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Simulated moving bed reactor for paraxylene production

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In this paper, a Simulated Moving Bed Reactor (SMBR) process for producing paraxylene (PX) is studied. A catalyst is validated for a liquid phase isomerization of xylene. An adsorbent and desorbent couple has been chosen, and simulations have been done to study the performances of the SMBR for PX production

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 more 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 by Takeuchi and Uraguchi (CO oxidation,(Takeuchi & Uraguchi 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 C_8 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 aromatics C_8 during the separation (Figure 1-b).

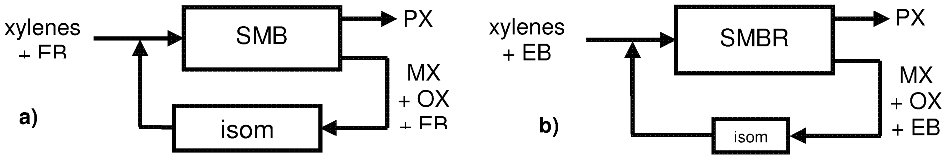

Figure 1 – Classical PX production plant (with an important isomerization loop) (a), PX production plant using SMBR(with a small isomerization loop) (b)

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Principles of SMB and SMBR

SMB principle

SMB, derived from the true moving bed (TMB), is an adsorption-based separation process based on a liquid-solid counter-current. For TMB, the solid phase flows down countercurrently to the mobile 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 mobile 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.

Main SMBR schemes

To operate a SMBR, a catalyst is mixed with the adsorbent or an adsorbent which can catalyze the reaction is used. The feed is composed of reactants and, while the reaction occurs, products are separated by adsorption: less adsorbed products are carried to the extract by the fluid phase and 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 (usually in the extract). Many publications established the efficiency of SMBR for A↔B+C but only few publications on A↔B reaction type were published.

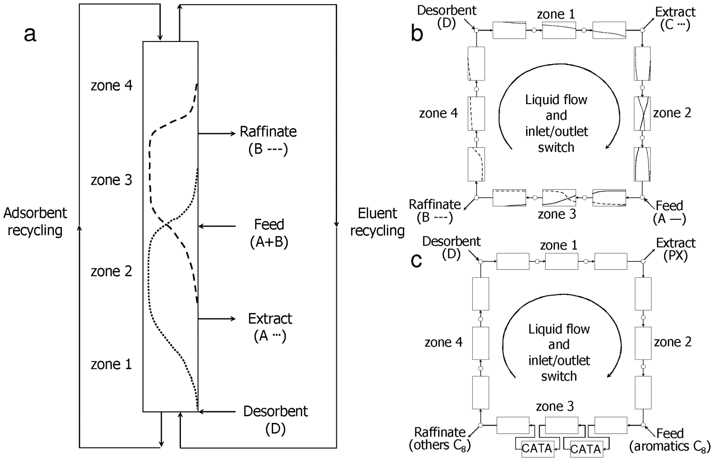

Figure 2 - Principle of TMB process for B/C separation (a), SMBR for the reaction A↔B+C (b) and SMBR for PX production (c)

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↔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 by Minceva 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 C. Zone 4 regenerates the desorbent by adsorbing B 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.

The SMBR for PX production

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

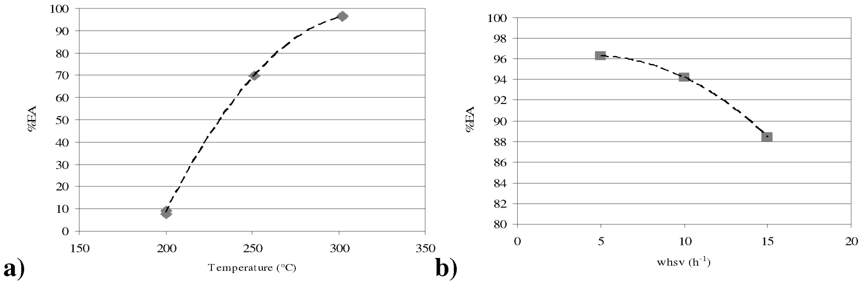

Figure 3 – Evolution of %EA for various temperature and whsv (pure OX feed)

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

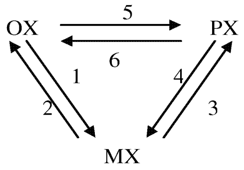

Figure 4 - Reaction scheme used for representing xylene isomerization

Chosen reaction scheme for the analytical model is shown on Figure 4. The direct OX↔PX reaction does certainly not occur but readily represents the secondary reactions that permit to product PX from OX without passing to MX as reactional intermediate. Classical mass balances, with a plug flow reactor model, for each six components give a differential equation system. A general solution of this system can be found analytically in steady state. 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 presented in table 1 (estimated using experimental data).

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}

TMBR simulation results

The TMBR model

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 Danckwert boundary conditions (Ruthven & Ching 1989) and intragranular mass transfer phenomena are represented by a double linear driving forces model (Da Silva, Silva, & Rodrigues 1999).

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

First TMBR results

The first results, presented in Figure 5-a, have been obtained with this model and the parameters presented in table 1. This TMBR is equivalent to a SMBR with 24 adsorption columns in a 5-9-7+6-3 configuration (6 reactors are inserted between each of the 7 adsorption beds of zone 3). This case has been simulated using the same operating conditions than those used with a classical SMB process without reaction. All the PX produced directly goes to the raffinate. In this case, adjusting the flow rates (Figure 5-b) 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 pollute the extract.

Table 1 – 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

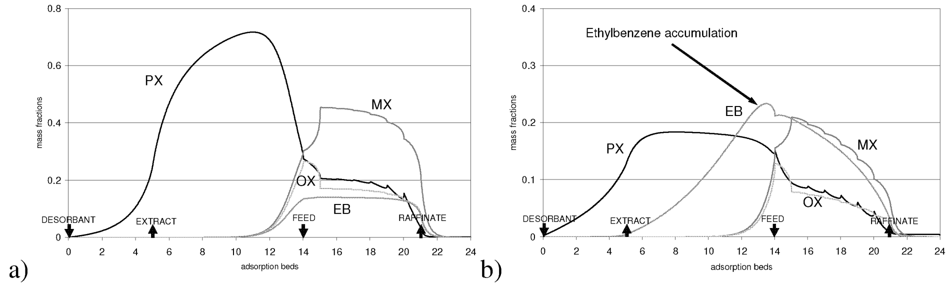

Figure 5 - Concentration profiles for TMBR with classical desorbent - a: with SMB operating conditions, b: with adjusted flow rates (lower C_8 aromatics feed)

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 to be used in our TMBR model (table 2).

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

Table 2 –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

SMBR interest for PX production

The feed, extract and zone 4 stream flowrates 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%).

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.

Conclusion

This work focuses on the use of 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. Since separation occurs in liquid phase, fixed bed experiments were carried out to establish the feasibility of liquid phase isomerization of C_8 aromatics and are presented in this paper. With SMBR scheme, 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 was implemented in a TMBR model.

Simulations have raised the problem of EB presence in operating a SMBR but the use of a new adsorbent in place of 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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