Effect of Murphree Tray Efficiency on Reactive Distillation Process for Ethyl Acetate

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ABSTRACT

A reactive distillation (RD) for the production of ethyl acetate (EtAc) from acetic acid (HAc) and ethanol (EtOH) using sulfuric acid as homogeneous catalyst is presented. To meet the industrial specification of HAc (≤0.01 wt%) and EtOH (≤0.2 wt%) in the product stream, a complete esterification process including a RD column with an overhead decanter and a stripping column are synthesized and studied by using the Aspen Plus® simulator. In a basic case, (Tang et al., 2003) perfect Murphree tray efficiency was assumed. To be more practical, the effect of the Murphree tray efficiency is considered in this study. Because of the effects of the non-ideality in Murphree tray efficiency, the heat duty of stripper and the organic reflux flow of RD column are adjusted to meet EtOH and HAc requirements in the product stream, respectively. It was found, output multiplicity occurred while this organic reflux flow rate is between 41 to 45 moles/sec and the Murphree tray efficiency is lower than 70%. As a result, the Murphree tray efficiency becomes a bifurcation parameter. As the tray efficiency is even lower, the existence of multiple steady-states is getting more obvious.

KEYWORDS

Murphree Tray Efficiency, Output Multiplicity, Reactive Distillation

INTRODUCTION

Ethyl acetate is an important organic solvent widely used in the production of varnishes, ink, synthetic resins, and adhesive agents. There are many papers on the subject of reactive distillation published in recent years, but those on the study of ethyl acetate production are quite scarce.

For the process design, Keyes (1932) was the first reported paper on an ethyl acetate process with a reactive distillation column in combination with a pre-esterification reactor, two recovery columns, and a decanter. The process is quite complex and containing quite a few process equipments.

For steady-state and dynamic simulation of EtAc RD column, Chang and Seader (1988) used homotopy-continuation method to solve the steady-state simulation on an EtAc RD column. Simandl and Svrcek (1991) used inside-outside method to simulate the EtAc RD column. Alejski and Duprat (1996) formulated a dynamic mathematic model of this RD column and validated the accuracy of the
simplified model via experimental data.

Bock et al. (1997) designed an uncatalyzed ethyl acetate process with excess ethanol containing a reactive distillation column and a pressurized recovery column. Although the high-purity EtAc product can be obtained from the bottom of the recovery column, the bottom of the RD column containing EtOH/H₂O needs further treatment.

Vora and Daoutidis (2001) studied the operation and control of a single RD column, but the top product is not pure enough and the bottom product stream contains all four components in the process, thus, it will be very difficult for further treatment of this stream.

Tang et al. (2003) studied the process including a RD column with an overhead decanter and a stripping column. High pure ethyl acetate product was obtained in the process with a hundred percent of Murphree tray efficiency. To be more practical, we study the process with different Murphree efficiencies from 0.8 to 0.5.

**PROCESS DESCRIPTIONS AND OUTPUT MULTIPLICITY PHENOMENA**

**Thermodynamic and Kinetic Model**

There are four azeotropes in this system including three homogeneous azeotropes of EtOH-EtAc, EtOH-H₂O, and EtOH-EtAc-H₂O and also one heterogeneous azeotrope of EtAc-H₂O. Table 1 shows the azeotropes of EtAc system and the compositions of each azeotrope. The selections of the form of the thermodynamic model and of its appropriate parameters are very important. A suitable NRTL (Non-Random Two-Liquid) model parameter set has been established with excellent prediction of the compositions and temperatures for the four azeotropes in this system. Vapor association of acetic acid due to dimerization and trimerization has also been included by using second virial coefficient of Hayden-O’Connell (1975) model in the vapor phase. In this paper, the NRTL model parameters from Tang et al. (2003) are used.

<table>
<thead>
<tr>
<th>Component</th>
<th>Experimental Composition</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol-Ethyl Acetate</td>
<td>(0.462,0.538)</td>
<td>71.81</td>
</tr>
<tr>
<td>Ethanol-Water</td>
<td>(0.9037,0.0963)</td>
<td>78.174</td>
</tr>
<tr>
<td>Ethyl Acetate-Water</td>
<td>(0.6885,0.3115)</td>
<td>70.38</td>
</tr>
<tr>
<td>Ethanol-Ethyl Acetate-Water</td>
<td>(0.1126,0.5789,0.3085)</td>
<td>70.23</td>
</tr>
</tbody>
</table>

The chemical reaction kinetic model is adopted from the paper by Alejski and Duprat (1996) with two set of parameters. One is for the situation with sulfuric acid as homogeneous catalyst, and the other is for the situation without catalyst. The kinetic equations are:

**With sulfuric acid as homogeneous catalyst:**
\[ r_1 = k_1 C_{HAc} C_{EtOH} - \frac{k_1}{K_c} C_{EtAc} C_{H_2O} \]  
(1)

\[ k_1 = (4.195 C_k + 0.08815) \exp(-6500.1/T) \]  
(2)

\[ K_c = 7.558 - 0.012T \]  
(3)

\[ \text{with } C_k \text{ as the catalyst concentration in } \%\text{vol. All concentrations are in } \text{mol/m}^3 \text{ and the forward reaction rate constant, } k_1, \text{ in } \text{m}^3/(\text{mol} \cdot \text{s}). The temperature is in K. The catalyst concentration in eq. (2) is assumed to be 0.4 vol\%.
\]

Without catalyst:

\[ r_1 = k_1 C_{HAc} C_{EtOH} - k_2 C_{EtAc} C_{H_2O} \]  
(4)

\[ k_1 = 0.485 \exp(-59774/RT) \]  
(5)

\[ k_2 = 0.123 \exp(-59774/RT) \]  
(6)

\[ \text{with the gas constant in J/(mol} \cdot \text{K).} \]

**Effect of the tray efficiency**

The base case of EtAc process with perfect Murphree tray efficiency has been established by Tang *et al.* (2003). From the base case, phase equilibrium in each stage is assumed in the Aspen Plus® simulation. In order to reflect actual industrial situation in the simulation, Murphree tray efficiency is introduced in the simulation to show the effect of tray efficiency on the results. According to the base case optimization procedure, the EtAc processes with different Murphree tray efficiency can be established. **Figure 1**, for example, shows the optimized results obtaining from the above phase equilibrium-based model to that of the simulation with Murphree tray efficiency of 60%. In the figure, more reactive and rectifying stages are needed for this case. The increasing of the rectifying and reactive stages of RD column and also increasing of the total stages of stripper for lower Murphree tray efficiency to achieve the same process performance in comparison with the equilibrium-based model is as expected.

![Figure 1. Ethyl acetate process configuration at 60% Murphree tray efficiency](image-url)
To meet the industrial specification of HAc(≤0.01 wt%) and EtOH(≤0.2 wt%) in the product stream, the organic reflux flow of RD column and the heat duty of stripper are adjusted. As using the heat duty of stripper to set the EtOH equal 0.2 wt%, it was assumed that the organic reflux flow rate can be adjusted to seek the HAc composition in the product streams to equal to 0.01 wt%. However the HAc composition can not be achieved by manipulating the organic reflux flow rate while fixing the EtOH product composition at 0.2 wt%. Output multiplicity occurred while organic reflux flow rate is changing from 41 to 45 mol/s and changing back from higher flow rate to lower one. Figure 2 shows the output multiplicity phenomenon for the Murphree tray efficiency from 80% to 50%. The output multiplicity phenomenon is more obvious when the Murphree tray efficiency is lower than 70%, while this phenomenon disappears at Murphree tray efficiency greater than 80%. Notice also from Figure 2 that the product specifications of HAc = 0.01 wt% can not be met for even a quite small changes of the organic reflux flow rate.

Figure 2. Multiple steady-states regions for different Murphree tray efficiencies from 80% to 50%.

We considered the EtAc process with 60% Murphree tray efficiency as shown in Figure 1 for further more detail study. The RD column (including reboiler) to achieve the same performance as the prefect Murphree tray efficiency will need 43 stages. The section from 21 to 43 stages is set as the reactive section and the other is set as the rectifying section. The stripper (containing reboiler) total stages are increased to 19 stages due to the lowering of the Murphree tray efficiency. The HAc and EtOH feed locations in the RD column are set at 21 and 42 stages respectively by the method of Tang et al. (2003). The HAc and EtOH feed flow are taken as 5.65 and 6.865 mol/s, and the two feed compositions of the HAc and EtOH are the same as that in Alejski and Duprat (1996) which containing some water in both feed streams. The mass fraction of HAc in the product stream is shown in Figure 3 which demonstrate the multiple steady-states region by manipulating organic reflux flow rate between 42.8 and 43.8 mol/s. Even though the region of the output multiplicity of the product stream is very small, the temperature and
composition profiles of the RD column are quite different.

**Figure 3. Multiple steady-states region for 60% Murphree tray efficiency.**

To compare the phenomena of multiple steady-states, the fixed organic reflux flow rate of 43.4 mol/s is chosen. The effect on the temperature profiles of RD column and stripper is shown in **Figure 4(a)** and **Figure 4(b)**. The temperature profiles of RD column have a large shift from high to low steady state while organic reflux flow rate is operated at the same value of 43.4 mol/s. The temperature profiles of stripper are quite similar at high and low steady states. Two different temperature profiles of RD column reflect different composition distributions in the RD column. As the result of the output multiplicity, temperature profiles of the RD column are more significant differed.

**Figure 4(a).** RD column temperature profiles and **Figure 4(b).** Stripper temperature profiles of high and low steady states at organic flow rate = 43.4 mol/s.

**Figure 5(a) and Figure 5(b)** compare the composition profiles of the different steady states. The HAc composition in the RD column at high steady state decayed slower from HAc feed stage to the top of the RD column than at the low steady state. Also, the water composition at high steady state has a peak
at the 7th stage while the low steady state does not show a peak water composition. The composition profiles at the rectifying section are very different for the two steady-states. The feed streams and the reboiler duty to the RD column are all the same except for the organic reflux flow composition. The different phenomena at the rectifying section may be caused by organic reflux flow composition. However, the reason of this phenomenon is still not clear.

The overhead stage compositions of RD column should be closed to the ternary azeotrope. However, the two steady-state composition profiles to approach the ternary azeotrope have different directions. The highest EtAc composition is on the 10th stage of RD column at high steady-state, and EtAc composition is decreased from the 10th stage to overhead stage. But the highest EtAc composition is on the overhead stage of RD column at low steady-state.

Figure 5(a). and Figure 5(b). RD column composition profiles at high and low steady-states; Figure 5(c). and Figure 5(d). Stripper composition profiles at high and low steady-states.
Even though the organic reflux flow may have a large impact for RD column, however, the difference of the reflux flow composition is not serious for stripper. The stripper having nearly the same compositions profile is shown in Figure 5(c) and Figure 5(d). The temperature and composition profiles are nearly the same in the stripper; however, the reboiler duty of stripper from low to high steady state is significantly increased from 884 kW to 1072 kW. Figure 6 shows the very different stripper heat duties are obtained by fixing the product EtOH composition at 0.2 wt %. Because the stripper feed stream EtOH compositions is different at the two steady-states.

**Figure 6.** The composition of stripper feed stream and reboiler duty at high and low steady-states.

From a viewpoint of material balance, high stripper reboiler duty leads to high overhead stream to the decanter and high feed stream to the stripper under the condition of fixing the reflux flow rate. The stripper only received the impact of the feed stream of stripper. The phenomena of multiple steady-states observed at the bottom product of stripper should be occurred at the RD column.

**CONCLUSIONS**

To be more practical, the effect of the Murphree tray efficiency is considered in this study. In our work, it was found that the output multiplicity occurred while the organic reflux flow rate is in the range of 41 to 45 mol/s and the Murphree tray efficiency is lower than 70%. It also demonstrated the difference of RD column temperature and compositions where the output multiplicity occurred. As the result from our simulation, when the tray efficiency is even lower, the existence of multiple steady-states is getting more obvious. This indicates that, if the tray efficiency could not be over 70%, the process will be operated under an open-loop unstable point, and more difficult control problem will be encountered. Based on this finding, the effect of Murphree tray efficiency will be an important concern in the design and control of this reactive distillation process.
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