Heterogeneous Azeotropic Distillation – Operational Policies and Control

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Abstract
In this work, heterogeneous azeotropic distillation process in batch column was studied. Batch column is a good alternative for separating non-ideal mixtures, when small amount of material is to be processed; continuous process becomes expensive, due to the operating costs, in these cases. The characteristics of the system (entrainer plus initial mixture) were analyzed in order to enhance the desired separation, different operating policies were discussed, a control strategy was proposed and the process was optimized considering the operating time and the energy consumption. The phenol/water separation was used as the case study. Simulations were performed using Hysys.Plant process simulator (AEA Technology).

Keywords: Batch Distillation, Process Dynamics, Azeotropic Systems.

1. Introduction
Batch columns are widely used in pharmaceutical and chemical industries, where high added value products, in small quantities, are to be produced. Batch columns are, also, used for solvent recovery due to its flexibility, which implies in economic incentives and waste minimization in industries. Continuous heterogeneous azeotropic distillation process for separating closed boiling point and azeotropic mixtures in its pure components is well known. However, batch operation implies in high complexity in terms of synthesis and operating strategies and, therefore, it is still a challenge. Donis et al. (2002) presented a feasibility study of heterogeneous batch distillation columns and pointed some advantages of this process: more design alternatives, simplified distillation sequences and a lower consumption of entrainer. Different ways to optimize batch columns were discussed in Lelkes et al. (1998) for extractive distillation process.

In this work, the main aspects of the heterogeneous azeotropic distillation in batch columns were studied. The first step was the problem implementation in the commercial process simulator, then it was proposed the operational policy and, as the last step, the control strategy to operate the column was defined. The operating policy and the
equipment sizing have large influence on the efficiency of the separation: operational
time, energy consumption and product recoveries.

2. Process Description

Heterogeneous azeotropic distillation is widely used to separate non-ideal mixtures. The
procedure is to add a new component (entrainer) in the system. The entrainer forms a
heterogeneous azeotrope with one or more components of the initial mixture. When the
azeotrope has minimum boiling point, it goes to the decanter and splits in two liquid
phases. The stream rich in the entrainer is recycled back to the azeotropic column.

In the batch mode, the first step is to define the way to operate the column. Different
options are possible to be used in conventional batch columns (without azeotropes):
constant distillate flow rate, constant reflux ratio and cyclic operation. When using
constant distillate or constant reflux ratio policies, energy is supplied to the reboiler and
the top product is continuously removed. The total operation is divided in periods.
When the top product is out of specification, the period is called “off-cut”. In the cyclic
operation, described by Sorensen (1999), the column operates in cycles: it operates at
total reflux until the top product composition remains unchanged, the energy in the
reboiler is interrupted and the condenser liquid is dumped. The cycle starts again until
the reboiler composition reaches the desired value. Figure 1 shows the scheme of batch
heterogeneous azeotropic column.

![Figure 1: Batch heterogeneous azeotropic distillation column](image)

3. Results

The results are based on simulations with optimized conditions. The optimization of the
process was made taking into account the interaction between operational time, energy
consumption and entrainer feed policy. The first item studied was the best position to
introduce the entrainer in the column. It was verified that the best entrainer feed
position is on the top stage of the column. Two operational policies for the column startup were considered:

- **Strategy 1** - The entrainer is introduced at the top of the column until fill up the trays; then heat is added at the reboiler to vaporize the charge. The column operates at total reflux until the desired top product composition is obtained. The top drawn valve is opened and the distillate is removed.

- **Strategy 2** - Heat is added and the column operates at total reflux until the steady-state is obtained. The entrainer is fed and when the top composition reaches the desired value, the entrainer feed valve is closed and the distillate valve is opened. The proposed operational policy takes into account cyclic and constant distillate flow rate strategy. Simulations show that using cyclic policy only, it takes longer time and the energy consumption is higher.

The next parameter to be optimized is the interaction between the batch time and the reboiler duty. These parameters are closely related: increasing the energy, the operating time decreases until the function reaches a minimum. From this point, the column becomes unstable, since the heaviest component (that must remain in the reboiler) tends to go to the top, making difficult to control the reflux, distillate and solvent flow rates. So, the higher the heat input is, higher is the number of total reflux cycles, due to the open/close valves procedure.

The case study was the phenol/water separation, using toluene as entrainer. Phenol and water forms a minimum boiling point azeotrope with 0.9793 water mole fraction. It is necessary to take phenol off the residual water because its high toxicity. This is a common problem in the phenolic resins production and in many other industrial processes presenting phenol. Toluene forms a heterogeneous minimum boiling point azeotrope with water. Table 1 shows the azeotrope boiling points of this system. It can be observed that there is no ternary azeotrope.

| Pure components and azeotropes boiling points for the phenol/water/toluene system at 1 atm |
|----------------------------------------------|-----------------|
| Water/Toluene                                | 84.34           |
| Phenol/Water                                 | 99.76           |
| Water                                        | 100.00          |
| Toluene                                      | 110.65          |
| Phenol                                       | 181.85          |

Table 2 shows the toluene/water azeotrope composition and the liquid phase split. Due to the characteristics of the liquid phase split, the separation is facilitated in the decanter. It was possible to have, practically, pure water and toluene.
Table 2: Water/toluene azeotrope composition and phase split at 1 atm

<table>
<thead>
<tr>
<th></th>
<th>Water mole fraction</th>
<th>Toluene mole fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binary azeotrope</td>
<td>0.55593</td>
<td>0.44407</td>
</tr>
<tr>
<td>Organic phase</td>
<td>0.00006</td>
<td>0.99994</td>
</tr>
<tr>
<td>Aqueous phase</td>
<td>0.99952</td>
<td>0.00048</td>
</tr>
</tbody>
</table>

**Control strategy**

The control strategy proposed for the batch heterogeneous azeotropic column consists of two flow controllers, one heat flow controller and one level controller. PID controllers were used. The controllers used were:
- Solvent flow rate controller
- Distillate flow rate controller
- Reboiler duty controller
- Condenser level controller (manipulating the reflux flow rate)
- An on/off controller was used to avoid the presence of phenol at the top of the column. When the temperature on stage 3 is upper than 84.34°C (toluene /water azeotrope – see Table 1), the controller closes the distillate valve and the column works on total reflux.

The initial charge to be processed was 98.89 kgmol of a phenol/water mixture with 0.50 phenol mole fraction. Thirty equilibrium stages were used to simulate the batch column (counted from top to bottom). The total condenser volume was 2 m³ and the set point to the condenser level controller was 25%. Table 3 shows that the first strategy was the best one due to the lower operating time. Table 4 shows the product compositions for strategy 1.

Table 3: Comparison between two operating policies.

<table>
<thead>
<tr>
<th></th>
<th>Strategy 1</th>
<th>Strategy 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reboiler Heat Duty (KJ/h)</td>
<td>5.0 x 10⁶</td>
<td>5.0 x 10⁶</td>
</tr>
<tr>
<td>Total reflux time (min)</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>Distillation time (min)</td>
<td>250</td>
<td>270</td>
</tr>
</tbody>
</table>

Table 4: Product vessel compositions to the phenol/water separation using toluene as entrainer – Strategy 1.

<table>
<thead>
<tr>
<th></th>
<th>Phenol mole fraction</th>
<th>Water mole fraction</th>
<th>Toluene mole fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reboiler</td>
<td>0.99999</td>
<td>0.00000</td>
<td>0.00001</td>
</tr>
<tr>
<td>Water storage</td>
<td>0.00000</td>
<td>0.99972</td>
<td>0.00028</td>
</tr>
<tr>
<td>Toluene storage</td>
<td>0.00001</td>
<td>0.00003</td>
<td>0.99997</td>
</tr>
</tbody>
</table>
Figure 2 shows the initial point, when the simulation is initialized. There is 98.89 Kgmol of the phenol/water equimolar mixture and the condenser is empty. Figure 3 shows when the steady state is obtained and the distillate valve is opened. Figure 4 shows that at the end of the simulation, pure phenol is obtained at the reboiler.

Figure 2: Start point to the strategy 1 simulation.

Figure 3: End of total reflux operation. At this point the distillate valve is opened.
4. Concluding Remarks

Batch heterogeneous azeotropic distillation problem was formulated in the simulator and simulations were performed. Important aspects were evaluated: entrainer characteristics and its feed position, operating policies and control strategy. The system considered is a very important application case, since only a heterogeneous binary azeotrope is formed, instead of a ternary one. This has advantageous implications on the phase split in the decanter. Different operational configurations were compared. It was found that the best option is to use cyclic policy and constant distillate flow rate. The composition profile was related to the temperature so that an efficient control strategy was proposed.

References