of triangle theory. However, SMB operation at the vertex point is unstable due to axial dispersion and mass transfer effect. Therefore, in this experiment, the operating point was selected at a point about 22% down from the vertex point in triangle (safety margin of 22%) to guarantee robust operation of the SMB process (Fig. 6). This point was biased toward the pure raffinate region in order to improve the purity of L-arabinose.

The ability of the SMB system composed of two pumps to provide stable flow to each column zones and product ports was examined by measuring the flow obtained at extract and raffinate port. The exact flow rate was calculated by dividing the volume by the switching time. The results show that two-pump SMB system was able to produce enough flow rates required for extract and raffinate port (Fig. 7). Therefore, any operating points in the triangle diagram might show similar separation results between two SMB systems (Fig. S4 and Table S1, supplementary information).

The experimental history profile of two-pump SMB was comparable to that of simulation (Fig. 8). It was observed that L-arabinose was slightly contaminated in the extract port in two-pump SMB system by simulation. This result was in agreement with the fronting phenomenon of L-arabinose in the extract zone (Fig. 5). However, higher purity of L-ribose obtained in the extract port by

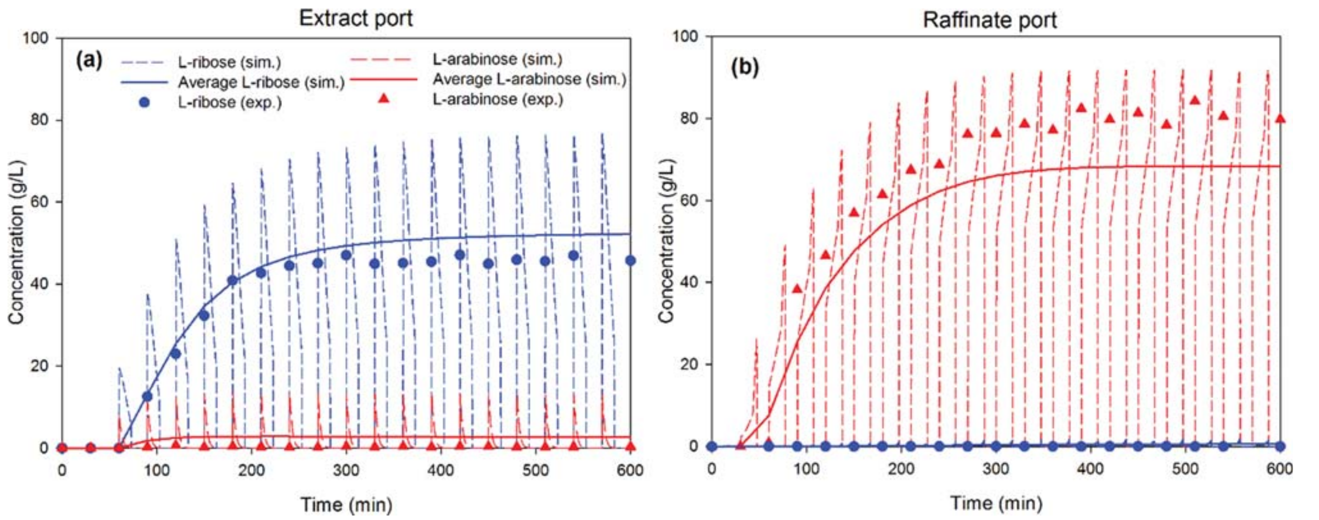

Fig. 8. History profile of extract (a) and raffinate in two-pump SMB (b).

Table 4. Experimental separation of L-ribose and L-arabinose by conventional and two-pump SMB

Parameter	L-ribose				L-arabinose			
	Conventional SMB		Two-pumps SMB		Conventional SMB		Two-pumps SMB	
	Sim.	Exp.	Sim.	Exp.	Sim.	Exp.	Sim.	Exp.
Purity (%)	99.99	98.94	96.37	99.38	99.93	99.82	99.24	99.98
Yield (%)	99.89	99.61	99.44	99.97	99.99	98.95	93.81	99.65
Enrichment (%)	53.30	53.27	54.77	46.33	88.29	85.78	71.37	80.74

Experiments and simulation were carried out with feed solution containing 95.03 and 95.66 g/L of L-arabinose and L-ribose, respectively. Process parameters were obtained with safety margin of 22% from the vertex point of triangle theory. The flow rates for column zones and product ports were obtained in Fig. 3

the two-pump SMB experiment compared to that of simulation indicated that L-arabinose was experimentally less contaminated in the extract port. This can be explained by that the mass transfer coefficient used in simulation was not able to predict exactly the results of experiments. Nevertheless, the purity, yield and enrichment of sugar obtained by two-pump SMB were comparable to those obtained by conventional SMB (Table 4).

CONCLUSIONS

Two-pump SMB system was developed by replacing the pumps that control the flow at raffinate and extract ports in conventional SMB with rotary valves. By appropriate operation of valves at these ports, it is possible to control the total flow rates at column zones and product ports identical to those in conventional SMB. Simulation and experimental studies showed that constant flow rates in each column zones and product ports required for robust SMB operation can be accomplished by selecting operating conditions relevant to an appropriate point inside the triangle shown in triangle theory and minimizing the frequency of valves opening/closing within one cycle of switching time. As a result, the purity, yield and enrichment of products obtained by two-pump SMB were comparable with those of conventional SMB. Moreover, separation cost with two-pump SMB would be more economical by reducing the installation and pump operating cost. The applicability of two-pump SMB system for the separation of other binary and ternary mixtures is undergoing study for full evaluation.

ACKNOWLEDGEMENTS

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SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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Supporting Information

Modified simulated moving bed chromatography with two pumps for sugar separation

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Table S1. Simulation results in conventional SMB and 2-pumps SMB at 2% safety margin

Parameter	Extract		Raffinate	
	Conventional	2-Pump	Conventional	2-Pump
Purity (%)	97.77	97.77	99.90	94.36
Yield (%)	97.68	93.82	98.43	96.32
Enrichment (%)	65.02	63.09	96.60	83.00

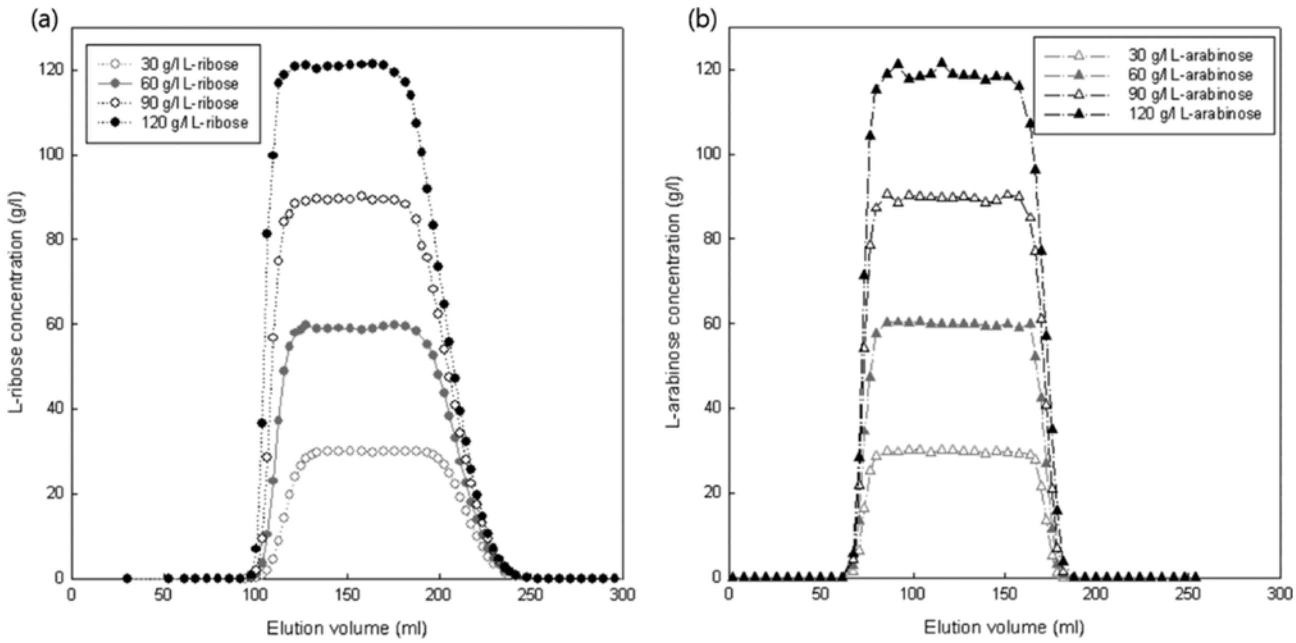

Fig. S1. Single-step frontal analysis of L-ribose (a) and L-arabinose (b).

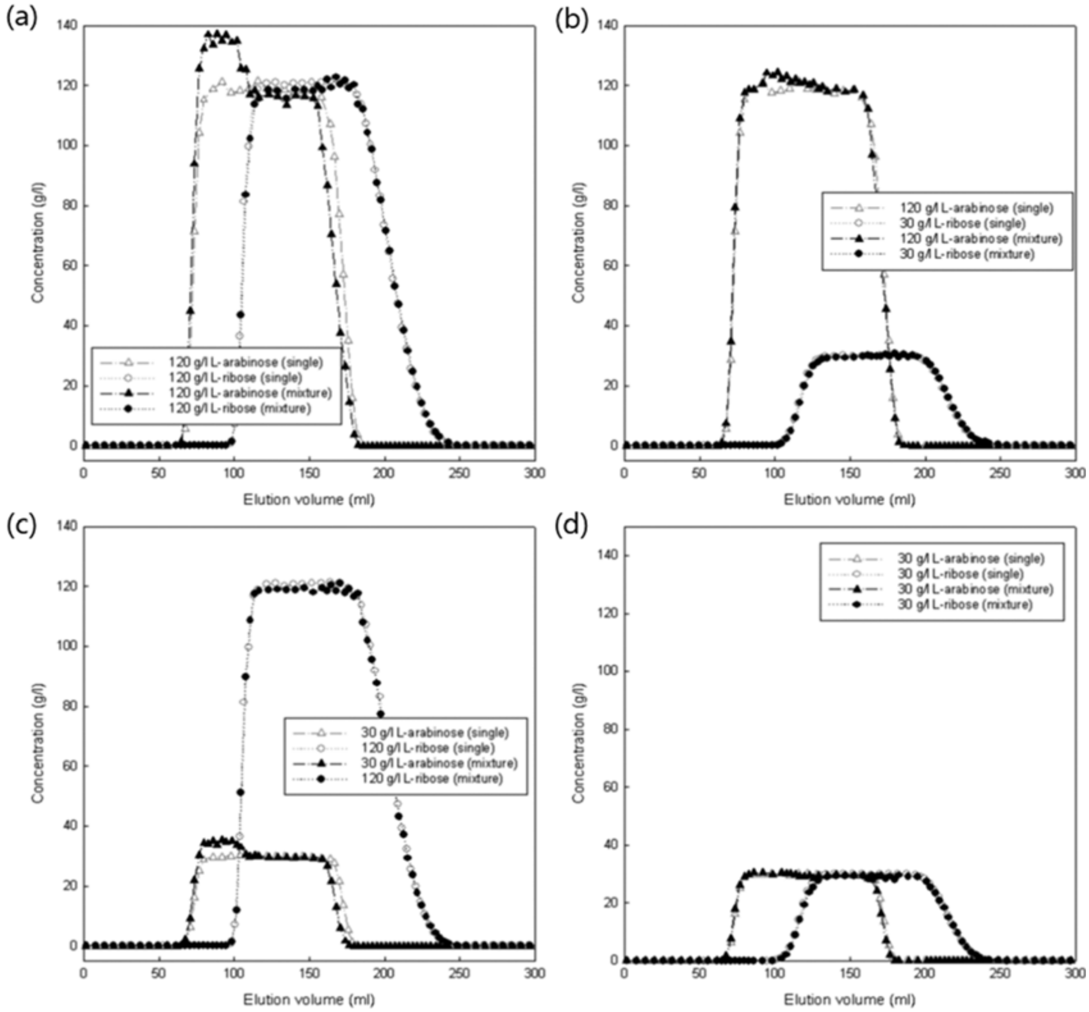

Fig. S2. Competitive interaction of L-sugars on Dow 50WX4-400 mesh. (a): 120 g/*l* L-ribose and 120 g/*l* L-arabinose, (b): 30 g/*l* L-ribose and 120 g/*l* L-arabinose, (c): 120 g/*l* L-ribose and 30 g/*l* L-arabinose, and (d): 30 g/*l* L-ribose and 30 g/*l* L-arabinose.

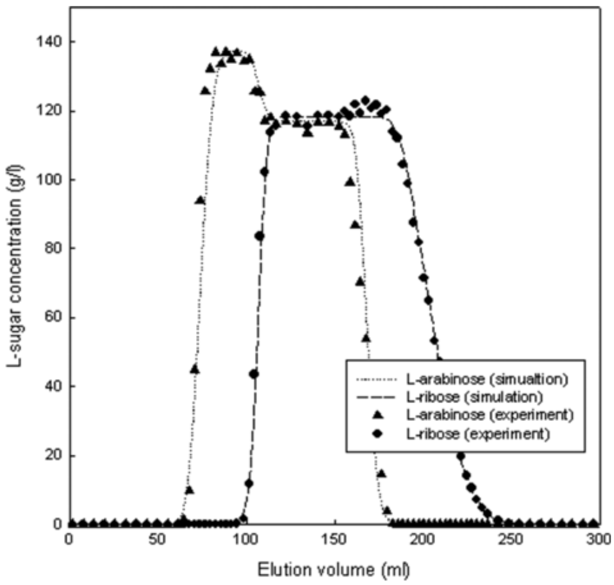

Fig. S3. Isotherm confirmation of sugars mixture by experiment and simulation. The sugar concentration was of 120 g/*l*.

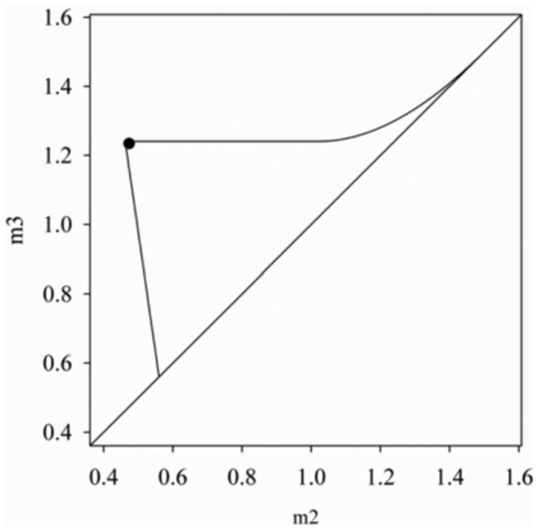

Fig. S4. Operating point with 2% safety margin in conventional SMB and two-pump SMB.