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Dynamic Study of the Synthesis of 1,1-Dibutoxyethane in a Fixed-Bed Adsorptive Reactor

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The synthesis of 1,1-Dibutoxyethane in a fixed-bed adsorptive reactor using Amberlyst 15 was studied for the first time. The adsorption of non-reactive pairs was investigated experimentally, at 25°C, by frontal chromatography in a fixed-bed adsorber. In order to avoid the immiscibility of the liquid phase, the liquid-liquid equilibrium for the mixture 1-butanol/water was studied. The multi-component equilibrium adsorption data was assumed to follow the modified Langmuir type isotherm. Reaction experiments of 1,1-Dibutoxyethane production and column regeneration were performed in the fixed-bed adsorptive reactor. This work will enable further developments in chromatographic reactors aiming at the 1,1-Dibutoxyethane process intensification.

INTRODUCTION

One important trend on chemical engineering and process technology is the process intensification, which consists in the development of innovative frameworks and techniques that improve the chemical manufacturing and processing, reducing equipment volume, energy consumption, or waste formation, leading to cheaper, safer and sustainable technologies (1). One of the basic components of process intensification is the multifunctional reactors, which combines reaction and separation in a single unit (2). Using independent equipments for reaction and separation processes, equipment and energy costs are usually higher. Therefore, the integrated reaction and separation process seems to be a better alternative to the conventional process leading to reduced investment costs and significant energy recovery and savings. These reactive separation techniques, such as chromatographic reactors (3) and reactive distillation (4), are widely used for reversible reactions, where conversion can exceed its equilibrium value; and for consecutive-competitive or parallel

reactions, where reaction yield and product selectivity can be largely enhanced.

By following this process intensification strategy, it is possible to develop competitive, efficient and environmentally friendly processes based on equilibrium limited reactions, as for example the use of reactive chromatography (SMBR) for continuous production of acetals (5,6) and esters (7).

Acetals can be produced by the acid-catalyzed addition of 2 mol of a monohydric alcohol and 1 mol of an aldehyde (8). The synthesis of oxygenated compounds, like acetals, is typically carried out with a strong liquid inorganic acid as homogenous catalyst; however, in spite of the high catalytic activity of homogeneous catalysis, they suffer from several drawbacks, such as their corrosive nature, the existence of side reactions, and the fact that the catalyst cannot be easily separated from the reaction mixture (9). The use of solid-acid catalysts, such as sulfated zirconia, clays, ion-exchange resins, zeolites, and zeotypes appears as a good alternative to the homogenous catalysis (10). Previous works report the use of ion-exchange resins for acetalization (11,12) and esterification reactions (13,14).

The objective of the present work is the study of the dynamic behavior of fixed-bed adsorptive reactor for the synthesis of 1,1-Dibutoxyethane (DBE), using the acid resin catalyst Amberlyst 15. The multicomponent Langmuir isotherm parameters are obtained by performing binary adsorptive experiments in the absence of reaction. The liquid-liquid equilibrium zone for the binary mixture 1-butanol/water was determined in order to avoid the immiscibility of the liquid phase during adsorption experiments. The mathematical model, that includes the interstitial fluid velocity variation, is validated by comparison with experimental reaction/regeneration experiments. The results obtained in this work provide new information about the adsorption of a reaction dynamics for the synthesis of 1,1-Dibutoxyethane in a fixed-bed reactor, which is very important in the future implementation of the process in a simulated moving-bed reactor (SMBR).

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EXPERIMENTAL

Experimental Setup

The experimental work was performed in a laboratory-scale jacketed glass column, packed with the sulfonic acid ion-exchange resin Amberlyst 15 (15). During the experiments, the column was maintained at constant temperature, through a thermostatic bath at 25°C. The experimental results were obtained by gas chromatography analysis of small samples, withdrawn at different times at the column outlet.

The characteristics of the fixed-bed reactor are presented in Table 1.

Catalyst

The catalyst used was the ion-exchange resin Amberlyst 15 (Rohm and Haas, France). The ion-exchange capacity is 4.7 meq/g of dry resin and the surface area is 53 m²/g. Ion exchange resins are produced by copolymerization with styrene and divinyl-benzene used as a cross-linking agent. The functional groups are attached to the polymeric matrix developed in the gel phase by long polystyrene chains fixed by bridges of divinyl-benzene, leading to a stable and rigid structure (17). When the dry resin contacts a fluid, it swells, and the swelling ratio depends on the interactions between the fluid and the resin and on the amount of the cross-links (18). For the Amberlyst 15 the swelling ratio for n-butanol, methanol, methyl acetate, and n-butyl acetate is, respectively 1.59, 1.58, 1.45, and 1.43 (19).

Chemicals

The reactants used were butanol (>99.9% pure) and acetaldehyde (>99.5% pure) (Sigma-Aldrich, UK).

Analytical Method

The samples were analyzed on a gas chromatograph (Chrompack 9100, Netherlands) and the compounds were separated in a fused silica capillary column (Chrompack CP-Wax 57 CB), 25 m × 0.53 mm ID, df = 22.0 μm using a thermal conductivity detector (TCD 903 A) for peak detection. The column temperature was programmed with a 5 min initial hold at 75°C, followed by a 25°C/min ramp up to 100°C, and held for 1.5 min. The temperature of the injector was set at 150°C. The carrier gas used was Helium N50.

TABLE 1
Characteristics of the Fixed-Bed Column

Solid weight	25 g
Length of the bed	12 cm
Internal diameter	2.6 cm
Radius of the particle	375 μm
Bed porosity	0.36 (16)
Bulk density	390 kg/m ³

Mathematical Model

The multicomponent Langmuir isotherm was considered in this work in order to describe the adsorption equilibrium.

$$q_i = \frac{Q_i K_i C_{p,i}}{1 + \sum_{j=1}^{NC} K_j C_{p,j}} \quad (1)$$

where Q_i and K_i represent the total molar capacity per volume of resin and the equilibrium constant for component i , respectively. The thermodynamic consistency of the Langmuir isotherm requires that the total molar capacity should be the same for all the components. However, experimental determination of capacity expressed in terms of volumes, masses, and moles of a component per gram of A15 showed that the assumption of a constant amount adsorbed is not suitable (20). Therefore, the Langmuir model is not a rigorous description of the physical phenomena of adsorption; however, previous works showed that the Langmuir model can satisfactorily represent the experimental adsorption data on ion-exchange resins (15,12). In order to better describe the adsorption on the swollen resin, an appropriate model, such as the modified Flory-Huggins model, should be used to predict the resin phase activities. However, for resins with a high degree of functionalization, such as A15, this model does not yield consistent results (20,21).

The dynamic behavior of the fixed-bed reactor used for the DBE production will be described by the mathematical model that considers the following assumptions and mass balances:

- Isothermal operation;
- The axial dispersed plug flow model is used to describe the flow pattern;
- The external and internal mass-transfer resistances for adsorbable species are combined in a global resistance;
- Constant column length and packing porosity;
- Velocity variations due to the changes in bulk composition.

Bulk fluid mass balance to component i :

$$\frac{\partial C_i}{\partial t} + \frac{\partial(uC_i)}{\partial z} + \frac{(1-\varepsilon)}{\varepsilon} \frac{3}{r_p} K_{L,i}(C_i - \bar{C}_{p,i}) = D_{ax} \frac{\partial^2 C_i}{\partial z^2} \quad (2)$$

Pellet mass balance to component i :

$$\frac{3}{r_p} K_{L,i}(C_i - \bar{C}_{p,i}) = \varepsilon_p \frac{\partial \bar{C}_{p,i}}{\partial t} + (1-\varepsilon_p) \frac{\partial \bar{q}_i}{\partial t} - v_i \rho_p r(\bar{C}_{p,i}) \quad (3)$$

The mathematical model is constituted of a system second-order partial differential equations related to bulk

concentration C (Eq. 2); a system of ordinary differential equations related to the average particle pores concentration $\bar{C}_{p,i}$ (Eq. 3); a system of algebraic equations regarding the multicomponent adsorption equilibrium between \bar{q}_i and concentration $\bar{C}_{p,i}$; together with the initial and Danckwerts boundary conditions:

$$t = 0 \quad C_i = \bar{C}_{p,i} = C_{i,0} \quad (4)$$

$$z = 0 \quad uC_i - D_{ax} \frac{\partial C_i}{\partial z} \Big|_{z=0} = uC_{i,F} \quad (5)$$

$$z = L \quad \frac{\partial C_i}{\partial z} \Big|_{z=L_c} = 0 \quad (6)$$

The subscripts F and 0 refer to the feed and initial states, respectively, u is the interstitial velocity, $K_{L,i}$ is the global mass transfer resistance coefficient of the component i , D_{ax} is the axial dispersion coefficient, t is the time variable, z is the axial coordinate, v_i is the stoichiometric coefficient of component i , ρ_b is the bulk density, and r is the rate of the chemical reaction given by:

$$r = k_c \frac{a_A a_B - \frac{a_C a_D}{K_{eq,A}}}{(1 + K_{S,D} a_D)^2} \quad (7)$$

where the activities of the components, a_i , are calculated based on the average concentration into the particle pores. The activity coefficients were calculated using the UNIFAC method (22). The equilibrium constant and the kinetic parameters were determined in a previous work (23) and are given by:

$$K_{eq} = 9.59 \times 10^{-3} \exp\left(\frac{1755.3}{T(K)}\right) \quad (8)$$

$$k_c = 2.39 \times 10^9 \exp\left(\frac{6200.9}{T(K)}\right) \quad (9)$$

$$K_{S,D} = 2.25 \times 10^{-4} \exp\left(\frac{3303.1}{T(K)}\right) \quad (10)$$

Moreover, the interstitial fluid velocity variation was calculated using the total mass balance assuming ideal liquid volumes additivity (16):

$$\frac{du}{dz} = -\frac{(1-\varepsilon)}{\varepsilon} \frac{3}{r_p} \sum_{i=1}^{NC} K_{L,i} V_{mol,i} (C_i - \bar{C}_{p,i}) \quad (11)$$

where $V_{mol,i}$ is the molar volume of component i .

The axial dispersion coefficient D_{ax} was estimated experimentally from the Peclet number:

$$Pe = \frac{uL_c}{D_{ax}} \quad (12)$$

The global mass-transfer coefficient was defined as:

$$\frac{1}{K_L} = \frac{1}{k_e} + \frac{1}{\varepsilon_p k_i} \quad (13)$$

The internal mass-transfer coefficient was estimated by the following expression (24):

$$k_i = \frac{5D_m/\tau}{r_p} \quad (14)$$

The external mass-transfer coefficient was estimated by the Wilson and Geankopolis correlation (25)

$$Sh_p = \frac{1.09}{\varepsilon} (Re_p Sc)^{0.33} \quad 0.0015 < Re_p < 55 \quad (15)$$

where $Sh_p = k_e d_p / D_m$ and $Re_p = \rho d_p u_0 / \eta$ are, respectively, the Sherwood and Reynolds numbers, relative to particle and $Sc = \eta / \rho D_m$ is the Schmidt number.

The infinite dilution diffusivities were estimated by Scheibel correlation (26)

$$D_{A,B}^0 (cm^2/s) = \frac{8.2 \times 10^{-8} T}{\eta_B V_{mol,A}^{1/3}} \left[1 + \left(\frac{3V_{mol,B}}{V_{mol,A}} \right)^{2/3} \right] \quad (16)$$

where $D_{A,B}^0$ is the diffusion coefficient for a dilute solute A into a solvent B, T is the temperature, $V_{mol,i}$ is the molar volume of component i , and η_B is the viscosity of solvent B.

For binary systems, the diffusion coefficient in concentrated solutions, $D_{A,B}$, was calculated using the Vignes equation (27)

$$D_{2,1} = D_{1,2} = (D_{1,2}^0)^{x_2} (D_{2,1}^0)^{x_1} \quad (17)$$

For multicomponent concentrated solutions the Perkins and Geankopolis mixing rule was used (28):

$$D_{A,m} \eta_m^{0.8} = \sum_{i=1, i \neq A}^n x_i D_{A,i}^0 \eta_i^{0.8} \quad (18)$$

where η_i is the viscosity of pure component i and η_m is the viscosity of the mixture. The mixture viscosity and components diffusivities were calculated at each time at every axial position.

The model equations were solved using the commercial software gPROMS (general PROcess Modeling System) version 3.1.5. The mathematical model involves a system

of partial and algebraic equations (PDAEs). The axial co-ordinate was discretized using the third-order orthogonal collocation in the finite elements method (OCFEM). The system of ordinary differential equations (ODE's), resulting from the axial discretization, was integrated over time using the DASOLV integrator implementation in gPROMS. Thirty finite elements were used for axial discretization. All simulations used a fixed tolerance equal to 10^{-7} .

Hydrodynamic Study of the Fixed-Bed Column

In order to determine the Peclet number and the bed porosity, tracer experiments were performed using a blue dextran solution (5 Kg/m^3). Samples of 0.2 cm^3 were injected under different flow rates and the column response was monitored using a UV-VIS detector at 300 nm. The bed porosity was calculated from the stoichiometric time of the experimental curves. The Peclet number was obtained by calculating the second moment of the experimental curves. Figure 1 shows the tracer experiments and the estimated values for bed porosity and Peclet number are presented in Table 2.

Adsorption/Desorption Experiments with Non-Reactive Pairs

The adsorption/desorption experiments were performed in a fixed-bed column. Before the beginning of each run, the column is previously saturated with pure 1-butanol. Then, the feed is changed to a binary mixture of 1-butanol/water or DBE/water, and the time evolution of the column outlet composition is evaluated until saturation with the new feed is achieved. After saturation, the column is regenerated with pure 1-butanol.

For the binary mixture 1-butanol/water we must avoid the formation of two liquid phases, depending on the temperature and composition conditions. The formation of

	Q (mL/min)	t_{st} (min)	ε	σ^2	Pe
Run 1	5	4.87	0.357	0.734	173.5
Run 2	8	3.05	0.358	0.152	173.0

two liquid phases with different densities can lead to back-mixing problems during the fixed-bed operation; so, the knowledge of liquid-liquid equilibrium for the mixture 1-butanol/water is of utmost importance in the study of fixed-bed adsorption.

Figure 2 shows the predicted liquid-liquid equilibrium zone for the binary mixture of 1-butanol/water using UNIFAC and UNIQUAC (29) for liquid-phase activity coefficients.

Taking into account these results, the adsorption/desorption experiments with 1-butanol/water binary mixtures were performed at 25°C , using 1-butanol molar fraction above 0.5, in order to avoid the formation of two liquid phases. Table 3 presents the experimental conditions for the adsorption/desorption experiments with binary mixtures of 1-butanol/water and 1-butanol/DBE.

The difference of densities between adsorbed and desorbed components can lead to hydrodynamic problems, which were overcome by using a Top-Down configuration, when the desorbed component is denser than the adsorbed component; and a Bottom-Top configuration, when the desorbed component is less dense than the adsorbed component.

Based on the experimental outlet column concentrations as a function of time, the total amount of species retained/leaving the column (amount in interparticle space + amount

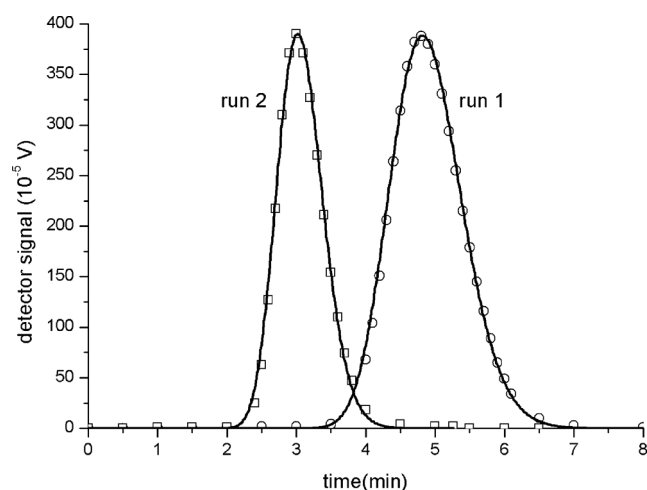


FIG. 1. Tracer experiments using blue dextran solution. Points are experimental values and lines are simulated curves.

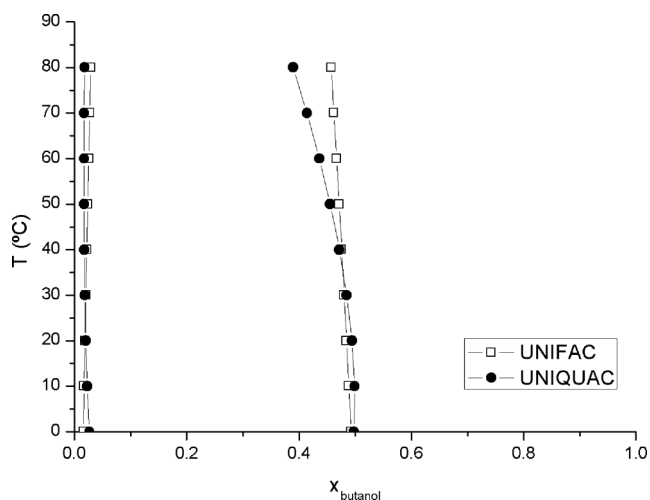


FIG. 2. Liquid-Liquid equilibrium phase diagram.

TABLE 3
Experimental conditions for adsorption/desorption with 1-butanol/water and 1-butanol/DBE at 25°C

Run	1-Butanol/DBE						1-Butanol/water			
	S1	R1	S2	R2	S3	R3	S4	R4	S5	R5
Q (mL/min)	9.0	9.0	8.0	8.0	8.0	8.0	8.0	8.0	9.0	9.0
C _{0,A} (mol/L)	10.87	7.0	10.87	7.46	10.87	6.16	10.87	9.69	10.87	9.39
C _{0,B} (mol/L)	0	1.69	0	1.49	0	2.07	0	5.98	0	7.53
C _{F,A} (mol/L)	7.0	10.87	7.46	10.87	6.16	10.87	9.69	10.87	9.39	10.87
C _{F,B} (mol/L)	1.69	0	1.49	0	2.06	0	6.0	0	7.54	0

in particle pores + amount adsorbed in the solid phase) are calculated by Eqs. (19) and (20), respectively, which are theoretically described by Eqs. (21) and (22), respectively.

$$n_{\text{exp}}^{\text{ads}} = Q \int_0^{\infty} [C_F - C_{\text{out}}(t)] dt \quad (19)$$

$$n_{\text{exp}}^{\text{des}} = Q \int_0^{\infty} [C_{\text{out}}(t) - C_F] dt \quad (20)$$

$$n_{\text{theo}}^{\text{ads}} = \{[\varepsilon + (1 - \varepsilon)\varepsilon_p](C_F - C_0) + (1 - \varepsilon)(1 - \varepsilon_p)[q(C_F) - q(C_0)]\} V_c \quad (21)$$

$$n_{\text{theo}}^{\text{des}} = \{[\varepsilon + (1 - \varepsilon)\varepsilon_p](C_0 - C_F) + (1 - \varepsilon)(1 - \varepsilon_p)[q(C_0) - q(C_F)]\} V_c \quad (22)$$

The adsorption parameters were optimized by minimizing the difference between experimental and theoretical values of number of moles adsorbed/desorbed. Table 4 presents the experimental and theoretical number of moles adsorbed calculated in each experiment. In order to close the mass balance in each adsorption/desorption experiments, the amount of a component desorbed during the desorption step has to be the same that was adsorbed during the adsorption step. For the experiments presented in

Table 4, the mass balance closes with an error lower than 5%.

Breakthrough experiments with acetaldehyde were not performed, because acetaldehyde reacts with itself to give an acetaldehyde trimer. Therefore, the adsorption parameters of acetaldehyde were determined by optimization of reaction data. The value of τ used in this work was 2.5, found by a “best fit” procedure to the adsorption experimental data.

The Langmuir isotherm parameters estimated by optimization are presented in Table 5.

The experimental and simulated adsorption/desorption results for the binary pair 1-butanol/DBE are presented in Fig. 3.

The experimental and simulated adsorption/desorption results for the binary pair 1-butanol/water are presented in Fig. 4.

Adsorptive Reactor

Reaction experiments were performed in a fixed-bed column; a binary mixture of 1-butanol/acetaldehyde was fed to the column previous saturated with 1-butanol, and the composition of reactants and products was measured at the column outlet at different times. After each reaction experiment, the column was regenerated with pure 1-butanol. In the reaction experiments, since the feed mixture is less dense than 1-butanol, the direction flow adopted was

TABLE 4
Experimental and theoretical values for the number of moles adsorbed/desorbed

Run	1-Butanol/DBE						1-Butanol/water			
	S1	R1	S2	R2	S3	R3	S4	R4	S5	R5
n _{exp,A} (mol)	-0.148	0.154	-0.132	0.138	-0.186	0.180	-0.150	0.150	-0.176	0.176
n _{exp,B} (mol)	0.065	-0.067	0.058	-0.060	0.081	-0.079	0.765	-0.759	0.897	-0.895
n _{theo,A} (mol)	-0.150	0.150	-0.132	0.132	-0.182	0.184	-0.153	0.153	-0.179	0.179
n _{theo,B} (mol)	0.065	-0.065	0.057	-0.057	0.080	-0.080	0.807	-0.805	0.941	-0.940
Δn_A (%)	-0.81	3.08	0.41	4.88	1.68	-2.28	-1.96	-1.74	-1.37	-1.71
Δn_B (%)	0.91	2.98	0.31	4.79	1.57	-2.40	-5.49	-6.07	-4.78	-5.12

TABLE 5
Multicomponent Langmuir isotherm parameters

Component	Q (mol/L _{wet.solid})	K (mol/L)
1-Butanol	8.5	7.5
Acetaldehyde	15.1	0.5
Water	44.9	12.1
DBE	5.8	0.4

from the top to bottom. In the regeneration step, since the reaction mixture is heavier than pure 1-butanol, the direction flow adopted was from the top to the bottom.

Figure 5 shows the time evolution of concentration in the column outlet during a reaction experiment. The reaction occurs inside the column between adsorbed

1-butanol and acetaldehyde; water and DBE are formed as products. However, water is preferentially adsorbed by the resin, whereas the DBE is soon desorbed and carried by the fluid phase along the column. The acetaldehyde is consumed above equilibrium conversion in the transient zone that corresponds to the reactive front that travels along the column (Fig. 6), and leaves the column between 12 and 25 minutes (Fig. 5). In Fig. 6 (at $t=10$ min and $x>10$ cm) it can be seen that the acetaldehyde is completely consumed. When the resin becomes saturated by the water, the selective separation between water and DBE is not possible anymore and the steady state is reached. In Fig. 5, the outlet column composition is constant and corresponds to the equilibrium composition for the conditions of the experiment ($C_{A,F}=8.44$ mol/l, $C_{B,F}=3.92$ mol/l, $T=25^{\circ}\text{C}$). In general, the steady state

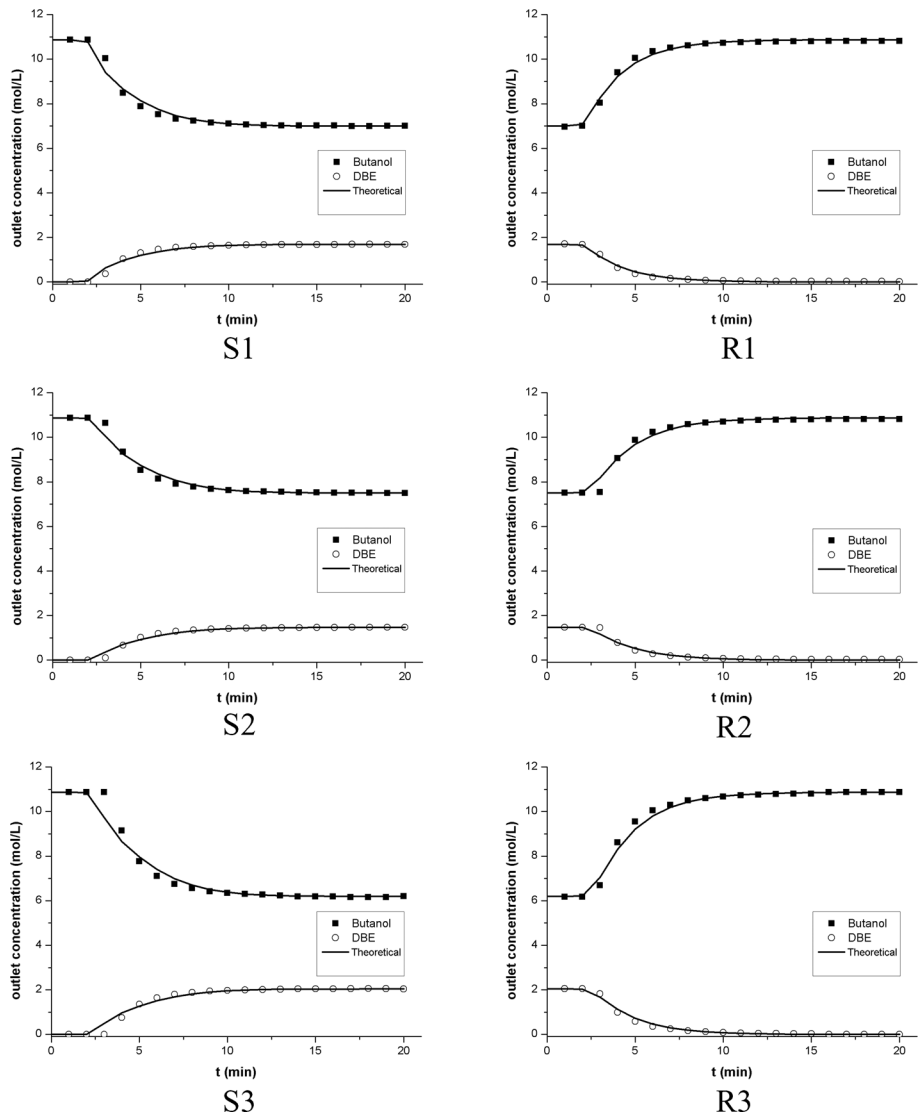


FIG. 3. Adsorption/desorption experiments with 1-butanol/DBE.

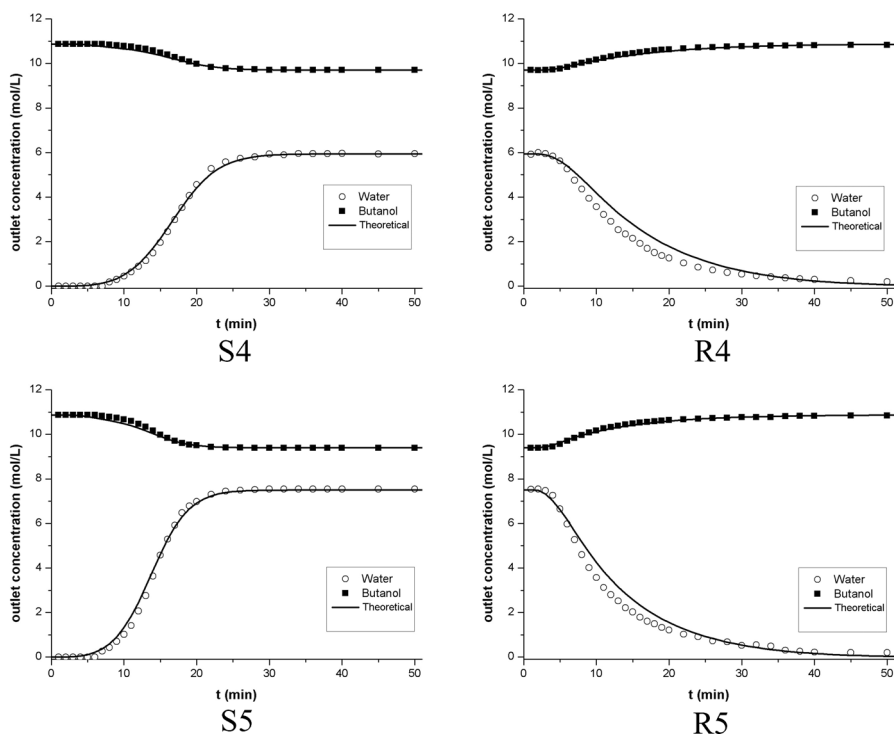


FIG. 4. Adsorption/desorption experiments with 1-butanol/water.

outlet composition, for different operating conditions will depend not only on the chemical equilibrium, but also on the residence time, the reaction rate, and mass-transfer rates.

By simulation it is possible to obtain concentration profiles inside the column during the reaction experiments (Fig. 6).

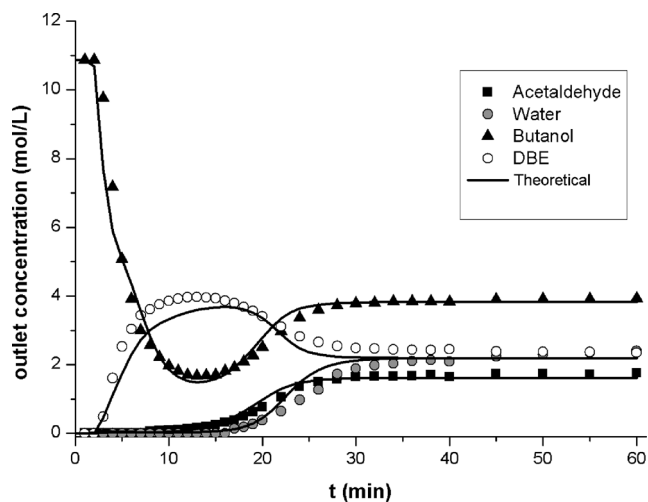


FIG. 5. Concentration histories in a fixed-bed adsorptive reactor, initially saturated with 1-butanol and then fed with 1-butanol and acetaldehyde. Experimental conditions: $Q = 8 \text{ mL/min}$, $C_{F,A} = 8.44 \text{ mol/L}$ and $C_{F,B} = 3.92 \text{ mol/L}$.

After the steady-state is reached, the column is regenerated with pure 1-butanol in order to remove the adsorbed species. Figures 7 and 8 show the concentration time evolution in the column outlet during reaction/regeneration experiments. In the regeneration experiments, DBE and acetaldehyde, due to their weak affinity with the resin, are easily removed. On the other hand, water is strongly adsorbed and, therefore, a large amount of 1-butanol is needed in order to totally remove the water.

CONCLUSIONS

Adsorption/desorption experiments in absence of reaction were carried out in a fixed-bed column with the non reactive binary mixtures of 1-butanol/water and 1-butanol/DBE, at 25°C . For the experiments with 1-butanol/water, it was necessary to study the liquid-liquid equilibrium in order to measure adsorption data in conditions of full miscibility. It was concluded that for a fixed-bed operation at 25°C , the molar fraction of 1-butanol should be higher than 50% in order to prevent the formation of two liquid phases. The adsorption parameters were estimated by minimizing the error between the experimental and the theoretical number of moles adsorbed/desorbed for all adsorption/desorption experiments.

For the chromatographic reactor, the mathematical model was derived assuming axial dispersion, isothermal operation, external and internal mass-transfer resistances,

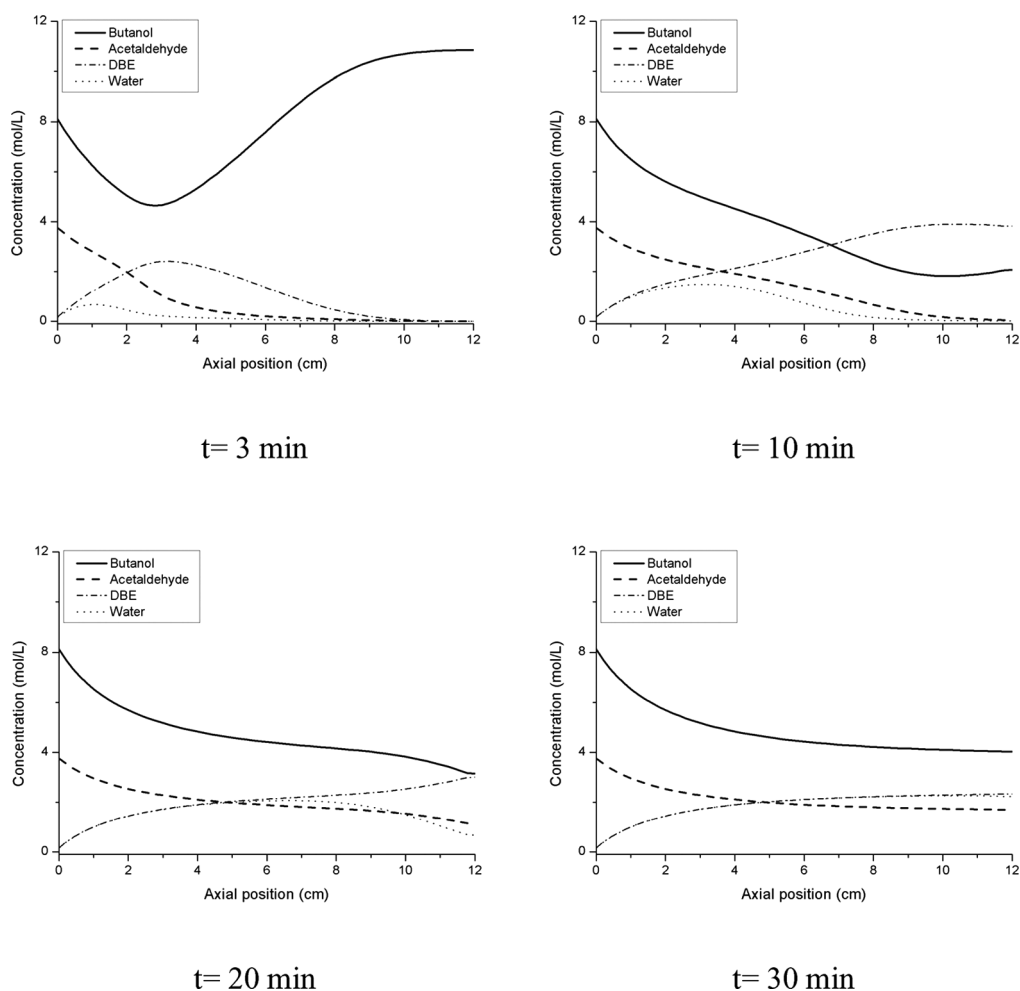


FIG. 6. Internal concentration profiles of all species in fluid phase inside the column, during the reaction experiment of Figure 5.

multicomponent Langmuir isotherm, and fluid velocity variations with the composition. The model equations were solved using the commercial software gProms. Reaction experiments were performed by feeding 1-butanol/acet-aldehyde mixtures to the column initially saturated with

1-butanol. It was observed that a good agreement between model predictions and experimental data. Experimental and simulated results of the adsorptive reactor show a selective separation between water and DBE over the resin, where DBE (the less retained component) is easily displaced by

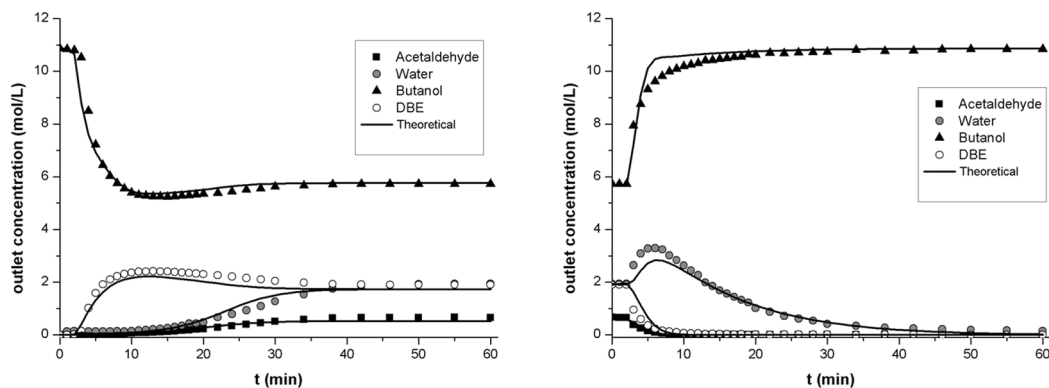


FIG. 7. Concentration histories in a fixed-bed adsorptive reactor, reaction (left) and regeneration (right) experiments. Experimental conditions: $Q = 9 \text{ mL/min}$, $C_{F,A} = 9.43 \text{ mol/L}$ and $C_{F,B} = 2.31 \text{ mol/L}$.

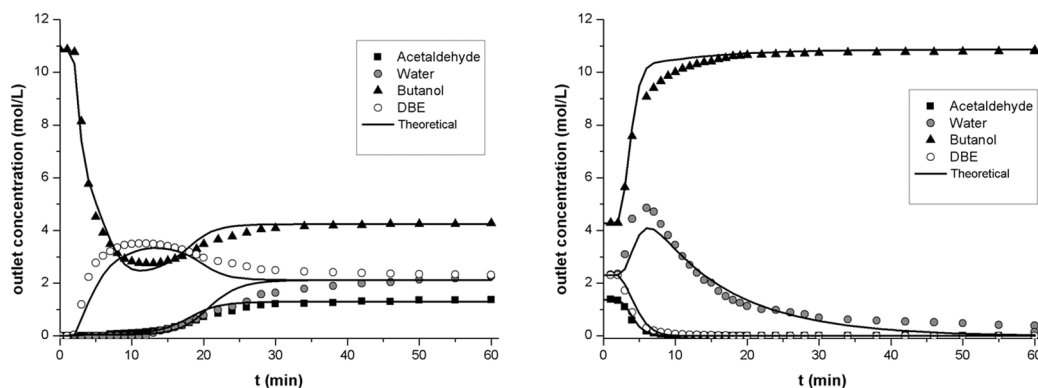


FIG. 8. Concentration histories in a fixed-bed adsorptive reactor, reaction and regeneration experiments. Experimental conditions: $Q = 9 \text{ mL/min}$, $C_{F,A} = 8.7 \text{ mol/L}$ and $C_{F,B} = 3.51 \text{ mol/L}$.

water, the more retained component. In view of these results, an integrated process of separation and reaction can be designed in order to enhance the conversion of this reaction. In fact, the removal of one product from the reaction medium will displace the chemical reaction towards more products formation.

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Notation

a	liquid phase activity
$\bar{C}_{p,i}$	average particle pore concentration, mol dm^{-3}
C_i	concentration, mol dm^{-3}
D_j	effective diffusivity, $\text{dm}^2 \text{min}^{-1}$
$D_{j,m}$	molecular diffusivity coefficient of a solute in a mixture, $\text{dm}^2 \text{min}^{-1}$
d_p	particle diameter, dm
K	adsorption constant, mol dm^{-3}
$k_{0,c}$	Arrhenius constant for Eq. (9), $\text{mol g}_{\text{cat}}^{-1} \text{min}$
$k_{0,s}$	Arrhenius constant for Eq. (10), $\text{mol g}_{\text{cat}}^{-1} \text{min}$
k_c	kinetic constant, $\text{mol g}_{\text{cat}}^{-1} \text{min}$
k_e	external mass-transfer coefficient, dm min^{-1}
K_{eq}	equilibrium constant
k_i	internal mass-transfer coefficient, dm min^{-1}
K_L	global mass-transfer coefficient, dm min^{-1}
K_s	equilibrium adsorption constant
n	number of moles, mol
Q	adsorption capacity, mol dm^{-3}
q	solid phase concentration, mol dm^{-3}
r	reaction rate, $\text{mol g}_{\text{cat}}^{-1} \text{min}$
r_p	particle radius, mm
t	time coordinate, min
T	temperature, $^{\circ}\text{C}$

t_{st}	stoichiometric time, min
u	interstitial velocity, dm min^{-1}
u_0	superficial velocity, dm min^{-1}
V	volume of solution, dm^3
V_{mol}	molar volume, $\text{dm}^3 \text{mol}^{-1}$
V_p	total volume of the particles, dm^3
X	conversion of the limiting reactant
x	molar fraction
z	axial position, dm

Greek letters

γ	activity coefficient
ε	bed porosity
ε_p	particle porosity
η	fluid viscosity, $\text{g dm}^{-1} \text{min}^{-1}$
ρ_p	particle density, g dm^{-3}
τ	tortuosity factor
ν	stoichiometric coefficient

Subscripts

A	butanol
B	acetaldehyde
C	DBE
D	water
i	relative to component i
p	relative to the particle

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