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.
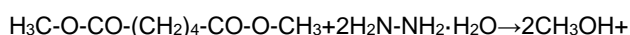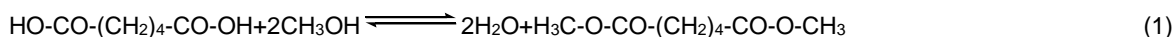
1. Introduction

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.

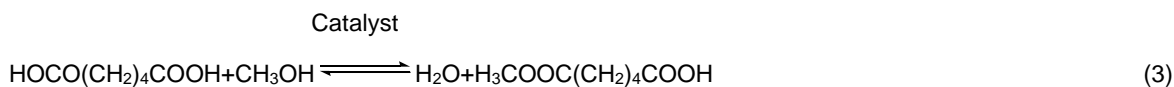## 2. Aspen simulation of ADH

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:

$$HO\text{-}CO\text{-}(CH_2)_4\text{-}CO\text{-}OH + 2CH_3OH \rightleftharpoons 2H_2O + H_3C\text{-}O\text{-}CO\text{-}(CH_2)_4\text{-}CO\text{-}O\text{-}CH_3 \tag{1}$$

$$H_3C\text{-}O\text{-}CO\text{-}(CH_2)_4\text{-}CO\text{-}O\text{-}CH_3 + 2H_2N\text{-}NH_2 \cdot H_2O \rightarrow 2CH_3OH +$$

$$H_2N\text{-}NH\text{-}CO\text{-}(CH_2)_4\text{-}CO\text{-}NH\text{-}NH_2 + 2H_2O \tag{2}$$

2.2 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.

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

Catalyst

$$HOCO(CH_2)_4COOH+CH_3OH \rightleftharpoons H_2O+H_3COOC(CH_2)_4COOH \tag{3}$$

Catalyst

$$HOCO(CH_2)_4COOCH_3+CH_3OH \rightleftharpoons H_2O+H_3COOC(CH_2)_4COOCH_3 \tag{4}$$

The reaction temperature is 70~75°C; with 1mol of adipic acid as the basis, the ratio of alcohol to acid is 4. After 1.5~2.0h of reflux reaction, distillation starts. First the unreacted methanol will be steamed out and recycled; then the esterification product - water will be steamed out; and finally the dimethyl adipate will be steamed 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.
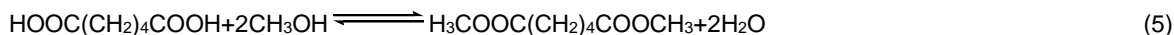
In the hydrazide reaction, the dimethyl adipate obtained from the esterification reaction is used as the raw material. With 1mol of dimethyl adipate as the basis, 4 mol of hydrazine hydrate and 4 mol of methanol are added to carry out the reaction under this condition. Finally, the conversion rate of dimethyl adipate is 100%. 2mol of hydrazine hydrate is consumed, and at the same time, 2mol 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 steamed 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 1kmol/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:

$$HOOC(CH_2)_4COOH+2CH_3OH \rightleftharpoons H_3COOC(CH_2)_4COOCH_3+2H_2O \tag{5}$$

$$HOOC(CH_2)_4COOH+CH_3OH \rightleftharpoons HOOC(CH_2)4COOCH_3+2H_2O \tag{6}$$

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 1bar.

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 0.125kmol/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 1kmol/h of dimethyl adipate generated, there will be 2kmol/h of dimethyl adipate and 1kmol/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%.
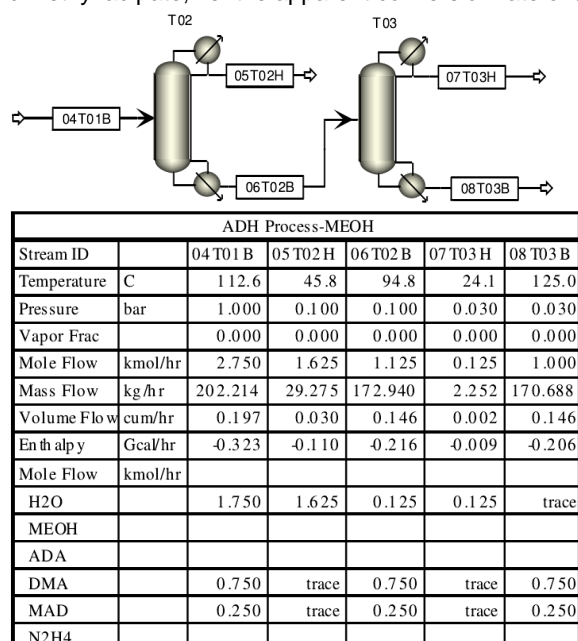

ADH Process-MEOH						
Stream ID		04 T01 B	05 T02 H	06 T02 B	07 T03 H	08 T03 B
Temperature	C	112.6	45.8	94.8	24.1	125.0
Pressure	bar	1.000	0.100	0.100	0.030	0.030
Vapor Frac		0.000	0.000	0.000	0.000	0.000
Mole Flow	kmol/hr	2.750	1.625	1.125	0.125	1.000
Mass Flow	kg/hr	202.214	29.275	172.940	2.252	170.688
Volume Flow	cum/hr	0.197	0.030	0.146	0.002	0.146
Enthalpy	Gcal/hr	-0.323	-0.110	-0.216	-0.009	-0.206
Mole Flow	kmol/hr					
H2O		1.750	1.625	0.125	0.125	trace
MEOH						
ADA						
DMA		0.750	trace	0.750	trace	0.750
MAD		0.250	trace	0.250	trace	0.250
N2H4						

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.

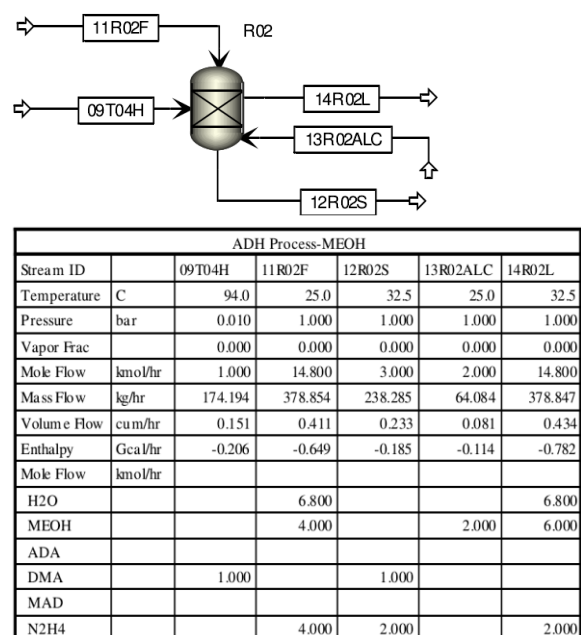| ADH Process-MEOH						
Stream ID		09T04H	11R02F	12R02S	13R02ALC	14R02L
Temperature	C	94.0	25.0	32.5	25.0	32.5
Pressure	bar	0.010	1.000	1.000	1.000	1.000
Vapor Frac		0.000	0.000	0.000	0.000	0.000
Mole Flow	kmol/hr	1.000	14.800	3.000	2.000	14.800
Mass Flow	kg/hr	174.194	378.854	238.285	64.084	378.847
Volume Flow	cum/hr	0.151	0.411	0.233	0.081	0.434
Enthalpy	Gcal/hr	-0.206	-0.649	-0.185	-0.114	-0.782
Mole Flow	kmol/hr					
H2O			6.800			6.800
MEOH			4.000		2.000	6.000
ADA						
DMA		1.000		1.000		
MAD						
N2H4			4.000	2.000		2.000

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_2H_4 and 3.4kmol/h of H_2O), 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.

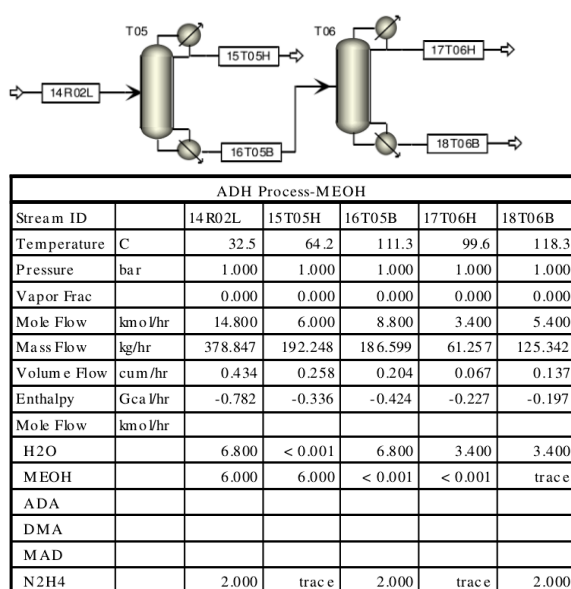| ADH Process-MEOH						
Stream ID		14R02L	15T05H	16T05B	17T06H	18T06B
Temperature	C	32.5	64.2	111.3	99.6	118.3
Pressure	bar	1.000	1.000	1.000	1.000	1.000
Vapor Frac		0.000	0.000	0.000	0.000	0.000
Mole Flow	kmol/hr	14.800	6.000	8.800	3.400	5.400
Mass Flow	kg/hr	378.847	192.248	186.599	61.257	125.342
Volume Flow	cum/hr	0.434	0.258	0.204	0.067	0.137
Enthalpy	Gcal/hr	-0.782	-0.336	-0.424	-0.227	-0.197
Mole Flow	kmol/hr					
H2O		6.800	< 0.001	6.800	3.400	3.400
MEOH		6.000	6.000	< 0.001	< 0.001	trace
ADA						
DMA						
MAD						
N2H4		2.000	trace	2.000	trace	2.000

Figure 3: Simulated result of filtrate distillation

From the data in the figure, we can see that, the amount of pure water finally evaporated from top of the column is 3.4kmol/h. 2kmol/h of N_2H_4 and 3.4kmol/h of H_2O remain at the bottom of the column, that is, 2kmol/h of 80% hydrazine hydrate, which is recycled to the hydrazide reaction. The temperature at the bottom of neither distiller exceeds 120°C.

3. Experimental verification of Aspen simulation computation

In this section, we analyze whether the mixture of dimethyl adipate and mono-methyl adipate can be recycled to achieve 100% apparent conversion rate of adipic acid and find out how many times the catalyst is reused.

3.1 Experimental process

Add 1mol of adipic acid, 5mol of absolute methanol and 2g of potassium bisulfate into the flask with a thermometer and a stirrer. After 1.5~2.0h of heating reflux reaction, start the distillation by gradually lowering the pressure, and steam out methanol, water and at last 0.25mol of dimethyl adipate. Add 0.25mol of adipic acid and 1.25mol of absolute methanol into the residual liquid, and continue the reflux reaction for 1.5~2.0h. After that, start the distillation by gradually lowering the pressure, and steam out methanol, water and at last 0.25mol of dimethyl adipate. For the residual liquid, repeat the above experiment and record the results of 6 experiments.

3.2 Experimental results and discussion

We conduct 6 experiments, which means the catalyst is used for 6 times. The total yield each time (the test result after each reaction and before the evaporation of methanol and water) is shown in Tab.1.

Table 1: Reuse result of catalyst

Time	1	2	3	4	5	6
Yield/%	82.61	83.84	84.93	85.29	84.62	85.58

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.
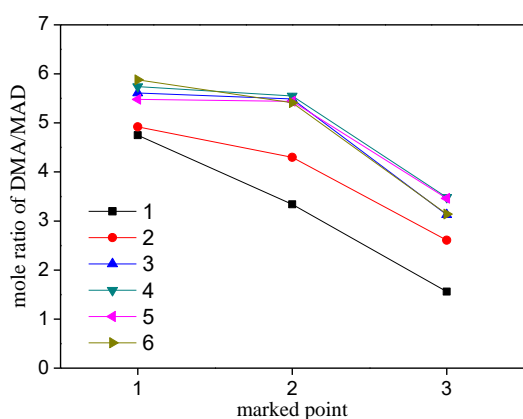

Figure 4: Graph of mole ratio of DMA/MAD

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 adipat, 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.

600

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