

# COMPARISONS OF RECYCLE CHROMATOGRAPHY AND SIMULATED MOVING BED FOR PSEUDO-BINARY SEPARATIONS

*Ju Weon Lee, Purdue University, West Lafayette, IN*  
*Phillip C. Wankat, Purdue University, West Lafayette, IN*

## Abstract

The simulated moving bed (SMB) process has been extensively used in industrial separations for binary and pseudo-binary separations. In pseudo-binary mixtures because the desired component is the most or least retained, the other components do not have to be separated. The UOP *Parex* process for *p*-xylene purification is an example. When non-target components have similar adsorption behaviors, the SMB has higher productivity and requires less desorbent compared to batch chromatography. However, these advantages are dependent on the difference of adsorption behaviors of the non-target components. When the most retained component is the target, productivity and desorbent consumption is related to the retention behaviors of the most and least retained non-target components, respectively.

In this research, the performance of batch chromatography with a single recycle stream is compared to a SMB process for pseudo-binary separations with competitive Langmuir isotherms. A ternary nucleoside separation was used as a model system for the simulation of batch and SMB processes. To determine the optimized operating condition of the SMB process, a multi-component hodograph transformation was numerically calculated to obtain the separation region in the  $m_{II}$ - $m_{III}$  plane and the regeneration region in the  $m_I$ - $m_{IV}$  plane. To compare the performances of SMB and recycle batch chromatography, each process was simulated with the optimized operating conditions with detailed Aspen Chromatography simulations.

## Introduction

SMB processes are commonly used for binary separations, such as chiral separations [1, 2]. It is well known that the SMB process is more efficient than batch chromatographic separations in terms of desorbent consumption and productivity [3]. Single-loop SMB processes have been extensively used for pseudo-binary separations. When non-target products have very similar adsorption behaviors, such as in the *Parex* process [4], it can be handled as a binary mixture. However, the advantages and disadvantages of SMB processes compared to batch chromatographic processes have not been extensively studied for pseudo-binary mixtures with a wide range of adsorption behaviors.

In this work, batch chromatography with a single recycle stream and 4-zone SMB processes are compared for pseudo-binary separations with different selectivities. Four nucleosides, 2'-deoxycytidine (dC), 2'-deoxyguanosine (dG), 2'-deoxythymidine (dT), and 2'-deoxyadenosine (dA), were studied as solutes with feed concentrations in the range of competitive Langmuir isotherms [7].

## Recycle Chromatography

In recycle chromatography, a single column can be used to separate pseudo-binary mixtures [5]. Fig. 1 shows a schematic illustration of recycle chromatography with one recycle stream. For separation of the most retained solute (C), pure component (A) mixed in desorbent can be recycled to help elute the other undesired component (B) and thus reduce the desorbent to feed ratio D/F. The recycle is timed so that A and B exit together (A/B). Therefore, there are three different streams leaving the column: *recycle*, *waste*, and *product*.

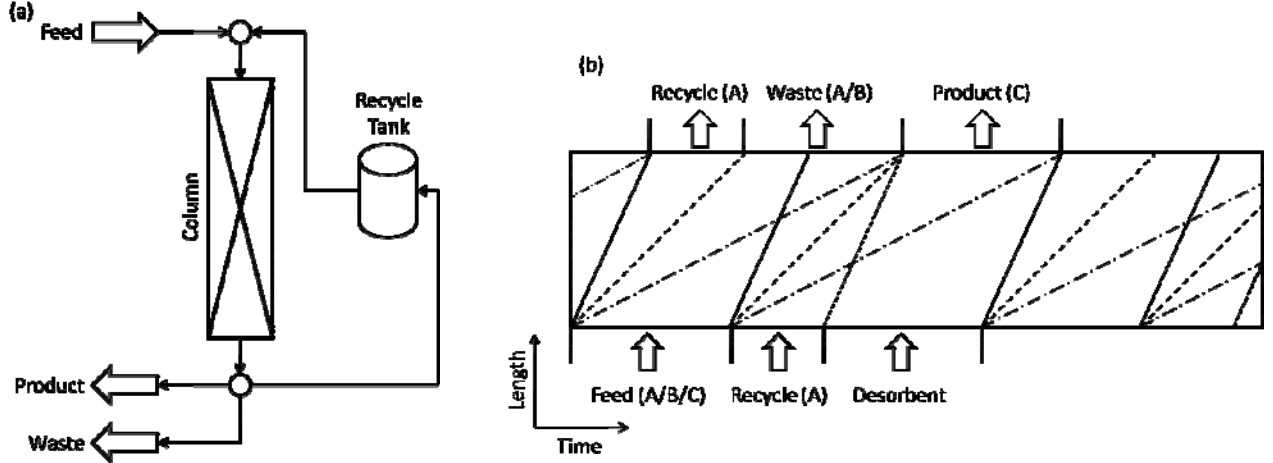


Fig. 1. Schematic illustration of recycle chromatography. (a) Flow diagram and (b) Migration traces of solute in the column.

The operating conditions of recycle chromatography are dependent on the elution bandwidth of each component. Changing the cut point will change the purity and yield. To determine the front and rear ends of elution band, cut points at 0.5% of peak height were used. By changing the flow-rate of the mobile phase, productivity and D/F of batch chromatography were varied. Recycle chromatography and SMB processes were compared at the optimized flow-rate which has maximum productivity and minimum D/F.

## SMB Process

Equivalent 4-zone SMB processes composed of 4 and 8 columns, which had the same total bed height as recycle chromatography, were studied. The operating points for  $m_{II}$  and  $m_{III}$  were chosen based on the even velocity trace which is obtained by the following forms [6]:

$$\frac{m_{II} - (\Delta q_{R,II} / \Delta c_{R,II})_{Max}}{\varepsilon_T + (1 - \varepsilon_T)(\Delta q_{R,II} / \Delta c_{R,II})_{Max}} + \frac{m_{III} - (\Delta q_{E,III} / \Delta c_{E,III})_{Min}}{\varepsilon_T + (1 - \varepsilon_T)(\Delta q_{E,III} / \Delta c_{E,III})_{Min}} = 0 \quad (1)$$

$$m_j = \frac{Q_j - \varepsilon_p Q_s}{(1 - \varepsilon_p) Q_s} \quad (2)$$

where  $m_{II}$  and  $m_{III}$  are, respectively, the flow-rate ratios of the liquid phase and the solid phase in zone II and III,  $c_{ij}$  and  $q_{ij}$  are, respectively, the concentrations of solute  $i$  in the mobile phase and the stationary phase of zone  $j$ ,  $\varepsilon_T$  is the total void fraction of the column,  $\varepsilon_p$  is the interparticle void fraction,  $Q_j$  is the

volumetric flow-rate of the liquid phase in zone  $j$ , and  $Q_S$  is the volumetric flow-rate of the solid phase, and solutes  $E$  and  $R$  represent the least retained component in the extract stream and the most retained component in the raffinate stream, respectively. The purity and yield of extract and raffinate streams are decided by the separation in zone II and III and the regeneration in zone I and IV. The maximum value of  $m_{III} - m_{II}$  was investigated with the same or higher purity and yield of target component as in recycle chromatography. With this value of  $m_{III} - m_{II}$ , the optimum  $m_I$  and  $m_{IV}$  values were obtained when SMB process had the same purity and yield as recycle chromatography.

## Results and Discussion

Three solute mixtures were selected for study of pseudo-binary separations (Table 1). For the most retained solute separation, dA was the target solute and the solute systems were dC/dT/dA, dG/dT/dA, and dC/dG/dA. The selectivities of (intermediate retained/least retained) and (most retained/intermediate retained) are 3.05/2.89, 1.30/2.89, and 2.35/3.74, respectively. The concentration of each component in the feed was fixed as 5.0 g/L.

Table 1. Isotherm parameters and kinetic coefficients of nucleosides [7].

Component	$a_i$ [-]	$b_i$ [L/g]	$a_p k_i$ [1/min]	$D_{e,i}$ [cm <sup>2</sup> /min]	$\alpha_{i-Ref.}$ = $a_i/a_{dC}$
dA	27.7	0.1	6	0.225	8.79
dT	9.60	0.1	30	0.225	3.05
dG	7.40	0.1	30	0.225	2.35
dC	3.15	0.1	60	0.225	1.00

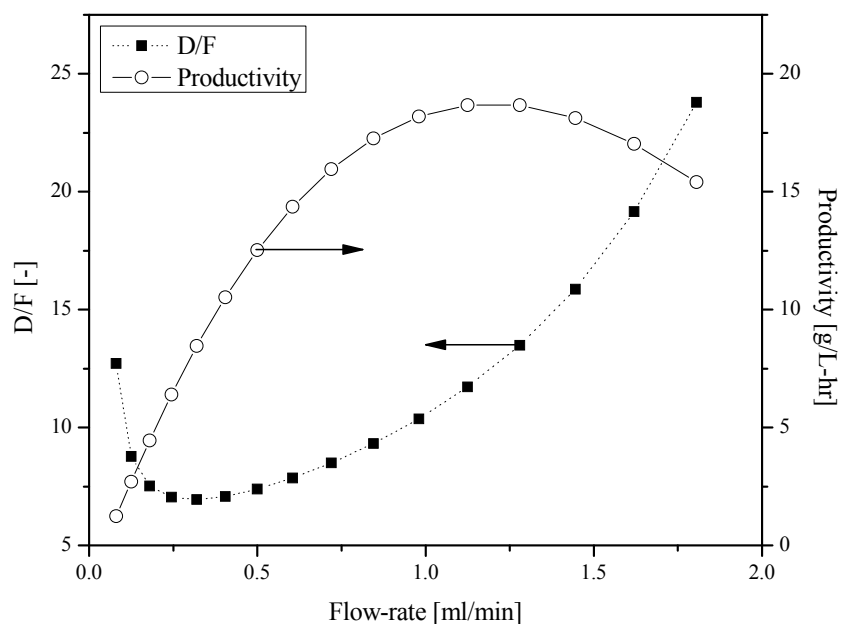


Fig. 2. Changes of D/F and productivity as a function of mobile phase flow-rate in recycle chromatography. Solute is dC/dT/dA and dA is target. Purity and yield of dA  $\geq 0.999$

In recycle chromatography, D/F and productivity depend on the mobile phase flow-rate because the efficiency, represented by HETP, depends on the flow-rate of the mobile phase. The apparent dispersion increases when the flow-rate increases. For constant purity, D/F and productivity have minimum and maximum values, respectively (Fig. 2). Table 2 shows the simulation results and the mobile phase flow-rates for the maximum productivity and the minimum D/F in recycle chromatography.

Table 2. Simulation results and mobile phase flow-rates for maximum productivity and minimum D/F in recycle chromatography to separate the most retained solute.

	Solutes	Conc. [g/L]	Flow-rate [ml/min]	D/F [-]	P* [g/L-hr]	$\Delta P^{**}$ [bar]	Purity [%]	Yield [%]
Max. P*	dC/dT/dA	5/5/5	1.196	12.493	18.744	4.500	99.896	99.933
	dG/dT/dA	5/5/5	1.232	13.794	18.685	4.633	99.936	99.883
	dC/dG/dA	5/5/5	1.677	11.678	29.035	6.307	99.927	99.915
Min. D/F	dC/dT/dA	5/5/5	0.308	6.942	8.147	1.159	99.936	99.961
	dG/dT/dA	5/5/5	0.308	7.620	8.016	1.158	99.942	99.932
	dC/dG/dA	5/5/5	0.307	5.568	10.032	1.156	99.956	99.967

\*Productivity, \*\* Pressure drop

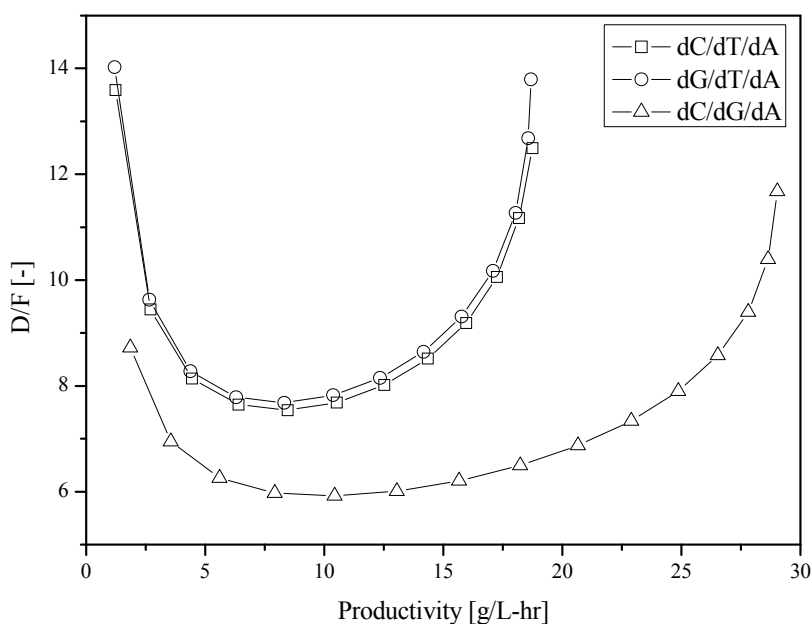


Fig. 3. Relationship between D/F and productivity in recycle chromatography to separate the most retained solute dA.

Figure 3 shows the relationship between D/F and productivity in recycle chromatography. The dC/dT/dA and dG/dT/dA systems show similar tendencies. Partially separated least retained solute (dC or dG) were recycled to be contained in the elution band of intermediate retained solute. There are only two outlet bands; one assigned for *waste* is the elution band which contains the least and intermediate

retained solutes. The other assigned for *product* is the elution band of the most retained solute. Therefore,  $D/F$  and productivity are strongly related to the separation of the most and intermediate retained solutes which are the same in the  $dC/dT/dA$  and  $dG/dT/dA$  systems. Figure 4 compares recycle chromatography and a 4-zone, 4-column SMB. For these three ternary mixtures,  $D/F$  of the 4-column SMB process is larger than recycle chromatography over the entire range of productivity. The maximum productivities of SMB process are also smaller than recycle chromatography. We will also show results for 8-column SMB systems that have a lower  $D/F$  than recycle chromatography for identical purities.

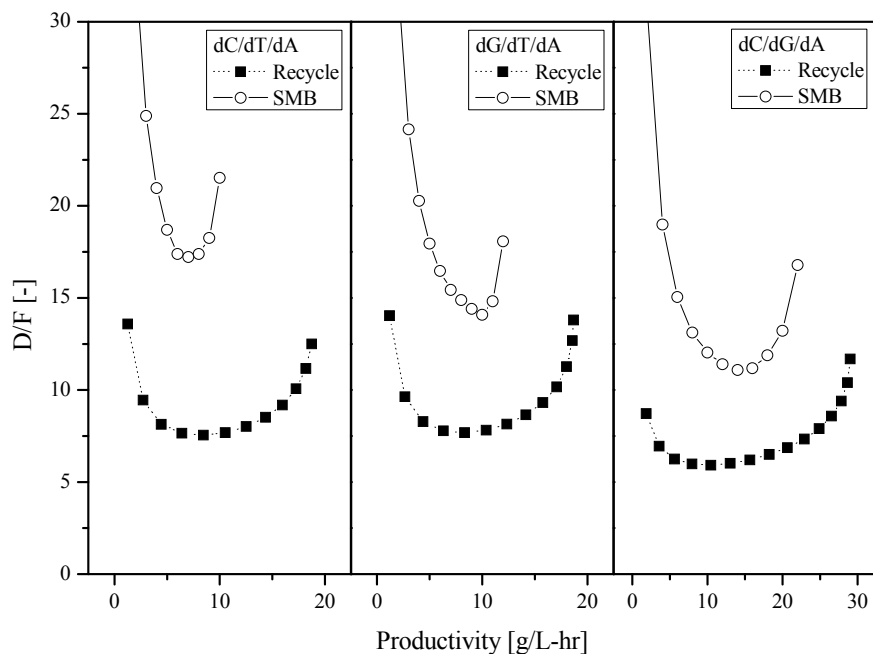


Fig. 4. Comparisons of  $D/F$  and productivity for recycle chromatography and 4-zone, 4-column SMB to separate the most retained solute.

## Conclusions

Recycle chromatography and 4-column SMB processes were compared for pseudo-binary separations when the most retained solute is desired. While the selectivity of non-target products is varied from 1.30 to 3.05, the performance of recycle chromatography is better than a 4-column SMB in terms of productivity and  $D/F$ . With 8 columns the performance of the SMB system was better than the performance of recycle chromatography.

## References

1. Pais, S.L., M.J. Loureiro, and A.E. Rodrigues (1997), "Separation of 1,1'-bi-2-naphthol Enantiomers by Continuous Chromatography in Simulated Moving Bed", *Chem. Eng. Sci.*, 52, pp. 245-257.
2. Francotte, E., P. Richert, M. Mazzotti, and M. Morbidelli (1998), "Simulated Moving Bed Chromatographic Resolution of a Chiral Antitussive", *J. Chromatogr. A*, 796, pp. 239-248.
3. Strube, J., S. Haumreisser, H. Schmidt-Traub, M. Schulte, and R. Ditz (1998), "Comparison of Batch Elution and Continuous Simulated Moving Bed Chromatography", *Org. Process Res. Dev.*, 2, pp. 305-319.
4. Broughton, D.B., R.W. Neuzil, J.M. Pharis, and C.S. Brearley (1970), "The Parex Process for Recovering Paraxylene", *Chem. Eng. Prog.*, 66, pp. 70.
5. Lee, J.W and P.C. Wankat (2008), "Optimized Design of Recycle Chromatography for Separation of a Single Component from a Ternary Mixture", *Ind. Eng. Chem. Res.*, *in press*.
6. Migliorini, C., M. Mazzotti, and M. Morbidelli (2000), "Design of Simulated Moving Bed Multicomponent Separations: Langmuir Systems", *Sep. Purif. Technol.*, 20, pp. 79-96.
7. Paredes, G., S. Abel, M. Mazzotti, M. Morbidelli, and J. Stadler (2004), "Analysis of a Simulated Moving Bed Operation for Three-Fraction Separations (3F-SMB)", *Ind. Eng. Chem. Res.*, 43, pp. 6157-6167.