Experimental and Simulation Study on the Reactive Distillation Process for the Production of Ethyl Acetate

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Abstract: A reactive distillation tower equipped with 10 catalyst-packed plates (9.8 cm³ of solid acidic catalyst packed on each plate), five equivalent separation trays above the catalyst packed plates, and three equivalent separation trays below the catalyst packed plates was used for reactive distillation experiments. The feed rates of acetic acid and ethanol were 2.65 and 3.71 mole/hr, respectively. When the reflux ratio was 3.0, the concentration of ethyl acetate at the top of the reactive distillation tower was 70 mole%. A final ethyl acetate product (over 98 wt%) was obtained through a further distillation. Modeling of the reactive distillation process was undertaken and a computer program was coded. Process simulations were conducted using the program; these simulation results explained the experimental measurements within 5% error.

Keywords: Reactive distillation process, ethyl acetate, simulation

Introduction

The reactive distillation process is one of the most widely used reactive separation processes. For example, the well-known MTBE (methyl tert-butyl ether) process is a reactive distillation process. Methanol is supplied at the top of the catalyst-packed plates of the reactive distillation tower and a C4 stream containing isobutene is supplied at the bottom of the catalyst-packed section. MTBE is produced from the bottom of the tower through the reaction of methanol and isobutene. In this process, the reaction and the MTBE purification are both conducted in a single unit.

The development of reactive distillation processes involving esterification, hydration, aromatic alkylation, nitration, and amidation reactions is an active area of research [1]. ETBE (ethyl tert-butyl ether) production has been reported using water containing ethanol and tert-butanol through a reactive distillation process [2]. A methyl acetate recovery process was developed by applying reactive distillation technology [3]. Butyl acetate and 2-methylpropyl acetate production, using acetate and the corresponding alcohols, through reactive distillation processes, have been studied [4,5].

Computer simulation studies are also an active field of investigation [6a, 6b]. They are necessary for the design of the optimum feed location, the number of separation trays, and the size of the catalyst-packed section. Computer simulation is also quite important for optimization of the operating conditions.

In this study, water containing ethanol and acetic acid were used as raw materials for the production of ethyl acetate. Normally, esterification reactions are reversible reactions. When the concentrations of reaction products in the mixture are low (reaction products are continuously removed), the forward reaction is enhanced. Thus, the reactive distillation process is suitable for this esterification reaction.

Modeling and Simulations

To simulate a reactive distillation process, modeling of the vapor liquid equilibrium for the constituting components and modeling of the reaction rate and heat of reaction are necessary. The heats of reaction of the systems investigated in this study were negligible.
Table 1. Binary Interaction Parameters

<table>
<thead>
<tr>
<th>Interaction parameter</th>
<th>a_{ij}</th>
<th>b_{ij}</th>
</tr>
</thead>
<tbody>
<tr>
<td>j</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>-18.477</td>
<td>13.991</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>-10.478</td>
<td>-11.188</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>12.343</td>
<td>21.416</td>
</tr>
<tr>
<td>Water</td>
<td>-9.7906</td>
<td>21.219</td>
</tr>
</tbody>
</table>

Vapor Liquid Equilibrium
A Non-Random Two-Liquid (NRTL) model was adopted for calculation of the vapor liquid equilibrium [7]. The model is expressed as follows:

\[
\ln \gamma_{ij} = \frac{\sum_j \tau_{ij} x_j G_{ij}}{\sum_i x_i G_{ij}} + \frac{\sum_j \sum_k \tau_{ij} x_{ik} G_{ij}}{\sum_i x_i G_{ij}} \left( -\frac{\sum_j x_{ij} G_{ij}}{\sum_i x_i G_{ij}} \right)
\]

(1)

where:

\[
G_{ij} = \exp \left( -a_{ij} \tau_{ij} \right)
\]

(2)

\[
\tau_{ij} = a_{ij} + b_{ij}/T, \quad a_{ij} = 0.3, \quad \tau_{ij} = 0, \quad G_{ij} = 1, \quad a_{ij} \neq a_{ji}, \quad b_{ij} \neq b_{ji}
\]

(3)

The binary interaction parameters for a_{ij} and b_{ij} are indicated in Table 1. These binary interaction parameters were obtained through bubble point temperature calculations. The objective function used for the regression of these parameters is was indicated as equation (4).

\[
Obj. = \left( -\frac{T_{\text{exp}}}{T_{\text{cal}}} \right) + (y_{1,\text{exp}} - y_{1,\text{cal}})^2
\]

(4)

Calculated values of the vapor liquid equilibrium for the binary system of ethanol and water at 1.01325 bar, as well as literature data, are shown in Figure 1. As shown in the figure, the NRTL model represented the phase behavior of the system well. The corresponding results for the binary system of water and acetic acid at 1.01325 bar are shown in Figure 2; the model also represents the literature data well. Similarly, calculations for the binary systems of ethyl acetate and ethanol, ethyl acetate and acetic acid, and ethyl acetate and water are shown in Figures 3, 4, and 5, respectively. Again, the NRTL models represent the phase behaviors of these systems well.

Reaction Rate
Ethanol and acetic acid react under acidic conditions to form ethyl acetate and water. The reaction is a well-known reversible reaction. The reaction rate can be expressed by the Langmuir-Hinshelwood equation [12],
which is shown in equation (5).

The reaction rate was measured using a batch reactor (volume: 300 mL; magnetic agitation, thermostated). Initially, known amounts of reactants were placed in the reactor and the temperature was maintained constant. After the insertion of the catalyst (Amberlyst-15), aliquots (less than 0.2 mL) of samples were analyzed using a gas chromatograph. Sampling was undertaken 2 or 3 times in each hour.

\[
-C_{EA} \frac{dC_{EA}}{dt} = k(C_{ET}C_{AA} - C_{EA}C_{WT})/K \quad (5)
\]

where \(C_{EA}, C_{ET}, C_{AA},\) and \(C_{WT}\) are the concentrations (moles/unit volume of catalyst) of ethyl acetate, ethanol, acetic acid, and water, respectively. The constants \(k\) and \(K\) are the backward and equilibrium reaction constants, respectively.

The reaction constants \(k\) and \(K\) at 343.15 K were 0.3967 (mol/cm\(^3\) cat)\(^{-1}\) min\(^{-1}\) and 3.965, respectively. The measured and calculated concentrations (mol/cm\(^3\) cat) of ethyl acetate with time are shown in Figure 6. The absolute average deviation between the measured and calculated concentrations was 8.8%.

**Modeling of the Reactive Distillation Tower**

An equilibrium plate model was used for simulation of the reactive distillation process. The mass and energy flows around a reactive distillation plate are indicated in Figure 7, where \(F, L, V, z, x,\) and \(y\) represent the flow rates of the feed (mol/hr), liquid, and vapor and the mole fractions of the feed, liquid, and vapor, respectively. \(\Delta H\) and \(r\) represent the heat of reaction and the reaction rate, respectively. \(H\) or \(h\) represents the enthalpy and the subscript \(p\) represents the plate number. In case of the separation tray, no reaction is involved.

The component and overall material balance equations are expressed in equations (6) and (7), respectively.

\[
I_{j,p-1} - I_{j,p} - v_{j,p} + v_{j,p+1} + f_{j,p} + V_{cat,p} r_{j,p} = 0 \quad (6)
\]

\[
L_{p-1} - L_p - V_p + V_{p+1} + F_p + V_{cat,p} \sum_j r_{j,p} = 0 \quad (7)
\]

The energy balance equation is expressed as
Table 2. Experimental Material Balance (mol/min)

<table>
<thead>
<tr>
<th>Stream</th>
<th>Acetic acid</th>
<th>Ethanol</th>
<th>Ethyl acetate</th>
<th>Water</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.055</td>
<td>-</td>
<td>-</td>
<td>0.005</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>0.063</td>
<td>-</td>
<td>0.008</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>0.012</td>
<td>0.051</td>
<td>0.009</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.004</td>
<td>-</td>
<td>-</td>
<td>0.064</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>-</td>
<td>0.0008</td>
<td>0.035</td>
<td>0.0006</td>
<td>ca. 96 mol % (ca. 98 wt%)</td>
</tr>
<tr>
<td>6</td>
<td>-</td>
<td>0.012</td>
<td>0.016</td>
<td>0.009</td>
<td></td>
</tr>
</tbody>
</table>

The coefficient matrix is tri-diagonal. The coefficients in equation 9 are expressed as

$$A_p = -1 (p=2, 3, 4, ..., N)$$

$$B_p = \begin{cases} 1 + \frac{V_iK_{p,1}}{L_1} & (p=1, \text{ Partial condenser}) \\ 1 + \frac{V_iK_{p,1}}{L_1} & (p=1, \text{ Total condenser}) \\ 1 + V_iK_{p,N} & (p=N, \text{ Kettle type reboiler}) \\ 1 + \frac{V_iK_{p,N}}{L_i} & (p=N, \text{ Thermosyphon type reboiler}) \end{cases}$$

The overall material and energy balance equation, together with the component material balance equation, equation 9, and the steady-state behavior of the reactive distillation column can be analyzed.

Figure 6. Measured and calculated ethyl acetate concentration variations with time at 343.15 K.

Figure 7. Material and energy flow around a reactive distillation tray.
Table 3. Conditions Used in the Simulation

<table>
<thead>
<tr>
<th>Condition</th>
<th>Value</th>
<th>Condition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of top separation trays</td>
<td>5</td>
<td>Column pressure drop (atm)</td>
<td>0.075</td>
</tr>
<tr>
<td>Number of catalyst-packed trays</td>
<td>10</td>
<td>Acetic acid feed rate (mol/hr)</td>
<td>2.65</td>
</tr>
<tr>
<td>Number of bottom separation trays</td>
<td>3</td>
<td>Ethanol (89 mol%) feed rate (mol/hr)</td>
<td>3.71</td>
</tr>
<tr>
<td>Feed temperature of acetic acid (K)</td>
<td>363.15</td>
<td>Catalyst packed on each tray (cm^3)</td>
<td>9.8</td>
</tr>
<tr>
<td>Feed temperature of ethanol (K)</td>
<td>352.15</td>
<td>Reflux ratio</td>
<td>3.0</td>
</tr>
<tr>
<td>Top pressure (atm)</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 8. Schematic illustration of the reactive distillation process.

Results

Reactive Distillation Experiments

The equipment used in this study featured a bottom separation section, a catalyst section, and a top separation section. The bottom and top separation sections were packed with 6 mm pall ring. The diameter and height of the bottom separation section were 4.5 and 50 cm, respectively. The diameter and height of the top separation section were 4.5 and 70 cm, respectively. The catalyst section was packed with Amberlyst-15 ion exchange resin. The diameter and height of the catalyst section were 6.0 and 120 cm, respectively. The catalyst section contained 10 trays. On each tray, 9.8 cm^3 of catalyst was packed (ca. 3 cm); the rest of the volume was empty.

While operating the reactive distillation system, the column pressure drop and reflux ratio were maintained constant at 1.1 psi (0.075 bar) and 3, respectively.

Figure 9. Calculated concentration and temperature profiles.

A schematic illustration of the equipment is shown in Figure 8. The experimental results are indicated in Table 2. The stream numbers in the Table correspond to the numbers indicated in Figure 8. At the top of the reactive distillation column, the concentration of ethyl acetate was ca. 70 mol% (refer to stream # 3 in Table 2). The concentration of ethyl acetate was higher than that in the azeotropic mixtures. In the experiment, the top product was collected and further distilled. The concentration of ethyl acetate in the final product was ca. 98 wt%.

Computer Simulation of the Reactive Distillation Process

Computer simulation on the reactive distillation column was conducted based on the experimental measurements. The conditions used in the simulation are indicated in Table 3. The calculated temperature and concentration profiles are indicated in Figure 9. The calculated top and bottom product concentrations were predicted well, within 5% error.
Conclusions

Reactive distillation experiments for the production of ethyl acetate from ethanol and acetic acid were conducted. The equipment used in this work featured 10 catalyst-packed plates (9.8 cm$^3$ of solid acidic catalyst packed on each plate), five equivalent separation trays above the catalyst-packed plates, and three equivalent separation trays below the catalyst-packed plates. In the experiment, the concentration of ethyl acetate in the top product was higher than those of in azeotropic mixtures. Over 98 wt% of ethyl acetate was obtained after further purification of the top product using a common distillation column. Process simulations explained the experimental measurements to within 5% error.

Acknowledgments

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Nomenclature

$F_i$: total feed flow to tray $i$
$L_i$: total liquid flow from tray $i$
$V_i$: total vapor flow from tray $i$
$Q_i$: heat added to tray $i$
$T_i$: temperature of tray $i$
$T_i^{exp}$: experimental bubble point temperature
$T_i^{cal}$: calculated bubble point temperature
$y_j^{exp}$: experimental bubble point composition
$y_j^{cal}$: calculated bubble point composition
$x_I^{exp}$: experimental liquid phase composition of phase I
$x_{L,j}^{exp}$: calculated liquid phase composition of phase I
$x_I^{exp}$: experimental liquid phase composition of phase II
$x_{V,j}^{cal}$: calculated liquid phase composition of phase II
$C_{EA}$: concentration of ethyl acetate (moles/unit volume of catalyst)
$C_{AA}$: concentration of acetic acid (moles/unit volume of catalyst)
$C_{WT}$: concentration of water (moles/unit volume of catalyst)
$k$: backward reaction rate constant
$K$: equilibrium reaction constant
$F, L, V, z, x, y$: flow rates of the feed (mol/hr), liquid, and vapor and the mole fractions in the feed, liquid, and vapor, respectively
$\Delta H$: heat of reaction
$r$: reaction rate
$Q_{k}$: objective function
$y_i$: activity coefficient of component $i$
$x_j$, $x_k$: liquid mole fraction of component $j$ and $k$
$a_{ij}$, $a_{ki}$, $b_{ij}$, $b_{ji}$, $a_{j}$, $G_{ij}$, $\tau_{ij}$: binary interaction parameters in the NRTL model

References