Application of Computer Simulation Technology in Chemical Synthesis of Resin Material ADH

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We use Aspen software to simulate the whole synthetic process of adipic dihydrazide (ADH) using methanol. The whole process is divided into esterification reaction and hydrazide reaction. In the esterification reaction, distillation adopts two-step evaporation, which can significantly reduce the temperature and energy consumption. The distillation product dimethyl adipate enters the next reaction module, indicating that esterification reaction can achieve 100% apparent yield in the hydrazide reaction. 2kmol/h 80% hydrazine hydrate can be used to achieve recycling of raw materials. The experimental results show that the ADH synthesis with methanol as the raw material simulated by Aspen is consistent with the experiment data, proving the effectiveness of the simulation.

1. Introduction

Adipic dihydrazide (ADH) is a good cross-linking agent which has been widely used. Medically, it is often used to crosslink with hyaluronic acid to prepare hyaluronic acid derivatives or as a drug carrier (Saleem et al., 2014; Basu et al., 2003; Xu, 2015. With people’s growing concern about environmental protection, water-based resin has been rapidly developing in recent years and is taking the place of solvent-based resin in various industries (Ďuranaa and Bystricky, 2002; Afanas’eva et al., 2006; Willis, 1991). ADH is a ketone-hydrazine crosslinking monomer, so its cross-linking with DAAM crosslinking is a typical room temperature self-crosslinking, which is widely used in water-based resin and can significantly improve the performance of water-based resin products (Zabierowski et al., 2016; Xue et al., 2016; Oh et al., 2008).

In this paper, we use Aspen to simulate the two-stage synthesis process of ADH with methanol as the raw material and prove the effectiveness of the Aspen simulation results through an experiment.

2. Aspen simulation of ADH

2.1 Synthesis principle for ADH

ADH is synthesized by the two-stage method, i.e. first methanol is used as the raw material to have esterification reaction with adipic acid to form dimethyl adipate, and then dimethyl adipate and hydrazine hydrate have the hydrazide reaction to synthesize ADH. The reaction equations are as follows:

\begin{align*}
\text{HO-CO-(CH}_2\text{)}_4\text{-CO-OH} + \text{2CH}_3\text{OH} & \rightarrow 2\text{H}_2\text{O} + \text{H}_3\text{C-O-CO-(CH}_2\text{)}_4\text{-CO-O-CH}_3 \\
\text{H}_3\text{C-O-CO-(CH}_2\text{)}_4\text{-CO-O-CH}_3 + \text{2HzN-NHz} + \text{H}_2\text{O} & \rightarrow \text{2CH}_3\text{OH} + \\
\text{H}_3\text{N-NHz-CO-(CH}_2\text{)}_4\text{-CO-NHz-NHz} + \text{2H}_2\text{O}
\end{align*}

2. Process design

Adipic acid and methanol and catalyst are added to the reactor. In the course of the reaction, 1mol of adipic acid and 2mol of methanol produce 1mol of dimethyl adipate. As the water generated in the reaction cannot be removed in time, the reaction cannot be carried out to the end, and it involves some extent of hydrolysis.

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Theoretically, the reactions involved in this process are as follows (Luo et al., 2000; Bouhadir et al., 1999; Oh et al., 2009).

Catalyst

\[
\text{HOCO(CH}_2\text{)}_4\text{COOH} + \text{CH}_3\text{OH} \rightarrow \text{H}_2\text{O} + \text{H}_3\text{COOC(CH}_2\text{)}_4\text{COOH}
\]  
(3)

Catalyst

\[
\text{HOCO(CH}_2\text{)}_4\text{COOCH}_3 + \text{CH}_3\text{OH} \rightarrow \text{H}_2\text{O} + \text{H}_3\text{COOC(CH}_2\text{)}_4\text{COOCH}_3
\]  
(4)

The reaction temperature is 70~75°C; with 1 mol of adipic acid as the basis, the ratio of alcohol to acid is 4. After 1.5~2.0 h of reflux reaction, distillation starts. First, the unreacted methanol will be steam out and recycled; then the esterification product - water will be steam out; and finally the dimethyl adipate will be steam out and used as the raw material in the next stage - hydrazide reaction. The residue at the bottom of the column residues is mono-methyl adipate, which can enter the next esterification reaction.

In the hydrazide reaction, the dimethyl adipate obtained from the esterification reaction is used as the raw material. With 1 mol of dimethyl adipate as the basis, 4 mol of hydrazine hydrate and 4 mol of methanol are added to carry out the reaction under this condition. Finally, the conversion rate of dimethyl adipate is 100%. 2 mol of hydrazine hydrate is consumed, and at the same time, 2 mol of methanol is generated. After the reaction is completed, the filtrate is filtered off and the residue is washed and dried to form a solid product. The filtrate enters the distiller for separation. Methanol is steam out from top of the column and recycled, and the mixture of hydrazine hydrate and water remaining at the bottom of the column enters the next distiller, where pure water is evaporated from top of the column, leaving hydrazine hydrate at the bottom.

2.3 Process simulation

Based on the process and conditions provided above, we use Aspen to simulate each unit. Regarding the property method, we adopt NRTL. The whole simulation process takes 1 kmol/h adipic acid as the basis and adopt *MET* as the unit system (Bouhadir et al., 2000; Yin et al., 2015; Tan et al., 2009).

2.3.1 Esterification reaction

We use the RStoic model and define the reaction equations as follows:

\[
\text{HOOC(CH}_2\text{)}_4\text{COOH} + 2\text{CH}_3\text{OH} \rightarrow \text{H}_3\text{COOC(CH}_2\text{)}_4\text{COOCH}_3 + 2\text{H}_2\text{O}
\]  
(5)

\[
\text{HOOC(CH}_2\text{)}_4\text{COOH} + \text{CH}_3\text{OH} \rightarrow \text{HOOC(CH}_2\text{)}_4\text{COOCH}_3 + 2\text{H}_2\text{O}
\]  
(6)

To make the computation simpler and more conservative, we set the two reaction conversion rates in the process simulation to be 75% and 25%, respectively; in other words, after the reaction, there will be 75% dimethyl adipate and 25% mono-methyl adipate. So the yield of dimethyl adipate is 75%. In the simulation, the alcohol to acid ratio is set to 5, the reaction temperature of the reactor 70°C and the pressure 1 bar. After the reaction, the mixture will go through three distillers to evaporate methanol, water and dimethyl adipate. The simulated result shows that in the three-stage distillation, the distiller consumes high amount of energy, which is costly. After analysis and repeated simulations, we adopt the two-stage distillation method. The first distiller evaporates most of the water under the original conditions, where the amount evaporated should be such that temperature at the bottom of the column will not be too high. The second distiller evaporates the small amount of water remaining at a lower pressure. As the amount is very small, fewer trays are needed. The load increase of the distiller caused by lower pressure will not significantly increase the cost. The parameters of the two dehydration columns are set as follows: T02: N=25, NF=10 and R=1; T03: N=10, NF=5 and R=2. The simulation results are shown in Figure 1.

From the data shown in the above figure, we can see that under the same pressure, the temperature at the bottom of T02 drops to 94.8°C, and the remaining 0.125 kmol/h is evaporated in T03, which has a lower pressure than T02. Due to the excessively low pressure, the water evaporated from top of T03 is at 24.1°C, which can no longer be used for condensation. Instead, freezing brine is used for that purpose. Due to the small amount of water remaining, the consumption of freezing brine is also small, which will not significantly increase the cost. The temperature at the bottom of T03 is 125°C, which means the temperature also drops significantly.

With the amount of dimethyl adipate evaporated becoming less and less, the temperature at the bottom of the column is gradually reduced, solving the excessive high temperature problem at the bottom of the column. At the top of the column, every time there is 1 kmol/h of dimethyl adipate generated, there will be 2 kmol/h of dimethyl adipate and 1 kmol/h of mono-methyl adipate remaining at the bottom. To make the material recyclable, the mixed ester is used as the base solution and added into the raw materials for esterification
reaction. Besides, additional 1kmol/h of adipic acid is also added. If after the reaction, there is still 3kmol/h of dimethyl adipate and 1kmol/h mono-methyl adipate left, we continue to evaporate 1kmol/h dimethyl adipate, and the rest can be recycled. In this way, the 1kmol/h adipic acid so added can be 100% converted to dimethyl adipate, i.e. the apparent conversion rate of adipic acid is 100%.

Figure 1: Simulated result of the two-step distillation dehydration

### 2.3.2 Hydrazide reaction

Since the resulting product ADH is solid, we use a separator to replace the reactor. We use the separator to separate the dimethyl adipate and hydrazine hydrate out as the consumption of the reaction, and at the same time, we add methanol into the separator as the product of the reaction. The other reaction product ADH does not appear in the simulation process, and the final result of the whole simulation process and the reaction are exactly the same. The simulation results of the reactor R02 are shown below.

Figure 2: Simulated result of hydrazide reaction R02
After the reaction, the stream 13R02L is equivalent to the filtrate. This stream needs to pass through two distillers. The first distiller T05 is a dealcoholization column, steaming out 6kmol/h of methanol, which is recycled to the esterification reaction. At the bottom of the column are water and hydrazine hydrate. In order to recycle hydrazine hydrate in the hydrazide reaction, we set the 2kmol/h material remaining at the bottom of T06 is 80% hydrazine hydrate (which contains 2kmol/h of N$_2$H$_4$ and 3.4kmol/h of H$_2$O), that is, the hydrazine hydrate used as the raw material. From this, we can calculate the amount of water to be evaporated from top of the column and achieve the recycling of hydrazine hydrate.

The parameters of the two distillers are set as follows: T05: N=35, NF=25 and R=1.2; T06: N=20, NF=10 and R=1. The simulation results are shown in Figure 3.

![Diagram of distillation process]

**Table 1: Reuse result of catalyst**

<table>
<thead>
<tr>
<th>Time</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield/%</td>
<td>82.61</td>
<td>83.84</td>
<td>84.93</td>
<td>85.29</td>
<td>84.62</td>
<td>85.58</td>
</tr>
</tbody>
</table>
From the table, it can be seen that after the third experiment, the yield is kept at about 85%, higher than those in the first and second experiments. This is because each time the residual liquid would contain mono-methyl adipate, which, through the next catalytic process, would turn into dimethyl adipate, gradually increasing the yield. Potassium bisulfate works as a catalyst after being dissolved in water and becoming acidic. Water is present throughout the reaction process, so potassium bisulfate works as a catalyst in the form of aqueous solution and in theory, would not be deactivated. From the data in the table, it can also be seen that the catalyst can still keep a high yield after being used for 6 times, so potassium bisulfate can be recycled as a catalyst.

In order to study the recycling of the remaining ester, we summarize the ratio between dimethyl adipate and monoester after the reaction, the evaporation of methanol and the evaporation of some DMA, as shown in Figure 4.

![Graph of mole ratio of DMA/MAD](image)

**Figure 4: Graph of mole ratio of DMA/MAD**

In Figure 4, the abscissa mark points 1, 2 and 3 indicate the ratios of dimethyl adipate to mono-methyl adipate after the reaction, the evaporation of methanol and water and the evaporation of DMA. It can be seen from the figure that the ratio between dimethyl adipate and mono-methyl adipate gradually increases in the three cases. When the third experiment, the ratio basically remains unchanged, indicating that the catalyst remains highly efficient and that there is not much change.

From the table, it can be seen that the ratio after the evaporation of methanol and water is lower than that after the reaction, mainly because a small amount of dimethyl adipate is hydrolyzed into mono-methyl adipate. After the evaporation of dimethyl adipate, the ratio between dimethyl adipate and mono-methyl adipate gradually increases with the number of experiments. At last, in the third experiment, this ratio remains basically unchanged and greater than 3. In the simulation process, this number is set at 2, meaning that the experiment effect is even better than the Aspen simulation result, and that the temperature at the bottom of the column will be lower.

It is feasible to use the remaining mixture of dimethyl adipate and mono-methyl adipate to reduce the temperature of the column. On one hand, it guarantees the high conversion rate, and on the other hand, it will control the temperature of the column within 120°C, which is an appropriate range. Besides, the product dimethyl adipate obtained from each experiment has a purity of over 99.5%. Therefore, the Aspen simulation computation of ADH synthesis with methanol as the raw material is consistent with the experiment data, proving the effectiveness of the simulation.

### 4. Conclusions

1. In the esterification reaction, distillation adopts two-step evaporation, which can significantly reduce the temperature and energy consumption. The distillation product dimethyl adipate enters the next reaction module, indicating that esterification reaction can achieve 100% apparent yield;
2. In the hydrazide reaction, 2kmol/h 80% hydrazine hydrate can be used to achieve recycling of raw materials.
3. The experimental results show that the ADH synthesis with methanol as the raw material simulated by Aspen is consistent with the experiment data, proving the effectiveness of the simulation.


