

IMPROVED PARAXYLENE PRODUCTION WITH SIMULATED MOVING BED REACTOR

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In this paper, a Simulated Moving Bed Reactor (SMBR) process for producing paraxylene (PX) is studied. Effects of various operating conditions and desorbents on the xylene isomerisation in liquid phase are given. A catalyst and a desorbent are validated for this reaction. This couple has been tested using True Moving Bed Reactor (TMBR) simulations, and the performances of this system are analyzed. The new adsorbent is tested and the concentration profiles of this more efficient SMBR system are presented.

1. INTRODUCTION

In the current energetic context, many studies are made in the field of process intensification. Process intensification consists in modifying processes to reduce investment and operating costs for cheaper and safer processes. Multifunctional reactors, which combine a reaction and a separation step in one single unit, constitute an important advance in process intensification. Coupling reaction and separation permits to reduce the operating costs for downstream purification step by shifting the chemical equilibrium. Many studies have been made in the last twenty years on reactive separation. If the most successful process is the reactive distillation, reaction and adsorption have been combined in numerous studies over the last ten years (especially in Simulated Moving Bed technology, SMB). First studied in 1976 for CO oxidation (Takeuchi et al. 1976), the Simulated Moving Bed Reactor (SMBR) was recently investigated for other systems in relation to the growing success of SMB industrialization. This paper deals with a SMBR applied to the isomerization and separation of C₈ aromatics for paraxylene (PX) production. In industrial plants, a SMB unit separates the isomers (PX from orthoxylene (OX), metaxylene (MX) and ethylbenzene (EB)) and an important flow is recycled to an isomerization reactor (figure 1-a). This recycle loop constitutes the major part of the SMB feed. SMBR should reduce the isomerization loop by isomerizing C₈ aromatics during the separation (figure 1-b).

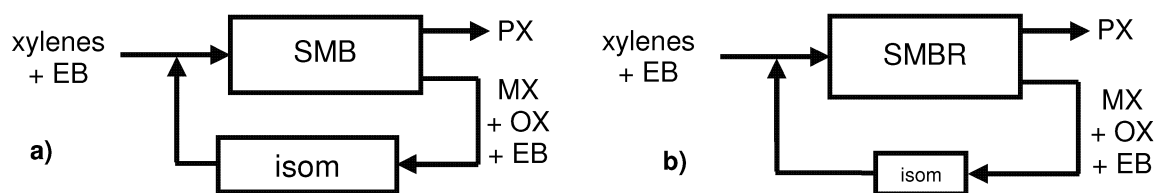


Figure 1: Classical PX production plant (with an important isomerization loop) (a), PX production plant using SMBR (with a small isomerization loop) (b)

2. PRINCIPLES OF SMB AND SMBR

2.1. SMB principle

The SMB, derived from the true moving bed (TMB), is an adsorption-based separation process based on a liquid-solid counter-current. For the TMB, the solid phase flows down countercurrently to the fluid phase stream. The feed mixture is introduced in the column and the most adsorbed component is carried by the solid to the bottom of the column (where it will be collected in the extract) whereas the less retained component is carried upward with the fluid phase and collected in the raffinate (figure 2-a). As a constant solid flow is not readily feasible, SMB is preferred. It is composed of several interconnected fixed beds (usually 24 for PX production) and the counter-current is simulated by a discrete switching of inlets and outlets. The first industrial use of SMB was for the petrochemical and sugar industries (Broughton B.D. et al. 1961). In the last years, many SMB applications appeared in the pharmaceutical industry (Juza et al. 2000).

2.2. Main SMBR schemes

A SMBR is operated with a catalyst mixed with the adsorbent or with an adsorbent which had catalytic properties (Dulot 2000; Lode et al. 2001; Takeuchi et al. 1977). The feed is composed of reactants and, while the reaction occurs, products are separated by adsorption: the less adsorbed products are carried to the extract by the fluid phase and the more retained products move to the raffinate with the simulated movement of the solid phase (figure 2-b). Ideally, this process permits to convert all reactants and obtain at least one pure product. Many publications established the efficiency of SMBR for $A \leftrightarrow B+C$ type reaction (sucrose inversion (Ganetsos et al. 1993; Kurup et al. 2005), esterification (Lode et al. 2001), toluene disproportionation (Dulot 2000), hydrolysis methyl acetate (Yu et al. 2005)) but only few papers on $A \leftrightarrow B$ reaction type were published.

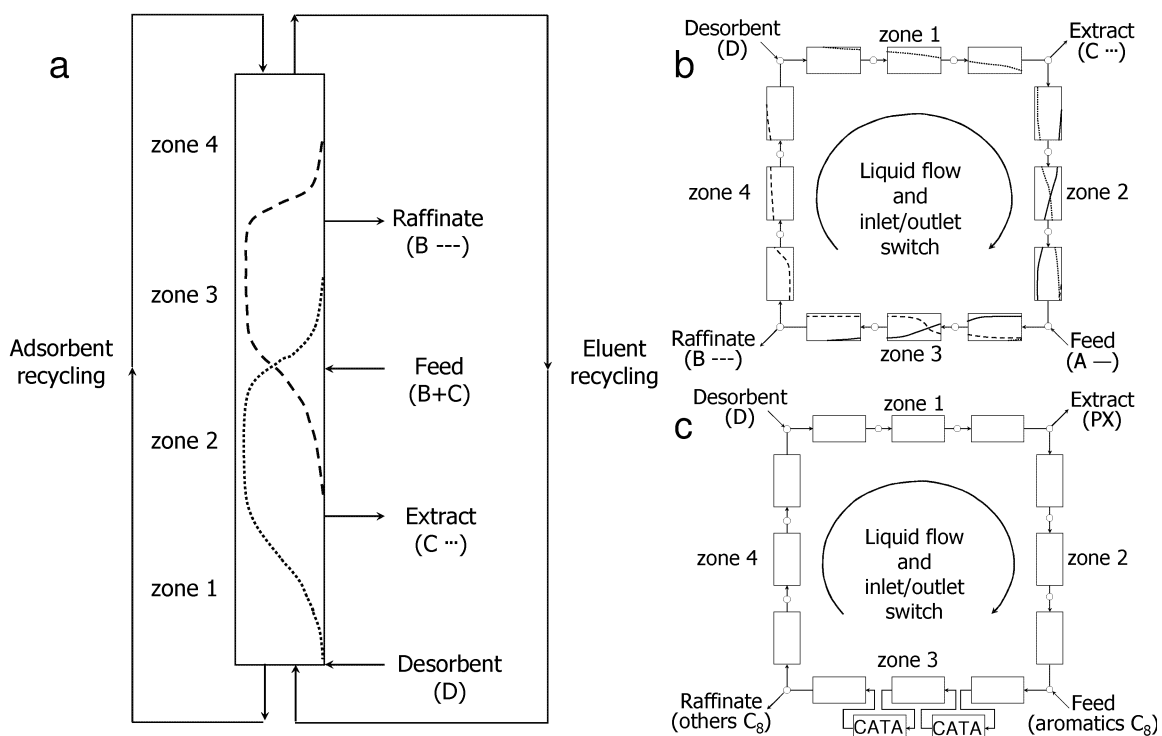


Figure 2: Principle of TMB process for B/C separation (a), SMBR for the reaction $A \leftrightarrow B+C$ (b) and SMBR for PX production (c)

2.3. SMBR scheme for PX production

For those systems, reaction cannot occur near the extract point if a high purity is required. So catalyst and adsorbent have to be separated. The first development for $A \leftrightarrow B$ reaction type concerned the isomerization of glucose into fructose by inserting reactors between the adsorption columns (Hashimoto et al. 1983). It was also used to simulate a SMBR for PX production (Minceva et al. 2008) but with a feed without ethylbenzene (EB). The four zones of classical SMB are present in this scheme. Zone 1 regenerates the adsorbent by desorbing PX. Zone 4 regenerates the desorbent by adsorbing the other isomers on the solid. Zone 2 separates PX from other isomers. Zone 3, where reactors are inserted, alternately separates and produces PX (figure 2-c). As xylene separation takes place in liquid phase, a liquid phase isomerization of xylene was studied to be able to connect catalyst beds to adsorption beds.

3. THE SMBR FOR PX PRODUCTION

3.1. Liquid phase isomerization of xylene

The catalyst used is a HZSM-5 zeolite packed in a fixed bed. First tests with paradiethylbenzene (PDEB, classical desorbent used in C_8 aromatics separation) and orthoxylene showed that PDEB isomerizes into ortho- and meta-diethylbenzene. Thus toluene (TOL) has been used as desorbent.

Reaction tests were carried out at 30 bar and with temperature ranging from 200°C to 300°C. Weight hourly space velocities (whsv) between 5 to 30 h^{-1} were tested, first with pure orthoxylene (OX) feed and then with a 50%OX/50%TOL feed. For each test, the Equilibrium Approach (%EA) was calculated (ratio between the PX produced and the PX at thermodynamic equilibrium). Equilibrium data employed for this calculation were published by Chirico and Steele (Chirico et al. 1997).

First tests with pure OX feed, carried out with a whsv of 5 h^{-1} , (figure 3-a) show that reaction has to be carried out at more than 250°C. Tests also show that %EA decreases when whsv increases (figure 3-b).

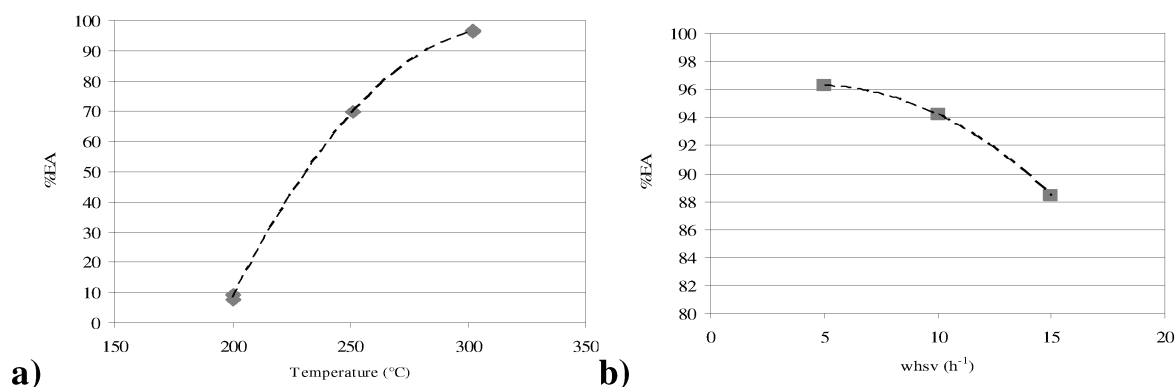


Figure 3: Evolution of %EA for various temperatures at a whsv=5 h^{-1} (a) and for various whsv at 300°C (b) for pure OX feed

Then, the effect of TOL presence on reaction was tested by using a 50%OX/50%TOL feed. The dilution with TOL does not affect the %EA. %EA decreases with the increase of whsv but remains acceptable with more than 75% at 30 h^{-1} and 300°C (figure 4).

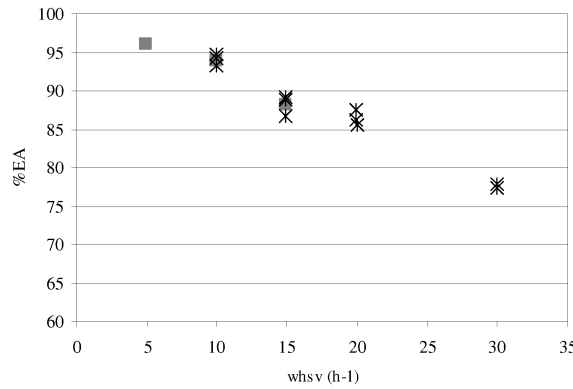


Figure 4: Effect of TOL dilution on %EA for whsv from 5 to 30 h⁻¹ at 300°C (without TOL: ■, with TOL: *)

Other tests show that the catalyst deactivation is very low and that regeneration permits to recover all the catalyst activity. Tests have also confirmed that EB, present in industrial feed, cannot be converted in liquid phase.

Those tests validate the HZSM-5 as a possible catalyst for PX production by SMBR. They also enable the estimation of parameters for a simplified analytical model for liquid phase isomerization of xylene.

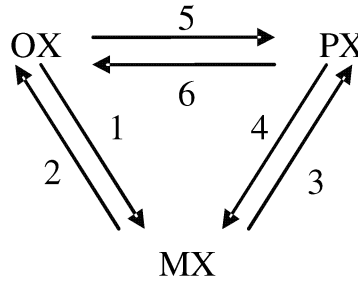


Figure 5: Reaction scheme used for representing xylene isomerization

The chosen reaction scheme for the analytical model is shown on figure 5. The direct OX \leftrightarrow PX reaction does certainly not occur but readily represents the secondary reactions that permit to product PX from OX without using MX as reactional intermediate. Classical mass balances, with a plug flow reactor model, for each component give, in steady state, a differential equation system (equation 1). The k_i are apparent kinetic constants of the reaction i given on figure 5. They include several fixed bed and catalyst parameters (equation 2).

$$\begin{cases} v \frac{dC_{ox}}{dz} = (k_6 - k_2)C_{px} - (k_2 + k_5 + k_1)C_{ox} + k_2C_{x0} \\ v \frac{dC_{px}}{dz} = (k_5 - k_3)C_{ox} - (k_3 + k_4 + k_6)C_{px} + k_3C_{x0} \\ C_{ox} + C_{mx} + C_{px} = C_{x0} \end{cases} \quad (1)$$

$$k_i = \frac{1 - \varepsilon_{reactor}}{\varepsilon_{reactor}} \rho_{catalyst} k'_{0i} \exp\left(\frac{-E_{ai}}{RT_{reaction}}\right) \quad (2)$$

A general solution of the system can be found analytically. It gives the outlet concentrations knowing the inlet concentrations and the whsv. This simplified model is implemented in the TMBR model with the kinetic parameters estimated using experimental data and presented in table 1.

Table 1: Kinetics parameters used in the model of liquid phase isomerization of xylene (at 300°C)

k_1	5.9900×10^{-3}	s^{-1}
k_2	2.1235×10^{-3}	s^{-1}
k_3	1.1464×10^{-3}	s^{-1}
k_4	2.5565×10^{-1}	s^{-1}
k_5	1.7758×10^{-2}	s^{-1}
k_6	1.4039×10^{-2}	s^{-1}

3.2. TMBR simulation results

3.2.1. The TMBR model

The TMBR model is based on a TMB model. The adsorber is considered isothermal. The external phase, the macroporous and the adsorbed phases are considered. External fluid phase is represented by an axial dispersed plug flow model with Danckwerts boundary conditions (Ruthven et al. 1989) and intragranular mass transfer phenomena are represented by a double linear driving forces model (Da Silva et al. 1999). An extended Langmuir model was chosen to characterize the adsorption equilibrium.

Modeling the TMBR process consists in splitting the 3rd zone and inserting reactors (Minceva et al 2008). For each reactor, the solid phase variables directly go to the next part of the 3rd zone but the variables describing the liquid phase pass through the isomerization model. The equations are solved by DASSL directly implemented in the Scilab software.

3.2.2. First TMBR results

The first results have been obtained with this model and the parameters presented in table 2. This TMBR is equivalent to a SMBR with 24 adsorption beds in a 5-9-7+6-3 configuration (6 reactors are inserted between each of the 7 adsorption beds of the 3rd zone) and with a switching time of 69.6 s. The corresponding concentration profiles are presented in figure 6.

Table 2: Geometrics, solids and flow parameters used in simulations

Reactors parameters		Adsorption beds parameters		Flows parameters (cm ³ /min)	
Length	0.8 m	Length	1.13 m	Feed	52
Diameter	0.033m	Diameter	0.015 m	Desorbent	92
Bed porosity	0.32	Bed porosity	0.317	Extract	49
Temperature	300°C	Temperature	180°C	Raffinate	89
Catalyst density	1150 kg/m ³	Adsorbent density	2180 kg/m ³	Recycle	194.5

This case has been simulated using the same operating conditions than those used with a classical SMB process without reaction. They have been chosen to obtain, with a TMB system, more than 99.9% of PX in the extract after distillation of the desorbent and a recovery of 97% of the xylene injected in the feed.

In the reactive case, all the PX produced directly goes to the raffinate (figure 6). The PX quantity in the extract is mostly the same (97% of the PX introduced in the feed). The optimal operating conditions for SMBR systems appear to be different than for SMB process. The flow rates have to be tuned in order to recover the PX created in the 3rd zone.

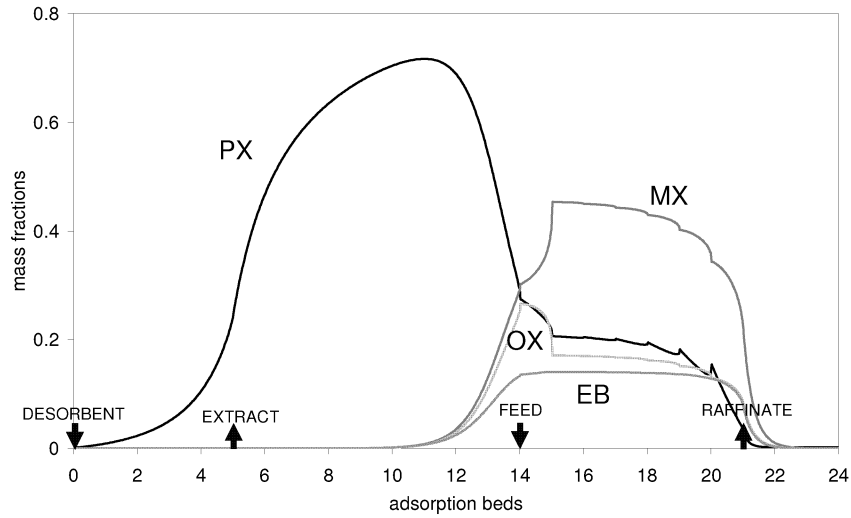


Figure 6: Concentration profiles for TMBR with classical adsorbent and SMB operating conditions

In this case, adjusting the flow rates to increase total xylene recovery (ratio between PX produced and total xylene introduced) raised a problem of purity due to the presence of EB. EB cannot be converted, and tends to accumulate in the 2nd zone and to pollute the extract (figure 7).

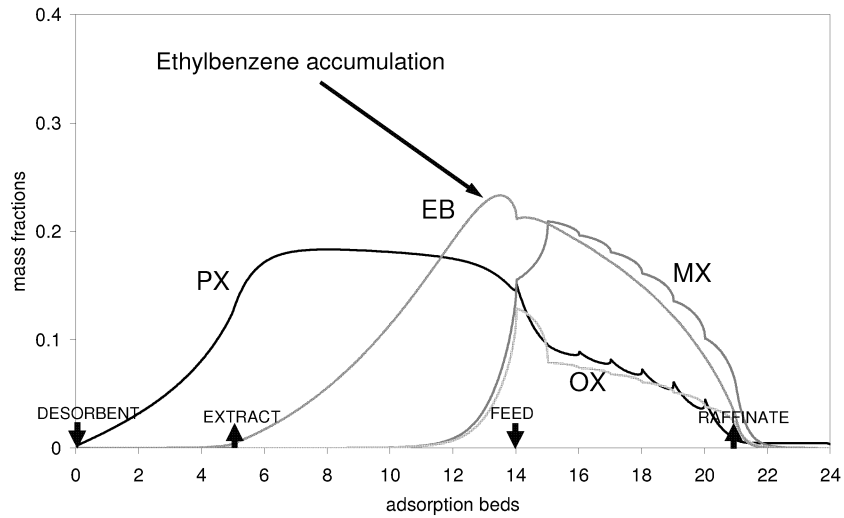


Figure 7: Concentration profiles for TMBR with classical adsorbent and adjusted flow rates (lower feed flow rate)

3.2.3. A new adsorbent

The proposed solution is to use a new adsorbent with a better PX/EB selectivity. This new adsorbent, a BaLSX zeolite, was validated using a breakthrough test method. The obtained results permit to determine transfer and selectivity parameters that can be used in our TMBR simulations (table 3).

The use of this new adsorbent allows much easier operating parameters adjustment as will be seen in the simulation results presented in the next part.

Table 3: Compared selectivities of the new and of the classical adsorbents

Selectivities of classical adsorbent		Selectivities of new adsorbent	
PX/MX	3.821	PX/MX	3.211
PX/OX	3.821	PX/OX	3.211
PX/EB	2.060	PX/EB	2.890
PX/TOL	1.796	PX/TOL	1.500

3.2.4. SMBR interest for PX production

The feed, extract and recycle zone flow rates have been adjusted and the simulation results show that the reduction of the isomerization loop can reach 35% to 90% with a total xylene recovery from 42% to 75% (with a constant PX purity of 99.9%). An example of the concentration profiles obtained for a total xylene recovery of 67.5%, which leads to a 86% reduction of the recycle loop, is presented on figure 8. This example was simulated with the flow rates given in table 2, except for the feed flow rate, which was divided by four, and for the raffinate flow rate, adjusted accordingly.

As the recycling stream can be efficiently reduced by using a SMBR, distillation and isomerization costs as well as energetic consumptions might be significantly reduced.

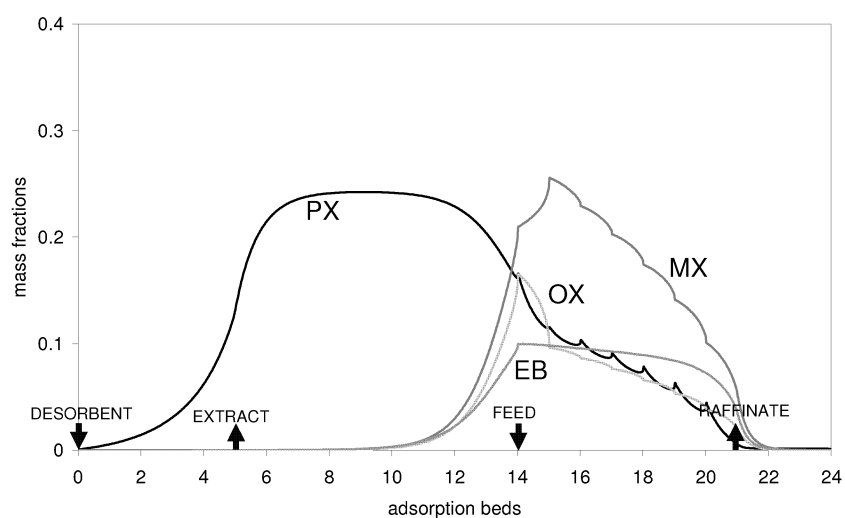


Figure 8: Concentration profiles for TMBR with the new desorbent and adjusted flow rates

4. CONCLUSION

This work focuses on the use of the SMBR process for PX production with industrial feed (i.e. containing EB). SMBR is implemented by inserting fixed bed reactors in the SMB scheme. Separation and adsorption are carried out in liquid phase. Fixed bed experiments were carried out to establish the feasibility of liquid phase isomerization of C₈ aromatics and are presented in this paper. With the SMBR system, the use of TOL instead of PDEB is preferred because of the isomerization of PDEB. The best operating conditions appear to be around 300°C for a whsv of 30 h⁻¹ but lower temperature can be used if catalyst quantity can be increased. Those tests also permit to write down a simple isomerization model that is implemented in a TMBR model. Simulations have raised the problem of EB presence when operating a SMBR but the use of a new adsorbent instead of the classical adsorbent allows an easier adjustment of SMBR.

The various simulated configurations and operating conditions show a great reduction of the isomerization loop volume (up to 90%). Total xylene recovery can reach 75% which corresponds to a consumption of more than 50% of the MX and OX feed. The results presented in this paper are very promising and motivate the continuation of this process study. Other configurations have to be tested, and a global scheme study as well as experiments on a pilot unit are needed to confirm those results and establish the interest of SMBR process for PX production.

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