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Reactive Chromatography for the Synthesis of 2-Ethylhexyl Acetate

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Abstract: Reactive chromatography (RC) combines reaction and chromatography in a single unit. Due to simultaneous separation of products it can be advantageously used for reversible reactions to obtain the enhanced performance. It is a promising alternative to reactive distillation when the components are temperature sensitive and less volatile. In the present work, we study the application of RC for the synthesis of 2-ethylhexyl acetate through esterification of acetic acid with 2-ethylhexanol. Amberlyst-15 has been used as a catalyst/adsorbent. Several aspects such as reaction kinetics, multicomponent adsorption equilibria, and reaction-separation study using fixed bed chromatographic reactor are covered. The kinetics was studied in a stirred batch reactor. The effects of various parameters such as speed of agitation, particle size, temperature, mole ratio of reactants, and catalyst loading have been investigated. Kinetic modeling was performed using modified activity based Langmuir-Hinshelwood-Hougen-Watson (LHHW) model. Non-reactive binary adsorption experiments were performed to determine the parameters of Langmuir adsorption isotherm by minimizing the errors between the experimental and predicted breakthrough curves. Further, the reactive chromatography experiments were performed to obtain the reactive breakthrough curves which indicate a clear potential for the use of reactive chromatography for this reaction. The obtained data has been compared with the predictions of mathematical model of the chromatographic reactor.

Keywords: Adsorption isotherm; cation exchange resin; 2-ethylhexanol; 2-ethylhexyl acetate; kinetic modeling; reactive chromatography

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INTRODUCTION

Integration of unit operation with chemical reaction has received significant importance in the recent years. The examples are reactive distillation, reactive chromatography, reactive extraction, membrane reactors etc. This approach results in a significant improvement in the process performance. The desired improvement can be seen in terms of yield, productivity, operating cost, energy saving, and safety. Reactive chromatography is one such operation which separates products and reactants based on adsorption to achieve enhanced performance. An exhaustive review on the literature on reactive chromatography is published by Lode et al. (1). Reactive chromatography is applicable to several heterogeneously catalyzed reactions e.g. esterification (2,3), acetalization (4,5), alkylations (6) etc. In case of reactive chromatography, special attention needs to be given to the choice of the adsorbents. There are different types of adsorbents used for reactive chromatography e.g. zeolites, activated carbon, alumina, immobilized enzymes, and ion exchange resin. Ion-exchange resins exhibit selective adsorption capabilities, high capacity, and significant catalytic activity. Hence, they have been used extensively in various applications of liquid phase reactive chromatography.

Esterification reactions are ubiquitous reactions especially in pharmaceutical, perfumery and polymer industries wherein both heterogeneous and homogeneous catalysts have been widely used. 2-Ethylhexyl acetate is an industrially important chemical with applications as a good solvent power for cellulose nitrate and many natural and synthetic resins. It can also be used in coatings for brushing, dip-coating and spraying, and for stove enamels. The main purpose of adding 2-ethylhexyl acetate is to improve flow and film formation. The product is also a good coalescing aid for emulsion paints. Another application for 2-ethylhexyl acetate is as an additive in cleaners and paint removers.

In this paper, we present a detailed study of the synthesis of 2-ethylhexyl acetate *via* fixed bed chromatographic reactor (FBCR) on laboratory scale. Reaction kinetics using batch reactor has been studied and a kinetic model is proposed. The non reactive binary adsorption experiments are performed in FBCR using Amberlyst-15 as an adsorbent to determine the multicomponent adsorption parameters. Kinetics and adsorption parameters are further used in the simulation of FBCR. The experimental data for FBCR is explained with the help of a mathematical model and the potential of RC for this reaction has been demonstrated.

REACTION KINETICS

The esterification reaction of 2-ethylhexanol and acetic acid in the presence of cation exchange resin as a catalyst (Amberlyst-15) can be represented as follows:

$$\underset{\text{(Acetic acid)}}{CH_3COOH} + \underset{\text{(2-ethylhexanol)}}{HO\text{-}CH_2(C_2H_5)CH(CH_2)_3\text{-}CH_3} \xleftrightarrow{\text{Amberlyst-15}} \underset{\text{(2-ethylhexyl acetate)}}{CH_3\text{-}COO\text{-}CH_2(C_2H_5)CH\,(CH_2)_3\text{-}CH_3} + \underset{\text{(water)}}{H_2O}$$

This reaction is slow and reversible. 2-ethylhexanol and 2-ethylhexyl acetate are sparingly soluble in water. The reaction being reversible, the simultaneous removal of product would shift the reaction in forward direction and reduce the load on downstream processing. Reactive distillation may not be a suitable option for this system as the product is less volatile. The relatively high boiling points of 2-ethylhexanol (b.p. 184°C) and 2-ethylhexyl acetate (b.p. 195°C) may be harmful for the thermally sensitive ion exchange resin catalyst. We propose to apply reactive chromatography for this system as it has a potential to separate components based on the difference in their affinity towards the cation exchange resin. Cation exchange resin also offers high catalytic activity for this reaction and hence plays a dual role of both catalyst and adsorbent.

Extensive reviews on reactions catalyzed by cation exchange resin have appeared in the literature (7). The use of ion exchange resin as catalyst for esterification reaction has been well studied (8,10). Recently the kinetics of extractive esterification of dilute acetic acid with 2-ethylhexanol in the presence of Amberlyst-15 has also been reported (11). This kinetics may not be of direct use in the present case since it was performed under dilute conditions. Therefore we study the kinetics of this reaction under the conditions of interest. The effect of various parameters like speed of agitation, particle size, temperature, mole ratio of reactants, and catalyst loading has been investigated.

Experimental Work

Materials and Catalyst

2-ethylhexanol (99.5% pure LR grade) was obtained from s.d. fine chemicals Ltd., Mumbai India. Acetic acid (99.7% pure AR grade) and isopropyl alcohol (99.5% pure AR grade) were obtained from Qualigens fine chemicals, Mumbai India. The purities of chemicals were verified by Gas chromatographic analysis and they were used without further treatments. The catalyst Amberlyst-15 was obtained from Rohm and

Table 1. Physical properties of Amberlyst-15

Shape	Beads
Average particle size (mm)	0.5
Internal surface area (m^2/g)	55
Capacity (meq /g)	4.7
Cross-linking density (% DVB)	20–25
Porosity (%)	36
Max. operating temperature (K)	393

Hass, France. The catalyst was dried in vacuum at 80°C for 6 hrs. The physical properties of Amberlyst -15 catalyst are listed in Table 1.

Apparatus and Procedure

All the experiments were conducted in a baffled glass reactor of volume $3.5 \times 10^{-4}\,m^3$ equipped with four-bladed disc turbine impeller. Glass reactor was dipped in a constant temperature oil bath and was equipped with a temperature sensor. The temperature in the reactor was maintained within $\pm 1\,K$ with respect to the desired temperature. The measured quantities of acetic acid and 2-ethylhexanol were charged to the reactor. Once the desired temperature was achieved, the sample was withdrawn and the catalyst was added in the reaction mixture. This time was considered as zero reaction time. The samples were withdrawn at specific time intervals and analyzed by Gas Chromatography.

Analysis

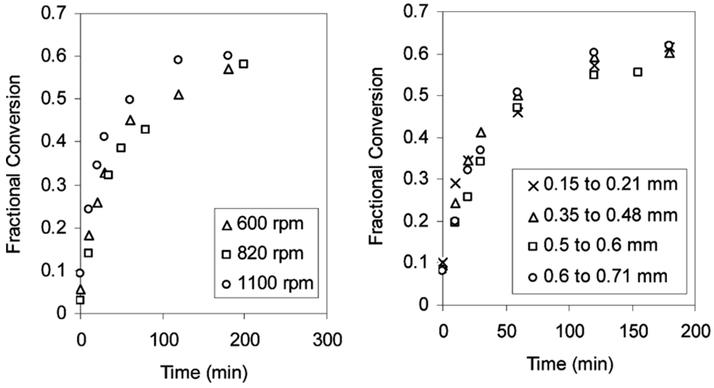
The samples were analyzed by a Gas chromatograph (GC-MAK-911) equipped with thermal conductivity detector. A 2 m long packed column Porapack-Q with hydrogen as a carrier gas at a flow rate of 30 ml/min, was used to separate the different components of the reaction mixture using isopropanol as an external standard. It should be noted that at higher conversion level (more than 0.7) samples are cloudy due to possible phase splitting; however addition of isopropanol makes the sample homogeneous. Injector and detector temperatures were maintained at 403 K and 493 K, respectively. Oven temperature was suitably programmed to get the best resolution and the least time for analysis. Oven temperature was initially maintained at 473 K for 2 minutes and then raised at a rate of 20 K/min up to 413 K and maintained there for 17 minutes. The retention times of all the individual components were confirmed by the respective authentic samples. Analysis of acetic acid was also performed independently by titration using 0.1 N NaOH to confirm the results of GC.

Results and Discussions

Elimination of Mass Transfer Resistance. The speed of agitation and particle size were varied to examine the effect of external mass transfer limitations and the role of the intra-particle diffusion, respectively. Fig. 1(a) shows the results obtained over a wide range of speed of agitation (600–1100 rpm) under otherwise similar conditions. It is clear from the figure that the speed of agitation shows very little effect on the rate of reaction. Hence, all the further runs were conducted at a speed of 1000–1100 rpm.

The resin particles of the available size were crushed and screened to obtain finer particles in a desired size range. Effect of particle size was studied over a range 0.15 to 0.71 mm under otherwise similar conditions. The results shown in confirm that the effect of particle size is negligible under the conditions of interest, which indicates that intra-particle diffusion limitations are insignificant. Hence, the resin was used in the supplied form for all of the other kinetic runs.

Effect of Temperature. Effect of temperature on the rate of formation of 2-ethylhexyl acetate was studied over a range of 348–373 K. As expected, Fig 2 shows that the fractional conversion of acetic acid increases with an increase in temperature.



(a) (b)

Figure 1. Effect of (a) speed of agitation (b) particle size, on conversion of acetic acid (Temperature = 373 K, Catalyst loading = 5% (w/w), 2EHOH: AcH = 1:1).

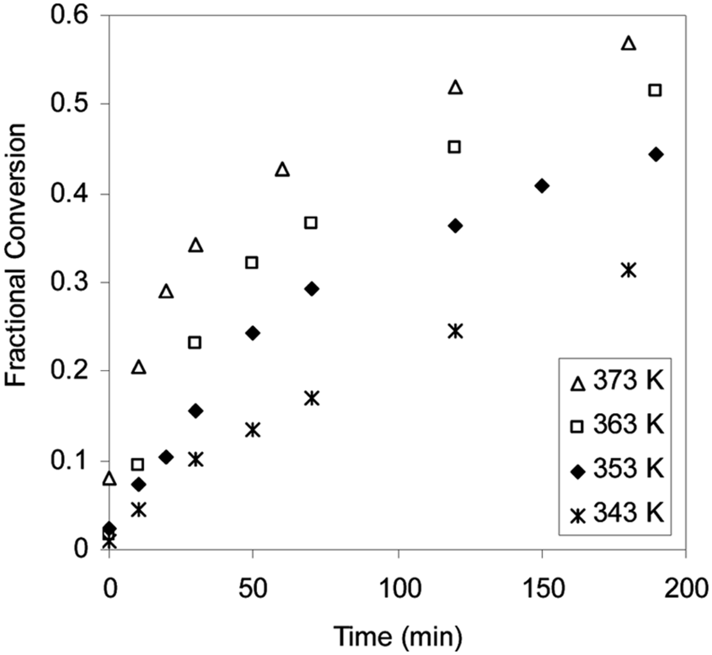


Figure 2. Effect of temperature on the acetic acid conversion (Catalyst loading: 5% (w/w), Speed of agitation: 1100 rpm, 2EHOH: AcH = 1:1).

Effect of Catalyst Loading. Figure 3 shows the effect of catalyst loading on the rate of the reaction. Catalyst loading was varied over a range of 0 to 20% w/w (wt of catalyst/wt of reactants) at 373 K, reactant mole ratio 1:1 and stirrer speed around 1100 rpm. It can be seen that the fractional conversion of acetic acid increases with an increase in catalyst loading due to a proportional increase in the number of active sites.

Effect of Mole Ratio. The mole ratio of 2-ethylhexanol to acetic acid was varied from 5:1 to 1:5 under otherwise similar conditions. Figure 4 shows that the fractional conversion of the limiting reactant increases with an increase in mole ratio. It was observed that fractional conversion of acetic acid goes up to as high as 95% for the mole ratio of 5:1.

Kinetic Modeling

Generally the kinetics of liquid phase reactions catalyzed by ion exchange resin is modeled by pseudo-homogeneous (PH) model,

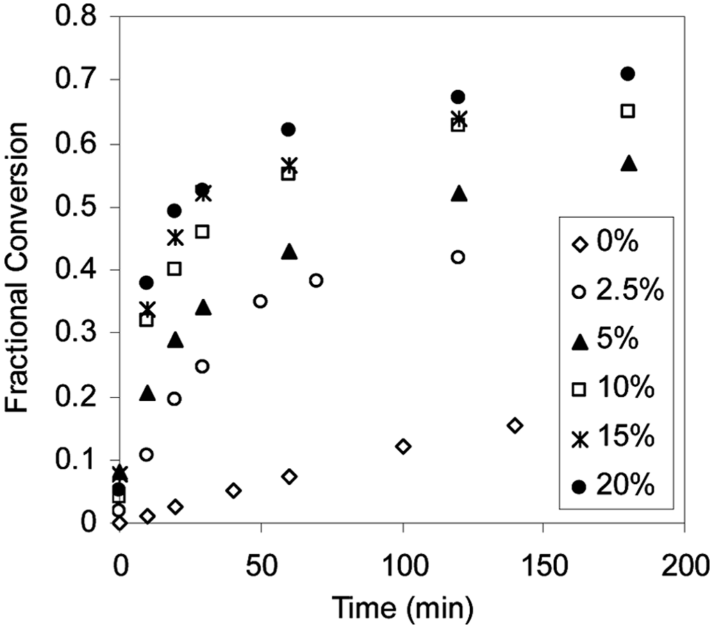


Figure 3. Effect of Catalyst loading (w/w) on the acetic acid conversion (Temperature = 373 K, Speed of agitation: 1100 rpm, 2EHOH: AcH = 1:1).

Langmuir-Hinshelwood (LH) model, Eley-Rideal (ER) model in the absence of any intra-particle diffusion limitations (9,7). Pseudo-homogeneous first order and second order models are generally applicable to highly polar reacting systems (12). We have used the Langmuir-Hinshelwood (LH) approach to explain our kinetic data available for different temperatures, catalyst loadings and mole ratios. Least square method was adopted to fit the kinetic data.

The parameters were estimated for the activity and concentration based kinetic models for which the rate expressions proposed for esterification reaction are as follows:

1) Concentration based LHHW model:

$$r_i = \left(\frac{V}{M_{cat}}\right)\frac{dC_i}{dt} = \frac{\nu_i(k_f C_{AcH} C_{2EHOH} - k_b C_{2EHAc} C_{H_2O})}{(1 + K_m C_{AcH} + K_w C_{H_2O})^2} \tag{1}$$

2) Activity based LHHW model:

$$r_i = \left(\frac{n}{M_{cat}}\right)\frac{dx_i}{dt} = \frac{\nu_i(k_f a_{AcH} a_{2EHOH} - k_b a_{2EHAc} a_{H_2O})}{(1 + K_m a_{AcH} + K_w a_{H_2O})^2} \tag{2}$$

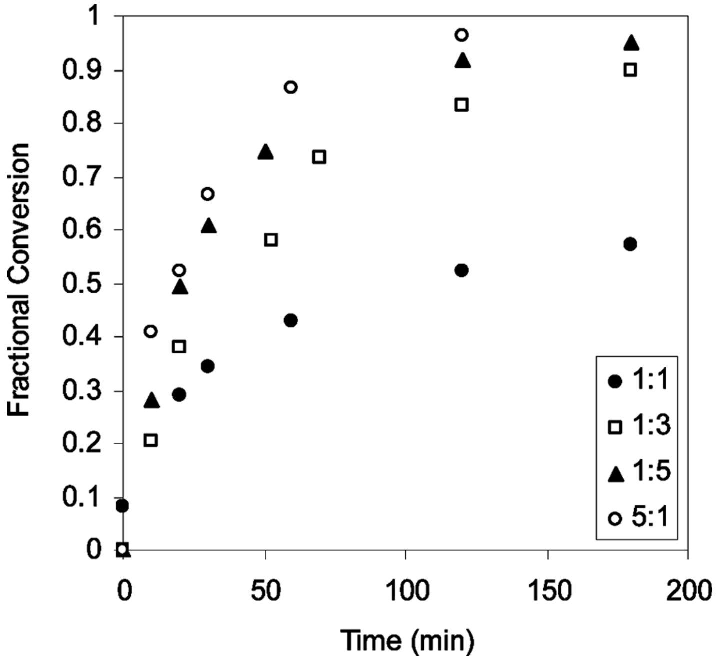


Figure 4. Effect of mole ratio (2EHOH: AcH) (Temperature = 373 K, speed of agitation: 1100 rpm, Catalyst loading = 5%).

Where, r_i and x_i are the rate of reaction and mole fraction of species i respectively. n, M_{Cat}, ν_i, V are the initial molar holdup, weight of catalyst, stoichiometric coefficient of species i and the volume of reaction mixture, respectively. a_{AcH}, a_{2EHOH}, a_{2EHAc}, a_{H_2O} are the activities of acetic acid, 2-ethylhexanol, 2-ethylhexyl acetate and water, respectively. Parameters K_m and K_w are the adsorption constants for acetic acid and water, respectively. Nonideal behavior of reaction mixture has been accounted for by taking activity $(a_i = x_i\gamma_i)$ of components. k_f and k_b are the forward and backward reaction rate constants. The temperature dependency of rate constants can be expressed as,

$$k_f = k_f^0 \exp(-E_f^0/RT) \tag{3}$$

$$k_b = k_b^0 \exp(-E_b^0/RT) \tag{4}$$

Where k_f^0, k_b^0 and E_f^0, E_b^0 are the Arrhenius pre-exponential factors and activation energies for forward and backward reactions, respectively. It is noted that affinities of Amberlyst-15 towards water and acetic acid are stronger than those of 2-ethylhexanol and 2-ethylhexyl acetate and

Table 2. Binary interaction parameters for UNIQUAC model (AspenPlus, 2001)

	Acetic acid	2-ethylhexanol	2-ethylhexyl acetate	water
Acetic acid	0	199.17	104.21	219.66
2-ethylhexanol	112.41	0	39.88	324.93
2-ethylhexylcetate	327.92	−91.65	0	540.63
Water	−73.44	−262.3	−182.55	0

hence the adsorption terms for 2-ethylhexanol and 2-ethylhexyl acetate are neglected in the model equations. It should be noted that the adsorption coefficients of the kinetic model are different than those determined later through breakthrough curve experiments. The adsorption coefficients in the kinetic model represent the interaction between species on the catalyst surface and that in the solution in the pores of the resin. The adsorption constants obtained from the breakthrough curves relate the concentration in bulk and that in the resin phase composed of pores and solid. The UNIQUAC model was used to calculate the activity coefficients of the components. The binary interaction parameters for few of the binaries i.e., acetic acid-2-ethylhexanol, acetic acid-water and 2-ethylhexanol-water, were obtained form Aspen data bank (13) using UNIQUAC model. For rest of the binaries UNIFAC method was used to calculate binary interaction parameters. The parameters thus obtained are given in Table 2 and Table 3.

The Aspen Custom Modeler (ACM) was used to estimate the parameters of LHHW model by regression. The program in ACM uses the least square method to minimize weighted absolute square error between the observed and modeled values. It determines the values of the parameters θ by solving the following minimization problem (13):

$$\mathrm{SSE} = \min\left\{\sum_{i=1}^{NDyn}\sum_{j=1}^{Nmeans}\sum_{k=1}^{M_{ij}} W_{ijk}^2\left(z_j(t_{ijk}) - z_{ikj}\right)^2\right\} \tag{5}$$

Subject to: $\theta^L \leq \theta \leq \theta^U$

Table 3. Volume parameters for UNIQUAC model (AspenPlus, 2001)

Components	R	Q
Acetic acid	2.19512	2.072
2-ethylhexanol	6.15095	5.208
2-ethylhexyl acetate	7.52406	6.352
Water	0.92	1.4

Table 4. Parameters of concentration based LHHW model (95% confidence limit)

Parameters	Values
E_f^0(J/mole)	72167.6 ± 1466.03
E_b^0(J/mole)	23582.9 ± 10370.8
k_f^0(Lt^2/Kg – mol – hr)	$2.18 \times 10^{11} \pm 1.67$
k_b^0(Lt^2/Kg – mol – hr)	9604.53 ± 28.78
K_m (Lt/mol)	0.081 ± 0.0066
K_w (Lt/mol)	0.36 ± 0.031
SSE	1.39×10^{-3}

Where $z_j(t_{ijk})$ are calculated by solving the model equations with the inputs and initial conditions corresponding to dynamic experiment i. The weight W_{ijk} is the user-specified value which reflects the importance of, or confidence in, the corresponding experimental measurement. In this case it has been assumed unity. The lower and upper bounds θ^L and θ^U are served to keep the parameters within physically realistic and/or mathematically acceptable limits. N_{Dym} is the total number of dynamic experiments performed; z_j is the number of variables, measured over all the experiments and which has dimension Nmeas. Mij is the number of measurements made in the experiment i (13).

Regression results obtained along with standard error in the parameters have been summarized in Table 4 and Table 5. Figure 5 shows parity plots for acetic acid, which show a good agreement between the predicted and experimental results. Parity plots and the obtained acceptable standard errors in the parameters prove that both the models perform satisfactory. These two models will be further used in the simulation of reactive chromatography and the choice of the model will be determined based on the agreement with the experimental results.

Table 5. Parameters for activity based LHHW model (95% confidence limit)

Parameters	Values
E_f^0(J/mole)	75783.2 ± 1484.21
E_b^0(J/mole)	40104.7 ± 14536.6
k_f^0(mole/Kg – hr)	$8.63 \times 10^{13} \pm 1.69$
k_b^0(mole/Kg – hr)	$1.88 \times 10^{7} \pm 110.49$
K_m	0.11 ± 0.06
K_w	1.29 ± 0.11
SSE	2.3×10^{-3}

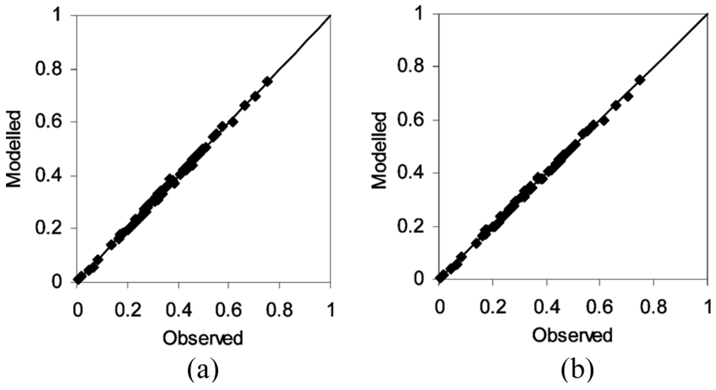


Figure 5. Parity plots for the mole fraction of acetic acid (a) Activity based kinetic model (b) Concentrations based kinetic model.

REACTIVE CHROMATOGRAPHY

Apparatus and Procedure

As shown in Fig. 6, the apparatus consists of a jacketed column of internal diameter 1.5 cm and height 70 cm packed with resins Amberlyst-15. Ethylene glycol was circulated through the jacket of the reactor to maintain the desired temperature. Temperature was measured at the top and middle of the reactor. Feed mixture was introduced from the bottom of the column at a constant flow rate using a peristaltic pump. Outlet samples were collected at fixed time intervals and were analyzed with the help of GC. Experiments were performed at isothermal temperature and atmospheric pressure. Figure 6 shows the experimental setup used for the fixed bed chromatographic reactor.

Multicomponent Adsorption Equilibria

When a liquid mixture is passed through the porous solid adsorbent material, all the components adsorb on the solid particles to an extent depending on their affinities towards the solid. If the physical adsorption is very fast compared to convection then local equilibria given by adsorption isotherm will exist close to the adsorbent surface at given temperature. Although there are many types of isotherms used in practice for liquid systems, normally three isotherms are very common and these are linear, Langmuir and Freundlich isotherms. An excellent review on measurement and analysis on liquid phase adsorption isotherm has been

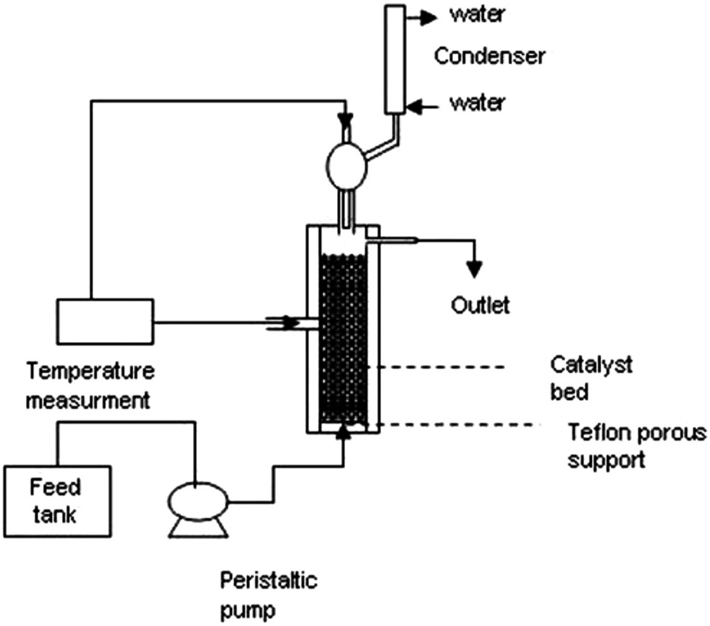
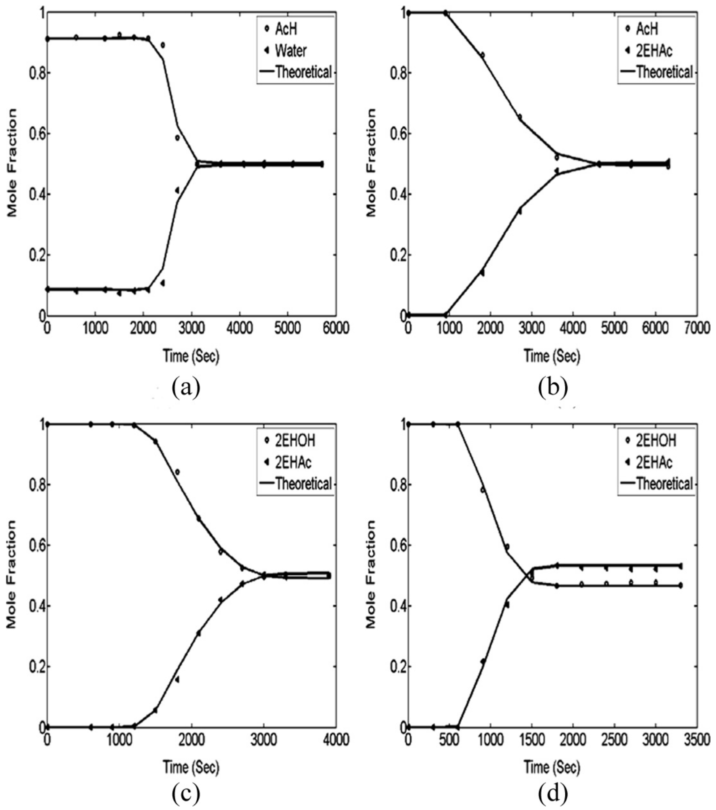


Figure 6. Experimental setup of reactive chromatography.

presented by Morgenstern (14). In our case, Langmuir isotherm model was assumed to govern the multicomponent adsorption equilibria and is given by equation (6).

$$\Gamma_i = \frac{K_i \Gamma_i^{\infty} c_i^L}{1 + \sum_{j=1}^{N} K_j c_i^L} \tag{6}$$

Γ_i and c_i^L are the concentrations of the ith component in the adsorbed and bulk liquid phases, respectively; K_i and Γ_i^{∞} are the adsorption equilibrium constant and capacity of component i respectively; and N is the total number of components in the liquid mixture. Adsorption isotherm can be determined by performing several experiments. There are various methods used to determine the adsorption isotherm and are summarized by Morgenstern (14). The static (batch and adsorption-desorption) methods are more tedious, less computationally expensive and sometimes inaccurate. Dynamic methods such as frontal analysis, perturbation method, inverse method etc. are found to be more accurate, computationally expensive but less time consuming (14). In our case, inverse dynamic method has been chosen for determining the adsorption parameters.



(a) (b)

(c) (d)

Figure 7. Binary adsorption experiments with model predictions (a) acetic acid-water, flow rate = 2 ml/min, mole ratio = 1:1, catalyst weight = 43.35 gms, T = 80°C; (b) acetic acid-2-ethylhexyl acetate, flow rate = 2 ml/min, mole ratio = 1:1, catalyst weight = 43.12 gms, T = 80°C; (c) 2-ethylhexanol-2-ethylhexyl acetate, flow rate = 2 ml/min, mole ratio = 1:1, catalyst weight = 45 gms, T = 80°C; (d) 2-ethylhexanol -2-ethylhexyl acetate, flow rate = 4 ml/min, mole ratio = 1:1, catalyst weight = 45 gms, T = 80°C.

Binary Adsorption Experiments

Adsorption parameters (K_i and Γ_i^{∞}) in equation (6) for all the components involved in the mixture are not available in the literature and hence the experiments were performed to estimate these values. Non-reactive binary mixtures were chosen such that the components are completely miscible. Three binary mixtures fulfilling these criteria are acetic acid-water, acetic acid-2-ethylhexyl acetate and 2-ethylhexanol-2-ethylhexyl acetate, respectively. The water-2-ethylhexanol binary was sparingly miscible and hence this combination was not used for the experiment. All these experiments were conducted in a fixed bed chromatographic reactor setup described before and the breakthrough curves are determined. The adsorbent was initially saturated with one of the components in the mixture and then the feed mixture was introduced to the column to obtain the breakthrough curves. These experiments were conducted at different temperatures and flow rates till the saturation is achieved.

Estimation of Adsorption Parameters

The breakthrough curves obtained are shown in the Fig. 8. For a four-component mixture Langmuir model requires the estimation of 8 parameters (K_i and Γ_i^{∞}). These parameters were obtained by minimizing the sum of squares of error between the experimental and predicted breakthrough curves. The mathematical model for the breakthrough curve is quite similar to FBCR model with the exclusion of the reaction terms. The model for the FBCR is described in the next section.

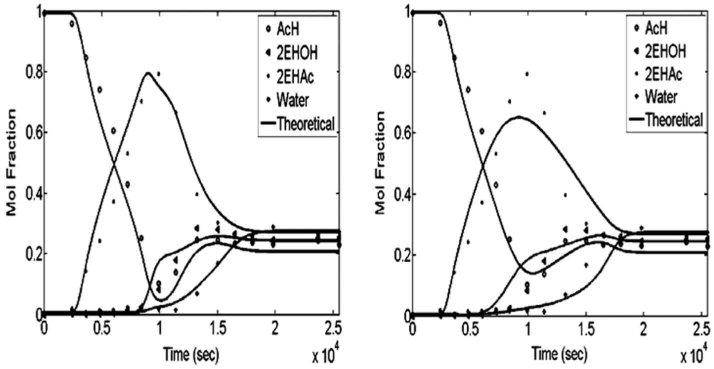
Adsorption parameters were estimated by using MATLAB function named Lsqnonlin. Lsqnonlin is the inbuilt function of MATLAB which can be directly used for non-linear least square regression. The adsorption parameters thus obtained are given in Table 6. Figure 7 shows a good agreement with the model results. The adsorption capacities were independently confirmed by measuring the area under the breakthrough curves.

Modeling of Fixed Bed Chromatographic Reactors

Various modeling approaches for FBCR are reported in the literature by considering the reaction, adsorption equilibria, mass transport between the fluid and solid phase and non-ideality in terms of axial dispersions (1,6). We use a model that accounts for the multi-component adsorption equilibrium, reaction kinetics and isothermal condition. The model also accounts for the axial dispersion in the reactor. It has been assumed that

Table 6. Estimated parameters of multicomponent Langmuir isotherm

Components	K(cm^3/mol)	Γ^{∞}(mmol/gm)
Acetic acid	413.20	22.35
2-ethylhexanol	284.52	7.4
2-ethylhexyl acetate	196.12	2.55
Water	1232.02	45.3



(a) (b)

Figure 8. Comparison of experiments (points symbol) and simulation (solid line) results of the FBCR (a) activity based kinetic model (b) concentration based kinetic model (Reactor height = 70 cm, reactor diameter = 1.5 cm, catalyst = 39.46 gms, flow rate = 1 ml/min, Mole ratio (2EHOH: AcH = 1:1), T = 80°C).

the resin phase concentration is in equilibrium with that in the bulk liquid. The change in the adsorbent volume due to swelling has been ignored, and the superficial liquid velocity of the liquid (v) is assumed to be constant.

The mathematical model for the fixed bed chromatographic reactor can be given by applying the mass balance for each component i, which turns out to be

$$\frac{\partial c_i^L}{\partial t} + \frac{(1-\varepsilon)}{\varepsilon}\rho_p\frac{\partial \Gamma_i}{\partial t} = -\frac{v}{\varepsilon}\frac{\partial c_i^L}{\partial z} + \varepsilon E\frac{\partial^2 c_i^L}{\partial z^2} + \frac{(1-\varepsilon)}{\varepsilon}\rho_p r_i \tag{7}$$

where c_i^L and Γ_i are the concentrations of the *ith* component in the bulk liquid phase and in the adsorbed phase respectively; E is the axial dispersion coefficient; ε is the interparticle bed void fraction, ρ_p is the adsorbent density, r_i is the net production rate of the *ith* component.

Danckwert's boundary conditions are given by equation (8) and (9),

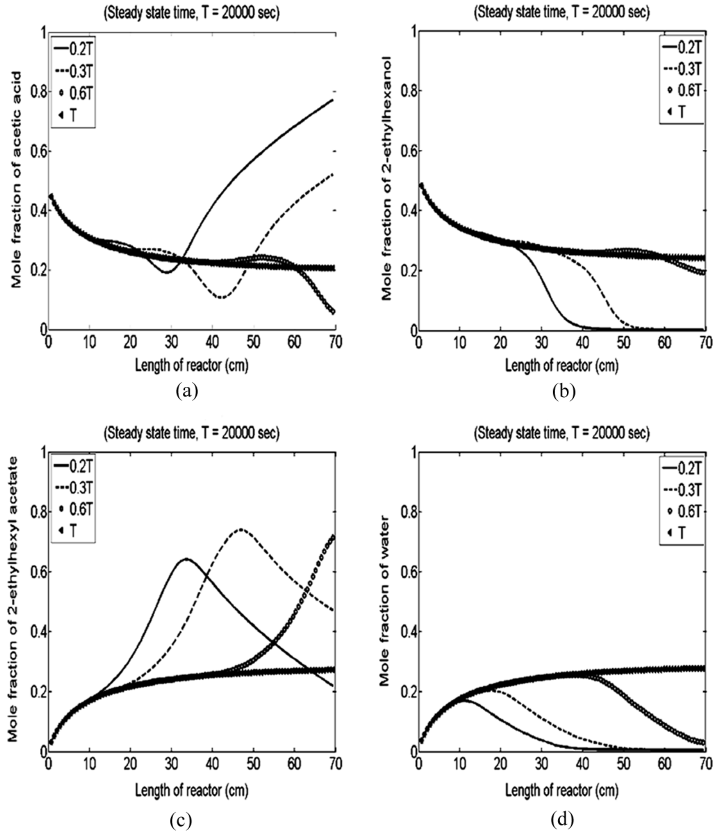
$$vc_i^F(t) = vc_i^L(0,t) - \varepsilon E\frac{\partial c_i^L}{\partial z}(0,t) \tag{8}$$

$$\varepsilon E\frac{\partial c_i^L}{\partial z}(L,t) = 0 \tag{9}$$

The initial conditions are,

$$c_i^L(z,0) = c_i^0(z) \tag{10}$$

Equation (7) was solved together with the boundary and initial conditions given in equation (8–10), the kinetic model given in equation (1) or (2) and the adsorption equilibria i.e. equation (6). The method of lines was used to solve the equations. Space discretization was performed using finite backward difference method to convert the set of PDEs to several coupled ODE-IVPs. The discretized equations were integrated using ode15s solver of MATLAB. Both the kinetic models developed, i.e. concentration based and activities based, were used to predict the results under the experimental condition. The correlation used to



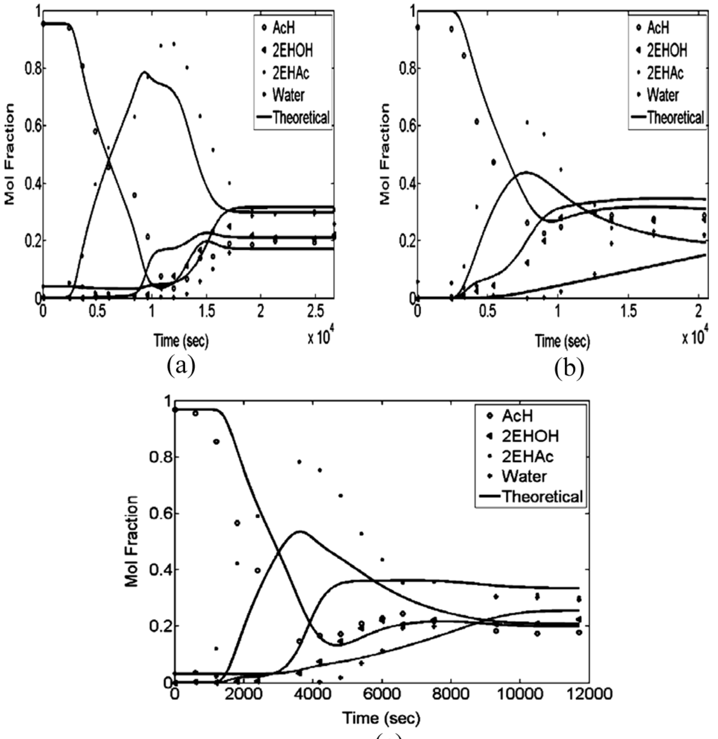
(a) (b) (c) (d)

Figure 9. Concentration profile of species inside the column at different time (a) Acetic acid (b) 2-ethylhexanol (c) 2-ethylhexyl acetate (d) water.

determine the model parameters e.g, axial dispersion coefficient; viscosities etc. are given in appendix.

Results and Discussions

Reactive chromatography experiments were performed in the same setup that is used for the adsorption experiment as shown in Fig. 6. Feed used was the mixture of 2-ethylhexanol and acetic acid which was continuously passed through the bottom of the fixed bed chromatographic reactor that is packed with Amberlyst-15 and initially saturated with acetic acid. The outlet concentration was measured with



(a)

(b)

(c)

Figure 10. Outlet mole fraction of the chromatographic reactor (a) (Temperatutre = 90°C, catalyst = 42 gms, flow rate = 1 ml/min); (b) (Temperatutre = 60°C, catalyst = 43.39 gms, flow rate = 1 ml/min); (c) (Temperatutre = 80°C, catalyst = 43.2 gms, flow rate = 2 ml/min); (Reactor height = 70 cm, reactor diameter = 1.5 cm, Mole ratio (2EHOH: AcH = 1:1)).

respect to time. From Table 6, the order of affinity of all the components towards resin are water > acetic acid > 2-ethylhexanol > 2-ethylhexyl acetate. The product, 2-ethylhexyl acetate with least adsorbtivity desorbs fast as compared to other components while water, which has highest adsorbtivity elutes, very late. This preferential adsorption leads to the separation of 2-ethylhexyl acetate and water, and also helps to increase the rate of reaction. Figure 8(a) shows the reactive breakthrough curves for each species and the corresponding model predictions using activity based reaction kinetics. A reasonable agreement was observed between model predictions and experimental predictions. Figure 8(b) depicts the same simulation and experimental result with concentration based rate model, which does not show very good agreement with experiments. The activity based rate model is thus recommended for simulations.

The breakthrough curves indicate a clear potential for the use of reactive chromatography as one can perform the operation for a suitable time period (say 10000 sec) to obtain the desired ester with relatively high purity and subject the column to regeneration. Here, two concentration fronts were observed namely reaction-adsorption front and reactive front. The profiles can be better understood by examining the concentration profile inside the column obtained by simulation using the experimentally validated model. Figure 9 shows the composition profiles for all species along the column length using the same operating

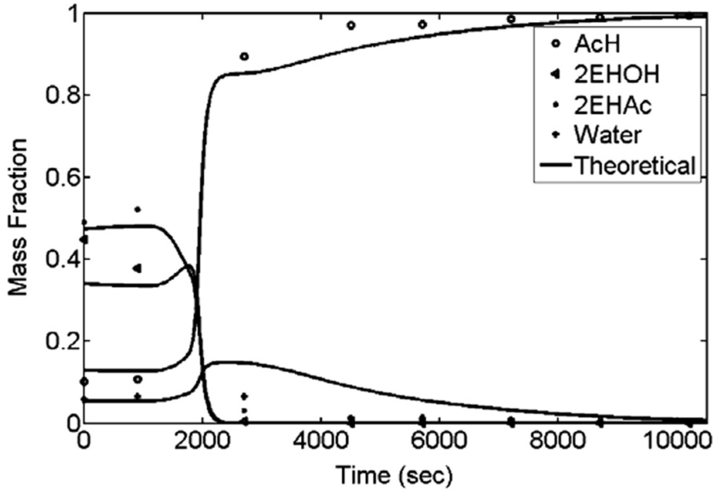
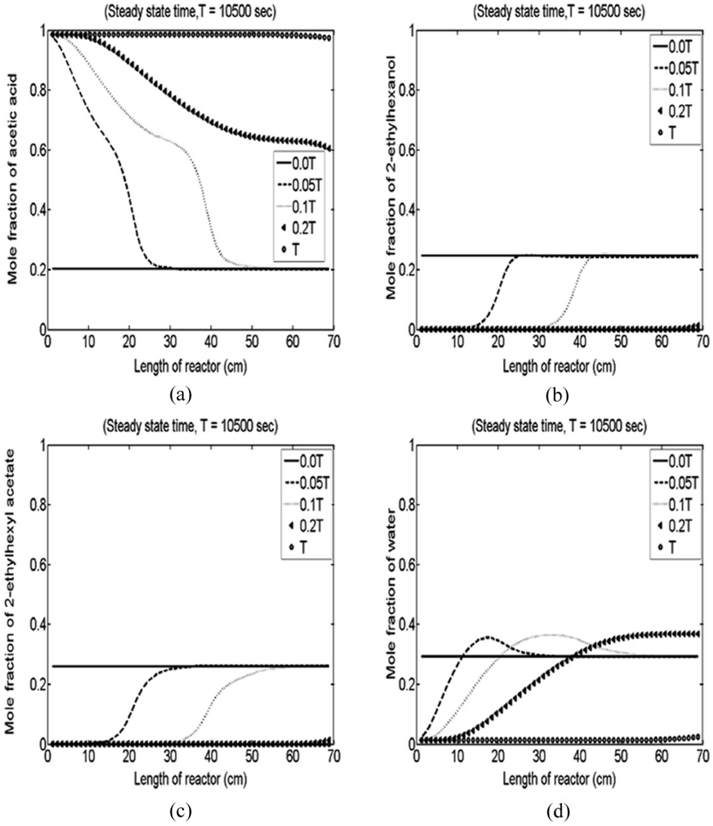


Figure 11. Regeneration experiment (Reactor height = 70 cm, reactor diameter = 1.5 cm, catalyst = 42 gms, flow rate = 2 ml/min, Temperature = 80°C).

condition mentioned in Fig. 8(a) at different times 0.2 T, 0.3 T, 0.6 T and at steady state time (T = 20000 sec), respectively. The shock waves for the individual components can be clearly seen to be traveling through the column. This behavior gets reflected in the outlet composition already shown Fig. 8.

Effect of various parameters like temperature and flow rate on the column dynamics was studied. The results of these experiments are shown in Fig. 10. It was observed from Fig. 10 that their qualitative behavior is the same but the width and the height of the peak for 2-ethylhexyl acetate increases with increase in temperature. It was expected because adsorption is inversely proportional to temperature. Figure 10(c) shows the



(a) (b) (c) (d)

Figure 12. Concentration profile of species inside the column at different time during regeneration experiments (a) Acetic acid (b) 2-ethylhexanol (c) 2-ethylhexyl acetate (d) water (Reactor height = 70 cm, reactor diameter = 1.5 cm, catalyst = 42 gms, flow rate = 2 ml/min, Temperature = 80°C).

effect of flow rate on the dynamics of breakthrough experiment, and as expected the peaks are sharper with increased flow rate. The model also captures these effects reasonably well. Considering the sensitivity of the results to the model parameters and the complexity involved in multicomponent adsorption accompanied by the reaction, we consider the predictions of this simplified model are reasonable.

Normally in reactive chromatography one of the reactants is chosen as the solvent used for regeneration. In this case acetic acid is considered to be the suitable solvent. Regeneration experiments were also performed by passing pure acetic acid feed through the saturated column once the steady state is achieved. Figure 11 shows the experimental and predicted profiles of the regeneration step, here we observe that 2-ethylhexyl acetate and 2-ethylhexanol being relatively less absorbable species desorbs fast and water with the highest affinity to adsorbent desorbs late. Model predictions in this case were also found to be satisfactory. Figure 12 shows the composition profiles for all the species along the column length using the same operating conditions mentioned in Fig. 11 at different times 0.0 T, 0.05 T, 0.1 T, 0.2 T and at steady state time (T = 10500 sec), respectively.

The movement of reaction front inside the column can be examined by determining the rate profile along the column length at different times.

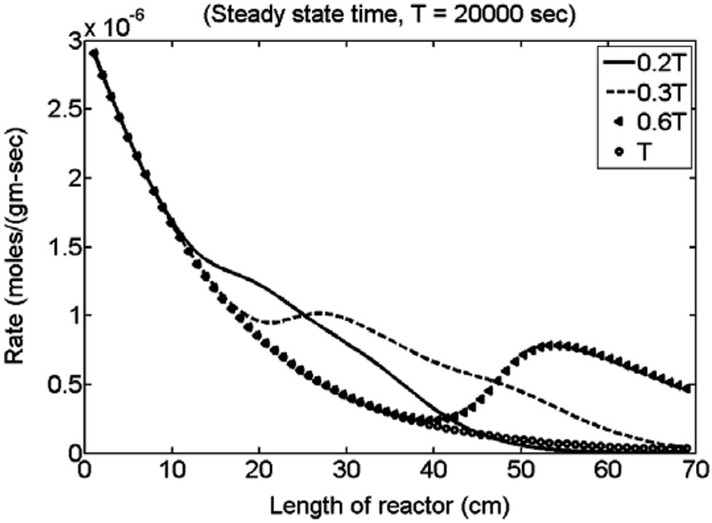


Figure 13. Reaction rate profile along the column length at different time (Reactor height = 70 cm, reactor diameter = 1.5 cm, catalyst = 39.46 gms, flow rate = 1 ml/min, Mole ratio (2EHOH: AcH = 1:1), T = 80°C).

Figure 13 shows the profiles of rate at times 0.2 T, 0.3 T, 0.6 T and steady state (T = 20000 sec). Here, we observe that rate in the dynamic regions (0.2 T, 0.3 T, and 0.6 T) are always greater than the rate obtained at steady state case. This implies that the overall conversion in the case of RC per weight of the catalyst is higher than the conventional steady state fixed bed reactor. It proves that the use of reactive chromatography for this system would enhance the overall process performance. The improvement will be realized not only through the enhancement in the rate and hence the reduced reactor volume but also through the partial separation of the species involved thereby reducing the capital and energy cost of downstream processing.

CONCLUSIONS

The esterification of acetic acid with 2-ethylhexanol is a reversible reaction and simultaneous removal of the product 2-ethylhexyl acetate and water through chromatography helps to enhance rate of reaction. The separation also helps to reduce the cost of downstream processing and hence reactive chromatography is the promising option for this reaction. Amberlyst-15, an ion exchange resin, is a suitable bifunctional material which plays the role of catalyst and as well as adsorbent. The mathematical model developed for the fixed bed chromatographic reactor explains the experimental results reasonably well and can be further used for the design of the continuous reactors such as simulated moving bed reactors (SMBR).

NOMENCLATURE

a_i	Activity of species i
C_i, C_i^L	Bulk concentration of species i, Mole/L
d_p	Particle diameter, mm
E	Axial dispersion coefficient, cm^2/sec
E_f^0, E_b^0	Activation Energy of forward and backward reaction, J/mole
k_f^0, k_b^0	Arrhenius pre exponential factor for forward and backward rate constant, mole/g.hr
k_f, k_b	Forward and backward rate constant, mole/g.hr
K_i	Adsorption constant of species i
K_m	Adsorption constant of acetic acid
K_w	Adsorption constant of water
M_{cat}	Weight of Catalyst, gm
n	Initial molar holdup
N_{Dym}	Total number of dynamic experiments

N_{Meas}	Total number of measurement per experiment
Q	Surface parameter of Uniquac model
q	Volumetric flow rate, ml/min
r_i	Rate of the reaction of species i, mol/(gm-sec)
R	Volume parameter of Uniquac model
v	Superficial velocity of liquid, cm/sec
V	Average Volume of liquid mixture, Litre
x_i	Mole fraction of species i
Z	Measured variable
SSE	Sum of Square Error
FBCR	Fixed bed chromatographic reactor

Greek Letters

υ_{i}	Stoichiometric Coefficient of species i
θ	Generic parameters
θ^L	Lower limit of parameters
θ^U	Upper limit of parameters
γ_i	Activity coefficient of species i
Γ_i^∞	Adsorption capacity of component i, mole/gm
Γ_i	Adsorbed phase concentration of component i, mole/gm
ρ_p	Density of dry adsorbent particle, gm/L
ε	Interparticle bed void fraction
$\mathrm{R_e}$	Reynolds's number
ρ_i, ρ_{mix}	Density of component i and liquid mixture, gm/L
μ_i, μ_{mix}	Viscosity of component i and liquid mixture, poise

Subscripts

AcH	Acetic Acid
2EHOH	2-ethyl hexanol
2EHAc	2-ethylhexyl acetate
H_2O	Water

REFERENCES

1. Lode, F.; Houmard, C.; Migliorini, C.; Mazzoti, M.; Morbidelli, M. (2001) Continuous annular chromatography. *Chem. Engg. Sci.*, *56*: 269–291.
2. Mazzotti, M.; Kruglov, A.; Neri, B.; Gelosa, D.; Morbidelli, M. (1996) Continuous chromatographic reactor: SMBR. *Chem. Engg. Sci.*, *51*: 1827–1836.
3. Gelosa, D.; Ramaioli, M.; Valente, G.; Morbidelli, M. (2003) Chromatographic reactors: Esterification of glycerol with acetic acid using acidic polymeric resins. *Ind. Eng. Chem. Res.*, *42*: 6536–6544.
4. Gandi, G.K.; Silva, V.M.T.M.; Rodrigues, A.E. (2006) Synthesis of 1,1-Dimethoxyethane in a fixed bed adsorptive reactor. *Ind. Eng. Chem. Res*, *45*: 2032–2039.

5. Zhang, Z.; Hidajat, K.; Ray, A.K. (2001) Application of simulated counter current moving bed chromatographic reactor for MTBE synthesis. *Ind. Eng. Chem. Res.*, *40*: 5304–5316.
6. Kawase, M.; Inoue, Y.; Araki, T.; Hashimoto, K. (1999) The simulated moving-bed reactor for production of bisphenol A. *Catalysis Today*, *48*: 199–209.
7. Chakrabarti, A.; Sharma, M.M. (1993) Cationic ion exchange resins as catalyst. *Reactive Polymers*, *20*: 1–45.
8. Mahajani, S.M. (2000) Reactions of glyoxalic acid with aliphatic alcohols using cationic exchange resins as catalysts. *React. Funct. Polym.*, *43*: 253–268.
9. Gangadwala, J.; Mankar, S.; Mahajani, S.; Kienle, A.; Stein, E. (2003) Esterification of acetic acid with butanol in the presence of ion - exchange resin as catalysts. *Ind. Eng. Chem. Res*, *42*: 2146–2155.
10. Teo, H.T.R.; Saha, B. (2004) Heterogeneous catalyzed esterification of acetic acid with isoamyl alcohol: kinetic studies. *Journal of Catalysis*, *228*: 174–182.
11. Ragaini, V.; Bianchi, C.L.; Pirola, C. (2007) Kinetics of esterification of diluted acetic acid with pure 2-ethyl-1-hexanol. *Chemical Eng. J.*, *131*: 257–262.
12. Saha, B.; Streat, M. (1999) Transeesterification of cyclohexyl acrylate with n-butanol and 2-ethylhexanol: acid treated clay, ion exchange resin and tetrabutyl titanate as catalysts. *Reactive and Functional Polymers*, *40*: 13–27.
13. AspenPlus. (2001) Aspen Technology Inc. ASPEN 11.1.
14. Morgenstern, A.S. (2004) Experimental determination of single solute and competitive adsorption isotherms. *J. Chromatogr. A*, *1037*: 255–272.
15. Chung, S.F.; Wen, C.Y. (1968) Longitudinal dispersion of liquid moving through fixed and fluidized beds. *AIChe J.*, *17*: 857–874.
16. Reid, R.C.; Sherwood, T.K. (1966) *The properties of gases and liquids: their estimation and correlation*; McGraw-Hill Book: NewYork.

APPENDIX: CALCULATION OF MODEL PARAMETERS

Voidage: Voidage of the bed was determined experimentally and it was found to be 0.42 which matches well with the one reported in the literature (Gelosa et al, 2003). The internal porosity of the resin particle reported by the supplier is 0.36.

Axial dispersion: Axial dispersion coefficients were estimated using the relation given by Chung and Wen (15) with the average particle diameter of 0.5 mm.

$$E = \frac{vd_p}{(0.2 + 0.011 R_e^{0.48})} \tag{A.1}$$

Here, R_e, ρ_{mix}, μ_{mix}, v, d_p are the Reynolds number, density of mixture, viscosity of mixture, superficial velocity and particle diameter, respectively.

$$R_e = \frac{vd_p\rho_{mix}}{\mu_{mix}} \tag{A.2}$$

$$\rho_{mix} = \frac{1}{\sum \frac{x_i}{\rho_i}} \tag{A.3}$$

Viscosity: Viscosity of liquid mixture was calculated by the given relation below (16).

$$\ln \mu_{mix} = \sum_i x_i \ln \mu_i \tag{A.4}$$

x_i, μ_i, ρ_i are the mole fraction in bulk liquid phase, viscosity and density of component *i* respectively. The viscosity of acetic acid, 2-ethylhexanol and 2-ethylhexyl acetate were calculated at given temperature by using Orrick and Erbar Method (16). Orrick and Erbar method employs the group contribution technique to estimate its parameters A and B in equation (A.5),

$$\ln \frac{\mu_i}{\rho_i M_i} = A + \frac{B}{T} \tag{A.5}$$

Here liquid viscosity is in cP, density at 20°C in gm/cc, M_i is molecular weight of component i and temperature are in gm/gmol and K, respectively. Makhija and Stairs correlation (16) were used to calculate viscosity of water being highly polar component.

$$\ln \mu_i = A' + \frac{B'}{T - T'} \tag{A.6}$$

Here A', B', T' are the parameters of their correlation obtained for different liquids over a particular temperature range.