Liquid-Phase Sorption-Enhanced Reaction Process

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A process for carrying out simultaneous liquid-phase reaction and separation of desired products is described. It uses a fixed packed column of an admixture of a catalyst and an adsorbent that selectively removes a reaction byproduct from the reaction zone. The adsorbent is periodically regenerated using the concepts of liquid-phase concentration swing adsorption. The integrated process allows production of multiple products at high purity with high conversions. For an endothermic reaction, the process permits much higher conversions of reactants to products at a substantially lower temperature than would be necessary by a plug-flow reactor using the catalyst alone. The concept is demonstrated for hydrolysis of methyl acetate to produce acetic acid and methanol.

Introduction

A gas-phase sorption-enhanced reaction process (SERP) was recently developed for directly producing a high purity reaction product at high conversion from an endothermic equilibrium-controlled reaction (Carvill et al., 1996; Hufton et al., 1999). The process used an admixture of a catalyst and an adsorbent in a packed column that acted as a simultaneous adsorber-reactor. The adsorbent selectively removed the undesired reaction products from the reaction zone. This increased the conversion and the rate of formation of the desired reaction product according to the Le Chatelier's principle. The adsorbent was periodically regenerated (adsorbed components removed) by using the principles of pressure swing adsorption (PSA).

The process was successfully used to produce: (a) CO by reacting CO_2 and H_2 (reverse water gas shift reaction, RWGS); (b) H_2 by reacting CH_4 and H_2O (steam-methane reforming, SMR). A major advantage of the SERP concept was that high conversions of both CO and H_2 products were achieved at a much lower reaction temperature than would be necessary if the reactions were carried out in a conventional plug-flow reactor using the catalyst alone. The specific design of the steps of the gas-phase SERP produced the desired products at a much higher purity than would be possible by the catalyst only case (which is governed by the thermodynamic chemical equilibria under the reaction conditions). Thus, the SERP concept reduced or eliminated the subsequent product purification steps.

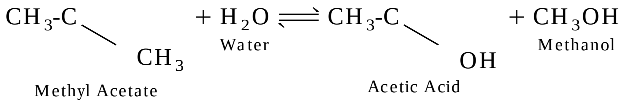
The above described advantages of carrying out equilibrium-controlled reaction using an admixture of a catalyst and an adsorbent can also be utilized to improve the equilibrium conversion of the desired reaction product in a liquid-phase reaction. Two recent publications proposed the use of continuous simulated moving bed (SMB) reactors where the catalyst also acted as the selective sorbent for an undesired reaction product (Mazzotti et al., 1996; Funk et al., 1996). Esterification of acetic acid with ethanol and hydrolysis of esters were studied as the liquid-phase equilibrium-controlled reactions by these authors. The advantages of Le Chatelier's principle for producing ethyl acetate by esterification of acetic acid over a mixture of a catalyst and an adsorbent (alumina) was also demonstrated using a liquid chromatography arrangement (Sardin and Villermaux, 1979).

The purpose of the present work is to propose a fixed-bed SERP concept for endothermic, equilibrium-controlled, liquid-phase reactions that can be used to produce essentially pure reaction products with high conversions while operating the reactor at a relatively low temperature.

Reaction System, Catalyst, and Adsorbent

Reaction system

We studied the equimolar hydrolysis of methyl acetate to form acetic acid and methanol in the liquid phase



$$CH_3\text{-}C(=O)CH_3 + H_2O \rightleftharpoons CH_3\text{-}C(=O)OH + CH_3OH \qquad (1)$$

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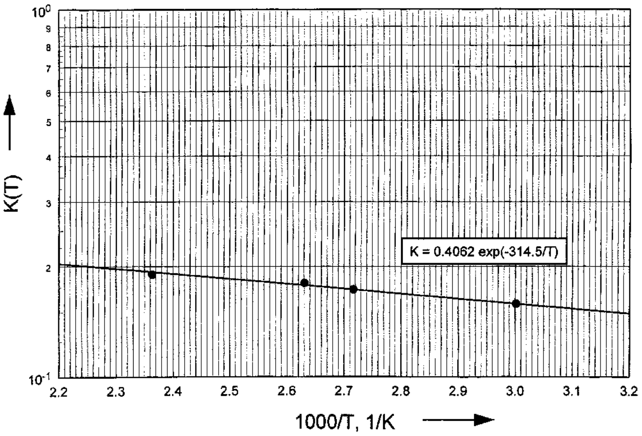

Figure 1. Temperature dependence of chemical equilibrium constant for methyl acetate hydrolysis reaction.

This reaction is endothermic with a heat of reaction of only 0.625 Kcal/mol. The equilibrium constant (K) for the reaction is defined by

$$K(T)=\frac{x^*_{CH_3OH}\cdot x^*_{C_2H_4O_2}}{x^*_{C_3H_6O}\cdot x^*_{H_2O}} \tag{2}$$

where x_i^* is the equilibrium bulk liquid-phase mole fraction of component i (methyl acetate, water, acetic acid, methanol). K is a function of temperature (T) only. Figure 1 shows the temperature dependence of K, measured in our laboratory, which can be described by the following relationship

$$K=0.4062\exp\left[-314.5/T\right] \tag{3}$$

Catalyst

A commercially available (Rohm and Haas Corp.) ion-exchange resin called Amberlyst A-15 was used as the catalyst for the reaction of Eq. 1. The reaction rate was virtually nil without the catalyst. The catalyst, however, was structurally stable only below 150°C.

Adsorbent

We used a commercial liquid-phase activated carbon (Calgon Corp.) called OL-Carbon as the selective adsorbent for acetic acid in the presence of methanol, methyl acetate, and water. Liquid-phase surface excess isotherms were measured on the carbon at 30°C for most of the binary pairs of interest using a standard technique (Sircar and Myers, 1971). A gas chromatograph was used to analyze the liquid mixtures before and after contact with the carbon. Figure 2 shows the binary surface excess isotherms. The acetic acid-methanol (Figure 2a), acetic acid-water (Figure 2b), and acetic acid-methyl acetate (Figure 2c) isotherms exhibit positive surface excesses for acetic acid in most of the concentration ranges indicating that acetic acid is selectively adsorbed over the other components from these mixtures (Sircar and Myers, 1970). The methyl acetate-methanol (Figure 2d) surface excess isotherm shows that methyl acetate is selectively adsorbed over methanol.

The differences between the pure component surface potentials (ϕ_i^o) for each binary mixture ($i=1{,}2$) of Figure 2 were

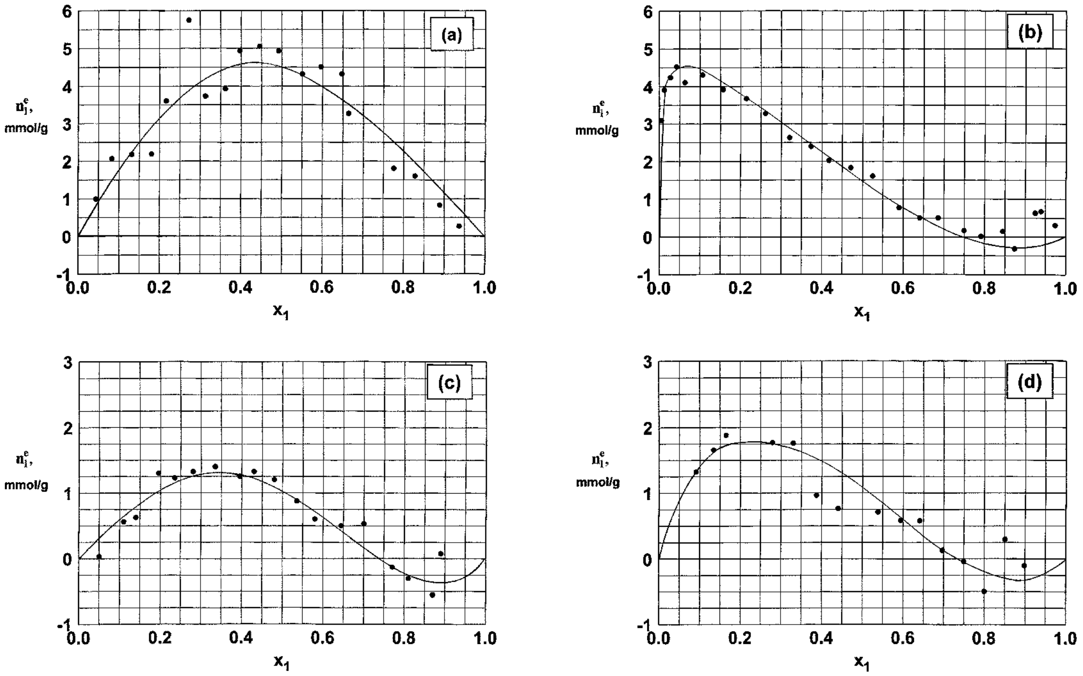

Figure 2. Binary surface excess isotherms on OL-Carbon at 30°C.

(a) Acetic acid (1) + methanol (2); (b) acetic acid (1) + water (2); (c) acetic acid (1) + methyl acetate; (d) methyl acetate (1) + methanol (2).

calculated using the integrated form of the isothermal Gibbs adsorption equation (Sircar and Myers, 1971)

$$\frac{(\phi_2^o - \phi_1^o)}{\mathrm{RT}} = \int_o^1 \frac{n_1^e da_1}{a_1 x_2} \tag{4}$$

where n_1^e is the surface excess of component 1 (binary system) at an equilibrium liquid-phase mole fraction of x_i for component i at temperature T. The variable $a_i(= x_i \gamma_i)$ is the activity of component i at x_i and T, and γ_i is the corresponding activity coefficient of component i. R is the gas constant.

Table 1 shows the values of the quantities $[(\phi_2^0 - \phi_1^0)/\mathrm{RT}]$ for the systems of interest. They were obtained by using Eq. 4, the experimental data of Figure 2, and the vapor-liquid equilibrium data for the binary pairs of interest (Gmehling et al., 1981). A positive value of the quantity $[(\phi_2^0 - \phi_1^0)/\mathrm{RT}]$ indicates that component 1 is more selectively adsorbed over component 2. The larger the value is of the difference between ϕ_1^0 and ϕ_2^0, the higher is the selectivity of adsorption of component 1 over component 2 (Sircar and Myers, 1970). Thus, Table 1 shows that acetic acid is very selectively adsorbed over water and ethanol by the OL-Carbon, and the selectivity of its adsorption over methyl acetate is moderate. Table 1 also shows that methyl acetate is selectively adsorbed over methanol by the carbon. It can be easily shown from the data of Table 1 that water is selectively adsorbed over methanol

$$\left[\left(\phi^o_{\mathrm{CH_3OH}} - \phi^o_{\mathrm{H_2O}}\right)/\mathrm{RT} = 4.7 \text{ mol/kg}\right]$$

and methyl acetate is selectively adsorbed over water

$$\left[\left(\phi^o_{\mathrm{H_2O}} - \phi^o_{\mathrm{C_3H_6O}}\right)/\mathrm{RT} = 12.1 \text{ mol/kg}\right]$$

by the carbon. Thus, the order of selectivity of adsorption on the carbon is acetic acid > methyl acetate > water > methanol. Consequently, the carbon can be used to selectively remove the acetic acid from the reaction zone for methyl acetate hydrolysis and that will favor the production of methanol by the liquid-phase SERP concept.

Batch demonstration of SERP concept

We measured the isothermal, liquid-phase kinetics of reaction 1 in a well-stirred batch reactor (thermostated glass beaker) in the presence of the catalyst only. An initial liquid mixture (71.5 g) of 35.5 mol % methyl acetate and 64.5 mol % water was contacted with the catalyst (7 g) at 53°C, and the bulk liquid-phase mole fraction of methanol was measured as a function of time. Figure 3a shows the results. The methanol composition in the reactor was initially zero and then it gradually increased to a constant level which was dictated by the chemical equilibria for the reaction at the reaction temperature. We then repeated the experiment under identical conditions but in the presence of the OL-Carbon (10 g). Figure 3b shows the results. Finally, the experiment was again repeated in the presence of the carbon, but without the catalyst. Figure 3c shows the results.

Table 1. Differences in Pure Component Surface Potentials on OL Carbon at 30°C

Binary Liquid Mixture	$(\phi_2^o - \phi_1^o)/\mathrm{RT}$ mol/kg
Acetic Acid (1) + Methanol (2)	20.3
Acetic Acid (1) + Water (2)	15.6
Acetic Acid (1) + Methyl Acetate (2)	3.5
Methyl Acetate (1) + Methanol (2)	4.0

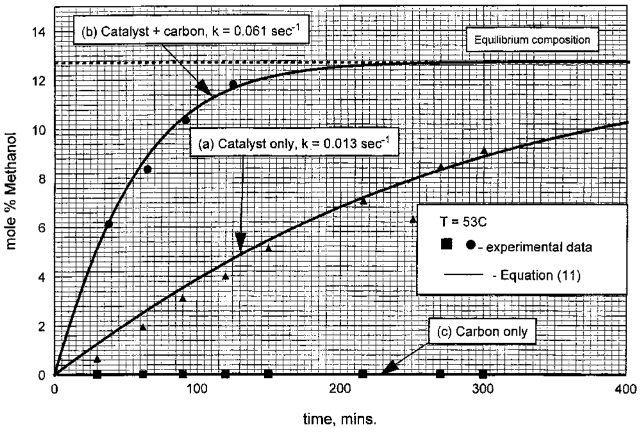

Figure 3. Batch reaction kinetics of methyl acetate hydrolysis at 53°C.

(a) With catalyst alone; (b) with catalyst and carbon adsorbent; (c) with adsorbent alone.

It may be seen from Figure 3c that there is virtually no formation of methanol in the absence of the catalyst at 53°C. The catalyst introduced a significant rate of reaction for the methyl acetate hydrolysis at that temperature (Figure 3a). The addition of the carbon in the presence of the catalyst further increased the rate of formation of methanol (Figure 3b). The carbon itself has no catalytic activity (Figure 3c). Thus, these experiments demonstrated that selective removal of acetic acid from the reaction zone by the activated carbon enhances the rate of forward reaction.

Reaction kinetic model

The rate of reaction for the hydrolysis of methyl acetate can be described by assuming that first-order mass action law governs the reaction. Thus, one may write

$$\frac{dx_{\mathrm{CH_4O}}}{dt} = \frac{dx_{\mathrm{C_2H_4O_2}}}{dt} = k_f[x_{\mathrm{C_3H_6O}} \cdot x_{\mathrm{H_2O}}] - k_b[x_{\mathrm{CH_4O}} \cdot x_{\mathrm{C_2H_4O_2}}] \tag{5}$$

$$K(T) = k_f/k_b \tag{6}$$

where $x_i(t)$ is the mole fraction of component i in the reactor at time t. The variables k_f and k_b are, respectively, the reaction rate constants for the forward and backward reactions.

Equations 5 and 6 can be combined to get

$$\frac{d\theta(t)}{dt} = -k\left[(1-K)\theta^2 + K\theta - Kx^o_{C_3H_6O}\cdot x^o_{H_2O}\right] \quad (7)$$

$$\theta(t) = \delta(t)/N; \qquad k = k_b \quad (8)$$

where N is the total number of moles of methyl acetate + water mixture in the batch reactor at the start of the experiment ($t = 0$). x^o_i is the mole fraction of component i in the reaction mixture at $t = 0$. $\delta(t)$ is the number of moles of methyl acetate reacted to form methanol at time t. It was assumed in deriving Eq. 7 that the initial reactant mixture was free of the products

$$\left(x^o_{CH_4O} = x^o_{C_2H_4O_2} = 0, \quad x^o_{C_3H_6O} + x^o_{H_2O} = 1\right).$$

The value of the parameter $\theta(t)$ approached θ^* when the system reached chemical equilibrium ($t \rightarrow \infty$). It follows from Eq. 2 that

$$\theta^* = \frac{\sqrt{A} - K}{2(1-K)} \quad (9)$$

$$A = K^2 + 4K(1-K)x^o_{C_3H_6O}\cdot x^o_{H_2O} \quad (10)$$

Equations 7–10 can be combined to obtain the transient compositions of the components in the batch reactor as

$$\frac{1}{\sqrt{A}}\ln\left[\frac{1-Z}{1+\lambda Z}\right] = -kt \quad (11)$$

$$Z = \theta(t)/\theta^*, \qquad \lambda = \left[\frac{1}{1+\dfrac{2K}{\left(\sqrt{A}-K\right)}}\right] \quad (12)$$

The instantaneous mole fractions of methanol and acetic acid at time t are given by the variable $\theta(t)$ and those for the methyl acetate and water are given by $[x^o_i - \theta(t)]$. The weight fractions of methanol at time t $[x^w_{C_2H_4O}(t)]$ can be calculated by

$$x^w_{C_2H_4O}(t) = \frac{\theta(t)\cdot M_{C_2H_4O}}{\Sigma x^o_i M_i} \quad (13)$$

where M_i is the molecular weight of component i.

The solid lines in Figures 3a and 3b represent the best fit of the experimental kinetic data using the above described model (Eqs. 9–13). The equilibrium constant (K) at 53°C was calculated using Eq. 3. The backward reaction rate constant ($k = k_b$) was then calculated from the data for a given set of values of x^o_i. They are reported in the figures. This exercise shows that the simplest reaction kinetic model given by Eq. 5 is adequate to describe the kinetics of methyl acetate hydrolysis reaction. Furthermore, the model shows that both the effective forward and backward reaction rate constants increased by a factor of five due to the selective removal of acetic acid by the activated carbon from the reaction zone. It should be emphasized that the reaction rate constants used in this analysis are empirical parameters, and they do not reflect the actual rate constants which must be determined by incorporating adsorption of all components of the system in the reaction mechanism. The purpose here is only to show that selective adsorption of reaction products enhances the effective forward reaction rate. The dashed line in Figure 3 shows the equilibrium mole fraction of methanol in the batch reactor calculated by Eq. 9, which was used to generate the curves (a) and (b) in Figure 3.

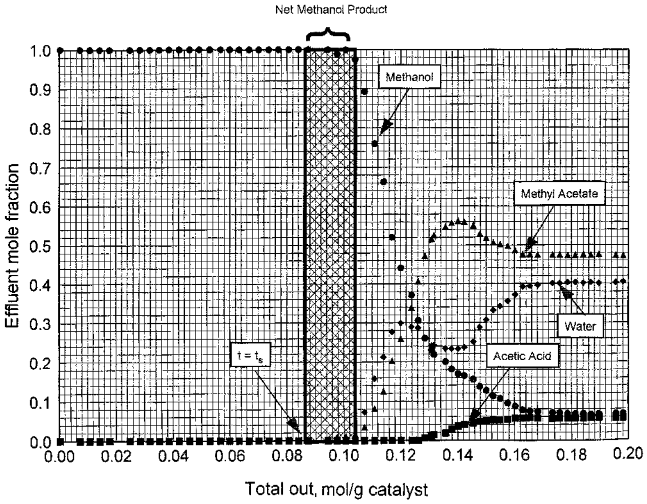

Figure 4. Reactor-adsorber effluent composition profiles during step (a) of SERP at 35°C.

Feed liquid mixture consisted of 54.25 mol % methyl acetate, 40.54 mol % water, and 5.21 mol % of methanol.

Column demonstration of SERP concept

A column dynamic experiment was conducted to further elucidate the liquid-phase SERP concept. A thermostated tubular reactor (1.25 cm internal diameter and 76.2 cm long) was packed with an admixture of 11.0 gms of Amberlyst A-15 catalyst and 6.5 gms of OL-Carbon (both approximately 0.05 cm diameter particles). The reactor was then filled with pure liquid methanol. A feed liquid mixture containing 54.25 mol % methyl acetate, 40.54 mol % water, and 5.21 mol % methanol was passed through the column at a molar flow rate of 1.08 mmol/cm^2/s (based on empty cross-sectional area of the column) and the composition of the column effluent was monitored as a function of time. The experiment was conducted at a temperature of 35°C. Figure 4 shows the experimental column effluent profiles. It plots the mole fractions of various components in the effluent liquid as a function of total mol of effluent liquid (mol/g of catalyst). It may be seen that the column effluent initially consisted of pure methanol over a period of time ($t = 0 - t^s$) and then the methanol concentration rapidly decreased to a constant mol fraction of 0.07. The mole fractions of water, acetic acid, and methyl acetate were negligible in the initial part of the column effluent ($t = 0 - t^s$) and they then increased to constant values of 0.406, 0.055, and 0.469, respectively. The mole fraction of methyl acetate went through a maximum value of 0.56

before it decreased to the final constant value of 0.469. The mol fraction of water went through a local maximum and a minimum before reaching a constant value of 0.406.

The total amount of methanol in the column at the start of the experiment was 0.086 mol/g of catalyst. The total amount of methanol introduced into the column with the feed liquid mixture during the time period of $0 - t^s$ was 0.0042 mol/g of catalyst. The total amount of pure methanol produced from the column during that time interval was 0.104 mol/g of catalyst. Thus, the net amount of pure methanol produced by the process was 0.0138 mol/g of catalyst (cross-hatched area in Figure 4).

The total amount of methyl acetate introduced into the column during time $0 - t^s$ was 0.0439 mol/g of catalyst. Therefore, the conversion of methyl acetate to methanol by hydrolysis was 31.4% for this experiment during the period where an essentially pure methanol product was withdrawn from the column.

A plug-flow reactor packed with the catalyst alone would yield a thermodynamic conversion (methyl acetate to methanol) of only 20.9% using the same feed liquid composition as that used in the above described SERP experiment. Furthermore, the reactor effluent (16.6% methanol, 42.9% methyl acetate, 29.2% water, and 11.3% acetic acid) in that case will not be pure methanol as for the SERP case. It can also be shown by using Eqs. 2 and 3 that the thermodynamic conversion of methyl acetate to methanol will be only 23% at a temperature of 150°C which is the upper temperature limit for the structural stability of the Amberlyst A-15 catalyst. Thus, the conversion of 31.4% achieved by the SERP concept using that catalyst at 35°C cannot be obtained at any practical temperature by using the catalyst alone.

Figure 5 shows the liquid-phase composition profiles of various components within the adsorber-reactor at time (t) during step (a) of the SERP. The mole fractions (x_i) of component i are plotted as functions of distance (z) from the feed end of the reactor. The effluent end of the reactor (EZ IV) is saturated (equilibrated) with methanol. The balance of the reactor holds two reaction-mass-transfer zones (RMTZ I and III) separated by an equilibrium zone (EZ II).

The liquid-phase compositions in the EZ II (x_i^*) are identical to those given by the effluent compositions of a steady-state reactor for the hydrolysis reaction using the catalyst alone where the feed liquid mixture has the same composition (x_i^o) as that of the SERP. Thus, x_i^* is governed by the values of x_i^o and the equilibrium constant for the hydrolysis reaction $[K(T)]$ at the reaction temperature.

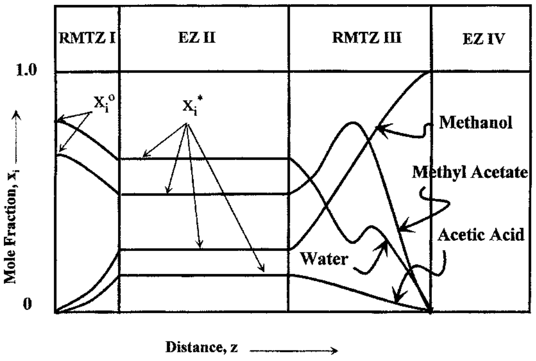

Figure 5. Composition profiles inside reactor-adsorber during step (a) of SERP.

The mole fractions of components in RMTZ I change from x_i^o to x_i^* due to simultaneous hydrolysis reaction and selective adsorption of reactants and products. The mole fractions of methyl acetate, water, and acetic acid decrease from x_i^* to zero in RMTZ III, while that for methanol increases from x_i^* to unity in that zone. The undesired reaction product (acetic acid) and the reactants are completely removed from the reaction zone by their selective adsorption on the carbon in RMTZ III. The RMTZ III progresses towards the effluent end of the reactor with increasing time during the step (a) of the SERP. The length of the EZ II increases with time in order to accommodate the selectively adsorbed components in RMTZ III. Consequently, the length of Section IV decreases with time.

The effluent from the reactor during step (a) of the process is essentially pure methanol until the leading edge of RMTZ III reaches the effluent end of the reactor. At that point (time $t = t^s$), the impurities like methyl acetate, water, and acetic acid appear in the effluent fluid. Thus, the effluent liquid quantity-composition profiles given by Figure 4 are mirror images of the concentration profiles in the reactor given by Figure 5.

The adsorbed methyl acetate is displaced by more selectively adsorbed acetic acid in RMTZ III causing a "roll over" effect (Sircar and Myers, 1986). This explains the composition profile of methyl acetate in RMTZ III where its mole fraction is equal to $x^*_{C_3H_6O}$ at the trailing edge of the zone, and then it increases to a value larger than $x^*_{C_3H_6O}$ before decreasing to zero at the leading edge of the zone. The profile of water composition is more complex. It displaces methanol in RMTZ III and then it is rolled over by methyl acetate and acetic acid. This creates the local maximum and minimum in the water breakthrough composition profile.

The three key potential advantages of the SERP concept described above for the liquid phase hydrolysis of methyl acetate to methanol are:

(a) Production of pure methanol product

(b) High conversion of methyl acetate to methanol at a relatively low temperature

(c) Higher rate of formation of methanol than the catalyst alone case.

All these advantages were achieved by selectively adsorbing one of the reaction products (acetic acid) from the reaction zone. It will obviously be necessary to periodically desorb the acetic acid from the carbon adsorbent so that it can be reused in a practical process. The recently developed concept of concentration swing adsorption (CSA), where the mole fractions of the adsorbed species of the superincumbent liquid phase in the adsorber are changed to effect adsorption and desorption (Sircar, 1991), will be used for this purpose. Thus, the cyclic process steps of the liquid-phase SERP concept will be as follows.

Liquid-Phase Sorption Enhanced Reaction Process Concept

(a) Sorption-Reaction Step: The feed liquid comprising of an equimolar mixture of methyl acetate and water is passed

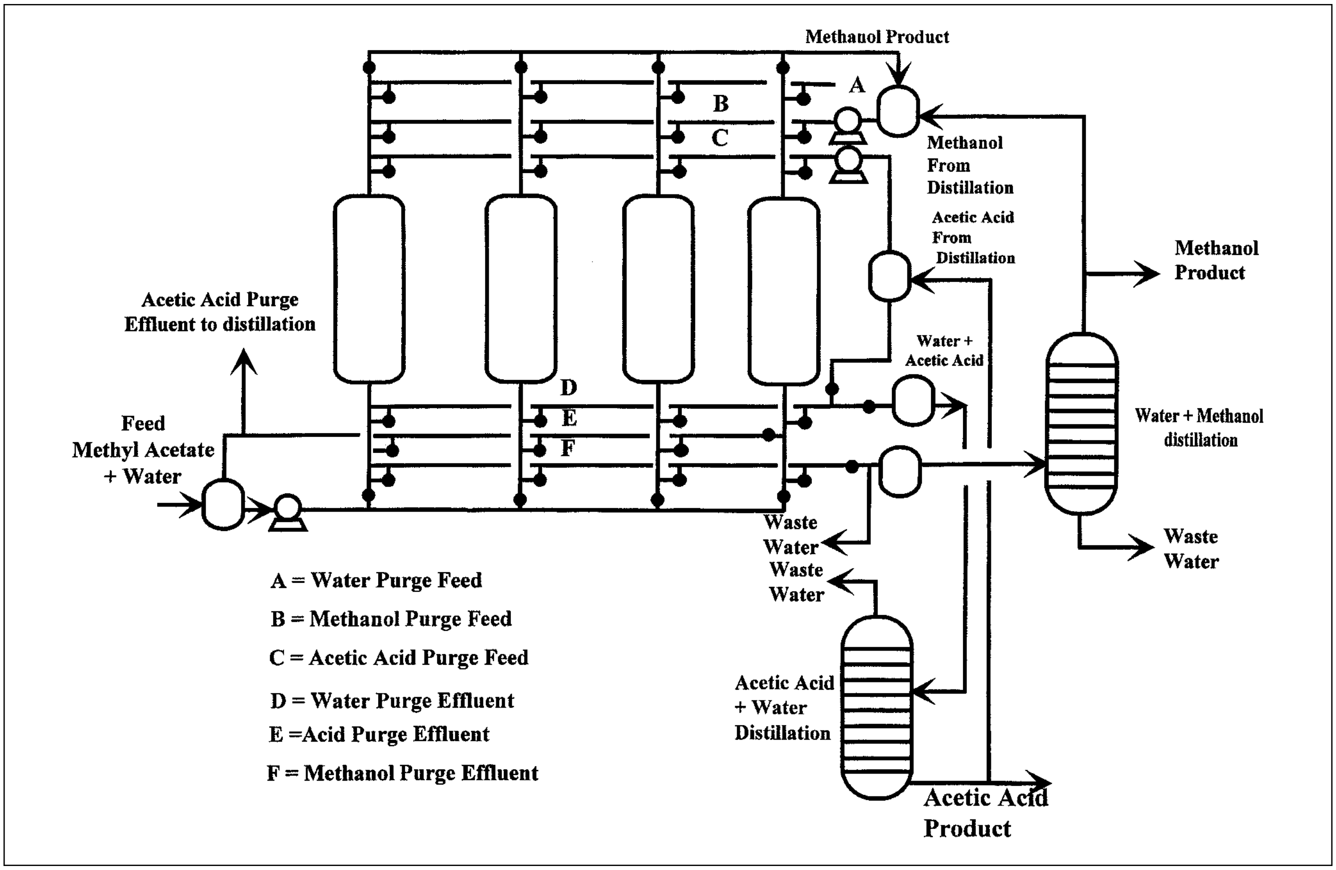

Figure 6. Process flow diagram for the liquid-phase SERP.

at the reaction temperature (T) through a packed-bed reactor containing an admixture of the hydrolysis catalyst and the carbon adsorbent. The reactor is initially saturated with pure methanol. A stream of essentially pure methanol is produced. A part of that effluent liquid is withdrawn as the methanol product and the balance is used as methanol rinse in step (d) of the cycle. Step (a) is continued until the mole fraction of methanol in the effluent liquid drops below a preset level.

(b) Acetic Acid Rinse Step: The reactor is purged with pure acetic acid in a countercurrent direction at temperature (T). The step is continued until the reactor is saturated with acetic acid. The effluent during this step is partly sent to a distillation column for separation. The methyl acetate and water products from that distillation column can be recycled as feed to the SERP. The remaining effluent from this step can be recycled as feed liquid in step (a) by mixing it with the fresh feed stream.

(c) Water Rinse Step: The reactor is then purged with pure water in a countercurrent direction at temperature T until the reactor is saturated with water. The effluent liquid during this step initially consists of high purity (99 + %) acetic acid, which is used as the feed stream for step (b). The latter part of the effluent during this step consists of a mixture of water and acetic acid which is sent to a distillation column for separation. A part of the high purity acetic acid product from the distillation column may also be used as the feed liquid to step (b), while the balance is withdrawn as the acetic acid product from the SERP.

(d) Methanol Rinse Step: Finally, the reactor is countercurrently rinsed with methanol at temperature T to displace the water from the reactor. The initial portion of effluent liquid during this step consists of water. The later part of the effluent consists of a methanol-water mixture which is separated by distillation. The methanol stream from the distillation column is used as rinse liquid for this step. The reactor is saturated with methanol at the end of this step, and it is ready to begin a new cycle from step (a).

The above described four-step SERP cycle produces two pure product streams (methanol and acetic acid) by hydrolysis of methyl acetate. All the advantages of the SERP concept are utilized by the process. A four-column adsorber-reactor system, operating in parallel, will be necessary to carry out the four-step cycle continuously. Each reactor will carry out a step of the cycle at any given time. Figure 6 shows the process. It consists of four parallel reactor-adsorbers, several liquid pumps, and storage tanks. The figure also shows the acetic acid-water and methanol-water-distillation columns.

Summary

The gas-phase sorption-enhanced reaction process (SERP) concept is applied to equilibrium-controlled liquid-phase reaction. The concept is based on Le Chateliers' principle that the rate of forward reaction and the conversion of reactants to products can be increased by selectively removing one or more reaction products from the reaction zone. A fixed-bed adsorber-reactor, which is packed with an admixture of the catalyst and an adsorbent, is used for this purpose. The adsorbent selectively removes some of the reaction products, and it is periodically regenerated by using the principles of concentration swing adsorption (CSA). The CSA concept triggers the adsorption and desorption of the selectively adsorbent components by deliberately changing their superincumbent liquid-phase compositions in a periodic manner. The SERP is integrated with several distillation columns which facilitate production of pure reaction products.

Catalytic hydrolysis of methyl acetate to form acetic acid and methanol, which is an endothermic equilibrium-controlled reaction, was studied to prove the liquid-phase SERP concept. A commercial ion-exchange resin (Rohm and Haas Amberlyst A-15) and a commercial activated carbon (Calgon OL) were used. Binary liquid-phase surface excess isotherms for the liquid pairs of interest were measured on the carbon. The selectivity of adsorption on the carbon increases in the order acetic acid > methyl acetate > water > methanol. Batch reaction kinetic data were measured to demonstrate that the net rate of forward reaction was increased by a factor of five due to the presence of the carbon adsorbent in the reactor. Column dynamic tests were carried out to show that the SERP concept can be used to directly produce a stream of essentially pure methanol with a high conversion of methyl acetate to methanol. The conversion of methanol by the process at 35°C was much higher (~ 31.4%) than that would be possible by using a plug-flow reactor with the catalyst alone (~ 21.0%) at the same temperature due to thermodynamic limitations. A much higher temperature (> 200°C), where the catalyst is unstable, would be necessary to match the methanol conversion achieved by the SERP concept when using a conventional plug-flow reactor with the catalyst alone. Furthermore, the reactor effluent, in that case, will be an equilibrium mixture of reactants and products. The proposed design of the SERP, on the other hand, was capable of producing two essentially pure product streams of methanol and acetic acid.

Acknowledgments

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Notation

a = bulk liquid-phase activity
x^w = weight fraction
z = distance in reactor-adsorber
$Z = (\theta/\theta^*)$
$\theta = (\delta/N)$
ϕ^o = surface potential of pure liquid adsorbate on the adsorbent
λ = function defined by Eq. 12
γ = liquid-phase activity coefficient

Subscript and superscript

o = initial condition of reactions
$*$ = equilibrium condition

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