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Flushing Flow Rates Analysis in Eight-Zone SMB Process for *p*-Xylene Separation

Pradana S. Sutanto[1], Young-il Lim[1]*, Jinsuk Lee[2]

[1]Department of Chemical Engineering, Hankyong National University, Anseong, 456-749, Korea, limyi@hknu.ac.kr
[2]SamsungTotal, Chungnam Seosan-si Daesan-up Dokgod-ri 411-1, 356-711, Korea.

The eight zone *p*-xylene (PX) simulated moving bed (SMB) utilizes three flushing sequences to prevent purity and recovery deterioration caused by transfer lines (or bed-lines) connecting rotary valve to adsorption beds. The application of flushing sequences makes the analysis and operation of this process more difficult and they rely on operation experience. In this study, effects of the flushing flow rates on SMB performance were investigated by sensitivity analysis at various axial dispersion intensities of dead volume. The concentration dynamics inside dead volume were solved by the method of characteristic (MOC). This study indicates that the flushing flow rates must be tuned properly in order to maximize PX recovery within desired purity.

Keywords: Simulated Moving Bed (SMB), Para-Xylene (PX), Dead Volume, Flushing, Sensitivity Analysis.

1. Introduction

Para-xylene (PX) is the most widely used of xylene isomers in petrochemical industries. PX is used as a raw material for terephthalic acid, which is used in the production of polyethylene terephthalate (PET) and polyester fibers (Beck and Haag, 1997). The demand of PX increases rapidly with 6% of average annual growth rate for the next decade. PX and other xylene isomers and ethylbenzene (EB) are produced from catalytic reformate, pyrolysis gasoline, or toluene disproportionation. Because of the close boiling point between PX and xylene isomers, the conventional distillation cannot be practically used for PX purification. Consequently, PX is separated via solvent extraction, crystallization, adsorption, and hybrid crystallization/ adsorption based processes (Minceva and Rodrigues, 2002). In 1960s, UOP developed Parex Simulated Moving Bed (SMB) adsorption process which has emerged as a superior technology for PX separation (Broughton and Gerhold, 1961). Nowadays, about 60% of PX worldwide is produced by SMB technology, such as UOP's Parex, Toray's Aromax, and IFP's Eluxyl (Minceva and Rodrigues, 2003).

SMB is a continuous counter-current multicolumn chromatographic process, which has been successfully commercialized in petrochemicals, sugars, pharmaceuticals, bio-molecules, and chiral separations (Rajendran et al., 2009). SMB utilizes the advantage of high driving force because of counter-current flow to achieve low solvent consumption, small apparatus size, low investment cost, and high yield (Azevedo, 2001). SMB was developed to overcome solid circulation problem in True Moving Bed

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(TMB), where liquid and solid flow in opposite direction (Pais et al., 1998), using a flow scheme that stimulates the continuous counter-current flow of adsorbent without actually moving it (Azevedo, 2001). This is achieved by holding the adsorbent as stationary phase while periodically moving the ports of introduction and withdrawal of liquids simultaneously to one column ahead (Azevedo, 2001). The ports divide the fixed beds of SMB into several zones, such as in conventional SMB which is divided into 4 zones by the inlet ports (desorbent and feed) and the outlet ports (extract and raffinate) (Lee et al., 2010).

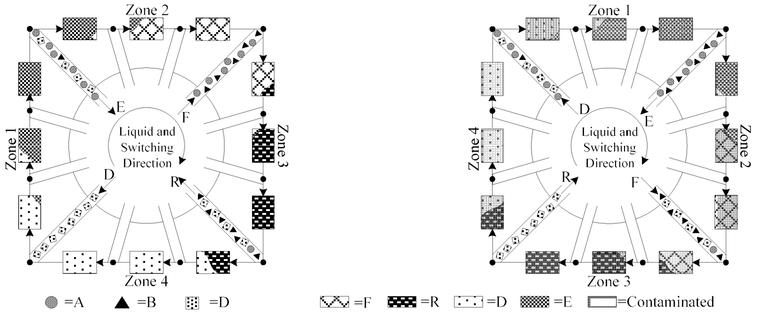
In the Parex SMB, each transfer line (or bed line) connecting rotary valve to adsorbent beds is shared for introduction and withdrawal of process streams. As a result, the bed line will be contaminated by the residue of other stream unless an appropriate action is taken (Minceva and Rodrigues, 2003). To overcome this problem, Parex unit uses internal and external line flushing sequences added to conventional four-zone SMB port switching, which increases the total number of SMB zones to seven or eight (Broughton and Gerhold, 1961). The dead volumes (i.e. extra-column dead volume and bed line) have to be properly taken into account in this practical application (Lim et al., 2010). Increasing the number of SMB zones makes the analysis and operation of the seven or eight-zone Parex process much difficult and they only rely on operation experience (Lee et al., 2010, Lim et al., 2010).

The dead volume (i.e., extra-column dead volume and bed-line) has to be properly taken into account in practical operations. Katsuo et al. (2009) performed the effect of extra-column dead volume on SMB using the frame of Triangle Theory. Migliorini et al. (1999) assessed the effect of the dead volume between column beds in lab-scale SMB. Grosfils (2009) classified the dead volumes into moving and fixed parts, i.e. bed head and bed tail as the moving parts and bed lines as the fixed parts. However, few studies have been addressed to the presence of the flushing streams for solving dead volume problems in the bed lines. Minceva and Rodrigures (2003) developed the model for the bed lines dead volume and flushing stream in the 7-zone Parex unit (Minceva and Rodrigues, 2003). Lim et al. (2010) examined the comparison between 7-zone and the 8-zone Parex performance. There remains a need for detail analysis to find optimal flushing flow rates and operational guidelines in a commercial Parex plant.

The present paper performs the sensitivity analysis for flushing flow rates at the 8-zone Parex unit. The effect of diffusion inside dead volume on flushing flow rates is also investigated. Dead volume including bed head (BH), bed tail (BT), and bed line (BL) is treated within the framework of an extended node model with a method of characteristics (MOC), while an explicit time-space conservation element and solution element (CESE) was used to solve the LDF adsorptive bed model. This study shows that flushing flow rates must be properly adjusted to maximize Parex recovery within desired purity.

2. SMB Process Description

The Parex process separates PX form its C_8 aromatic isomers using p-diethylbenzene (PDEB) as desorbent. Mono or dual metal ion exchanged Y or X zeolite is used as adsorbent (Minceva and Rodrigues, 2002). The Parex process is designed to recover more than 97 wt% of the PX from feed with minimum extract purity of 99.7 wt%.



a) Configuration at the last of 1^{st} shifting *b) Configuration at the beginning of 4^{th} shifting*

Figure 1: Schematic diagram of four-zone SMB unit (A: strong adsorbed component, B: less adsorbed component, D: desorbent, E: extract, F: feed, R: raffinate)

Conventional 4-zone SMB with bed-lines connecting the rotary value to adsorption beds is shown in Figure 1a. Zone 1 regenerates the adsorbent by desorption of strong adsorbed component. Zone 2 desorbs less strong adsorbed components and prevents these components to reach the extract port. Zone 3 adsorbs strong adsorbed components and prevents these components to exit through raffinate port. Zone 4 cleans the desorbent by adsorption of less strong component (Azevedo, 2001). Figure 1b shows the contamination of the bed-lines that occurs at conventional 4-zone SMB, which implies the requirement for a flushing system on SMB (Minceva and Rodrigues, 2003).

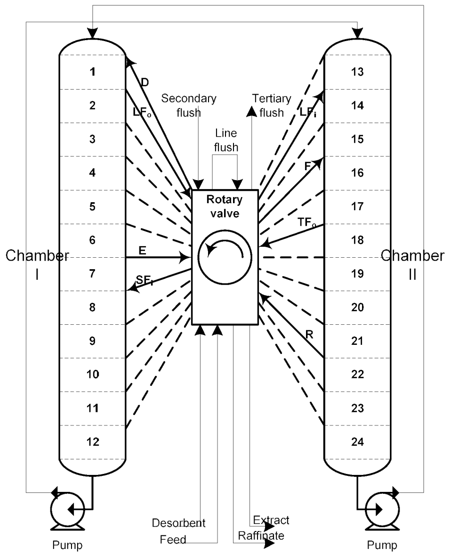


Figure 2: Schematic diagram of 8-zone PX SMB process (LF_o: line flush outlet, E: extract, SF_i: secondary flush inlet, LF_i: line flush inlet, F: feed, TF_o: tertiary flush outlet, R: raffinate).

Application of a flushing system to the Parex unit increases the number of SMB zones into eight. Figure 2 shows a typical 8-zone Parex unit with 24 adsorption beds and 24 bed-lines connecting the rotary valve to the beds. The rotary valve shifts the injection and withdrawal points in SMB operation by one-bed. The pump provides liquid circulation from the bottom of a chamber to the top of another chamber. Usually, extract and raffinate streams come out from the SMB unit with high desorbent content, which is separated in distillation columns later. The 8-zone SMB applies 3 flushing sequences i.e. line flush flows (LF), secondary flush-inlet flow (SF_i), and tertiary flush-outlet flow (TF_o) (Lim et al., 2010). The location of LF, SF_i, and TF_o ports is designed in such a way to give best performance by utilizing the mediums which would not affect extract purity (Minceva and Rodrigues, 2003).

The LF and SF_i sequences are applied to prevent extract contamination by xylene isomers residue from the feed stream. LF consists of a line flush-outlet flow (LF_o) and a line flush-inlet flow (LF_i), which utilizes internal SMB liquid medium to push the trapped feed into the unit. The LF_i stream trapped inside the bed line, which contains mainly PX and desorbent, is flushed into the unit by the SF_i to ensure no contamination in the extract line. PX can be used as a SF_i medium, but desorbent is usually used for the sake of process economics. A drain-out flow of TF_o, which has more PX than the raffinate stream, is preferably used to make the initial bed-line composition of feed similar to the fresh feed composition. Therefore, the 8-zone SMB is designed and operated to increase recovery and extract purity in the industrial-scale unit.

Table 1: Simulation parameters for 8-zone p-xylene SMB process

Design parameters			
bed configuration	1-5-1-6-2-2-4-3	ε_b	0.39
L_c (m)	1.1	L_{BH} (m)	0.02 for each bed-head
d_c (m)	4.1	L_{BT} (m)	0 0 0 0 0 0 0 0 0 0 0 0.12 0 0 0 0 0 0 0 0 0 0 0 0.12
ρ_p (kg/m^3)	1390	V_{BL} (m^3)	0.145 for each bed-line
Operating parameters			
Q_D (m^3/min)	2.89	Components (5)	PX (product), MX, OX, EB, PDEB (desorbent)
Q_{LFo} (m^3/min)	0.1668 (varying from 0.02-0.3)	C_F (kg/m^3)	171, 360, 92, 101, 0
Q_E (m^3/min)	1.8	C_D (kg/m^3)	0, 0, 0, 0, 724
Q_{SFi} (m^3/min)	0.145 (varying from 0.02-0.3)	C_{SFi} (kg/m^3)	0, 0, 0, 0, 724
Q_{LFi} (m^3/min)	0.1668 (varying from 0.02-0.3)	τ (min)	1.15
Q_F (m^3/min)	1.45	N_{switch}	480 (20 cycles)
Q_{TFo} (m^3/min)	0.13 (varying from 0.02-0.17)		
Q_R (m^3/min)	2.5545 (varying from 2.54-2.67)		
$Q_{recycle}$ (m^3/min)	5.39		
Model parameters			
D_{ax} (m^2/min)	$1.0\times10^{-3}v_L$	Pe	1100
$D_{ax,dead}$ (m^2/min)	$(1, 2, 3, 4, \text{or } 5)\times10^{-3}v_L$	Pe_{dead}	1100, 550, 367, 275, or 220
k_i (min^{-1})	2.0 for each component		
a_i (-)	316 68 56 91 317	b_i (m^3/kg)	1.07 0.23 0.19 0.31 1.29
Computational parameters			
N_{mesh}	20	N_{time}	60
Δz (m)	0.058	Δt (min)	0.019
$N_{CFL,max}$	0.532		

Table 1 shows the operating parameters of the PX SMB unit for this study. The 4-zone flow rates were taken from (Minceva and Rodrigues, 2003). For sensitivity analysis of flushing flow rates on process performance at various dead volume axial dispersions ($D_{ax,dead}$), the flow rates of line flush-outlet (Q_{LFo}), line flush-inlet (Q_{LFi}), secondary flush-inlet (Q_{SFi}), and tertiary flush-outlet (Q_{TFo}) vary within certain range.

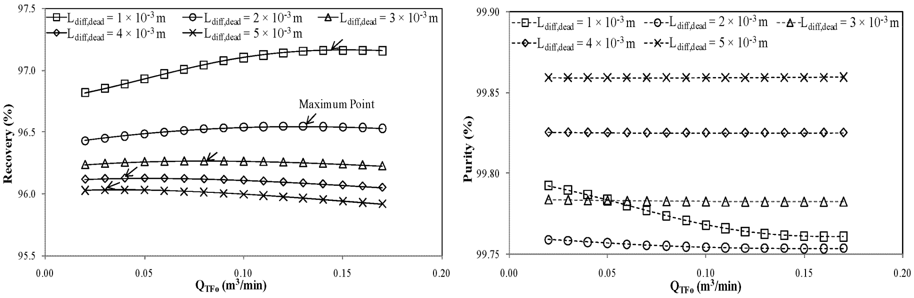
3. Simulation Results and Discussion

Two process performance indicators, purity and recovery, were evaluated for each run.

$$\text{Purity (\%)} = 100 \times \frac{\overline{C}_{E,PX}}{\overline{C}_{E,PX} + \overline{C}_{E,MX} + \overline{C}_{E,OX} + \overline{C}_{E,EB}} \tag{1}$$

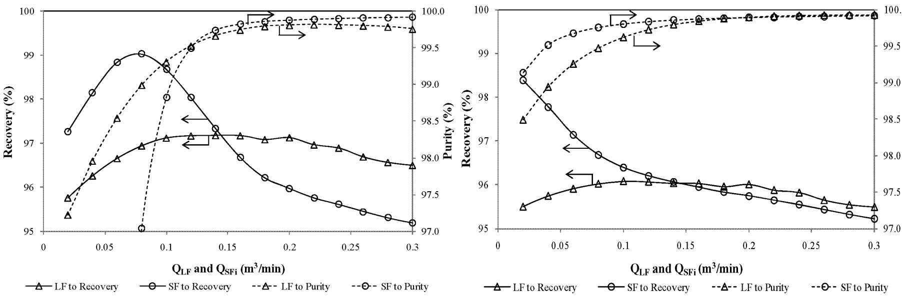
where $\overline{C}_{E,i}$ is the time-averaged of fluid component *i* concentration in extract stream.

$$\text{Recovery (\%)} = 100 \times \frac{\overline{C}_{E,PX} Q_E}{Q_F C_{F,PX} + C_{SF_i,PX} Q_{SF_i}} \tag{2}$$



a) Recovery versus Q_{TFo} *b) Purity versus Q_{TFo}*

Figure 3: Sensitivity of Q_{TFo} on extract recovery and purity for 1×10^{-3} m ≤ $L_{diff,dead}$ ≤ 5×10^{-3} m at fixed Q_{LF}=0.1668 m^3/min and Q_{SFi}=0.145 m^3/min



a) $L_{diff,dead}$=1×10^{-3}m, Q_{TFo}=0.145 m^3/min *b) $L_{diff,dead}$=5×10^{-3}m, Q_{TFo}=0.04 m^3/min*

Figure 4: Sensitivity of Q_{LF} and Q_{SFi} on extract recovery and purity for $L_{diff,dead}$=1 × 10^{-3} and 5 × 10^{-3} m at optimum Q_{TFo}. (Q_{SFi}=0.145 m^3/min when Q_{LF} varies, and Q_{LF}=0.1668 m^3/min when Q_{SFi} varies)

4. Conclusion

Properly adjusted Q_{TFo}, Q_{LF} and Q_{SF} improve recovery and purity, while the excessive flushing flow rates decrease the recovery due to PX loss. High axial dispersion in dead volume reduces effectiveness of flushing flow rates. This research provides a comprehensive study on the flushing technique in the eight-zone PX SMB to understand complex relationships between the flushing flow rates for industrial application.

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