Novel energy saving strategy for separating acetic acid – water in extractive distillation with N-methyl acetamide as entrainer

Xinqiang You, Changjun Peng and Honglai Liu
State Key laboratory of Chemical Engineering and Department of Chemistry, East China University of Science and Technology, Shanghai 200237, China
E-mail: youxinqiang208@163.com; hlliu@ecust.edu.cn

Abstract. The design of homogeneous extractive distillation for acetic acid (AA) dehydration with N-methyl acetamide (NMA) as entrainer was investigated. It belongs to the classification of 0.0-1. The main challenge is that NMA and AA will lead to another pinch point, probably leading to energy cost and total annual cost (TAC) increase. Through analyzing thermodynamic insight, we have proposed a new strategy: low recycling entrainer purity for the extractive distillation of class 0.0-1 with no univolatility line existing. The strategy could save energy cost by avoiding the approach of the pinch point between AA and NMA. We have run sequence iterative optimization method for the process optimization. The total eleven variables are optimized. Results show that energy consumption and TAC are reduced by 50.6% and 52.1%, respectively. The results also reveal that a suitable shift of the feed tray locations improves the efficiency of the separation, even when less entrainer is used.

1 Introduction
Acetic acid (AA), as an important solvent or reagent, is widely used in a lot of chemical processes and the aqueous solution of acetic acid is produced as by-products [1]. The dehydration of aqueous acetic acid in an economical way is of great importance for the industries practice. However, it is difficult to separate the mixture by simple distillation because the relative volatility between water and acetic acid is very close to unity. Since the vapor-liquid equilibrium of acetic acid and water is not sensitive enough to the pressure variation to undertake pressure swing distillation, azeotropic distillation or extractive distillation are required. Both of them demand the addition of a third component in order to alter the relative volatility among water and acetic acid.

According to Küürüm and Fonyo [2], azeotropic distillation can be used advantageously to separate acetic acid from feeds having greater than 35-45wt% acetic acid in water. The design and control of equal molar acetic acid-water separation via heterogeneous azeotropic distillation was studied, and iso-butyl acetate was found to be the best azeotropic entrainer [3]. For more dilute feeds, solvent extraction is used before azeotropic distillation with solvents such as ethyl acetate, isopropyl acetate and diethyl ether. However, extraction is limited by phase separation and distribution of other components. Besides, the amount of azeotropic agent in azeotropic distillation is great, which causes much energy consumption for the vaporizing the agent.
Extractive distillation, as an alternative process, shows relative low energy consumption because of relative low reflux ratio, facilitation in design and control. For the dehydration of AA in extractive distillation, there are plants of publications focus on the choice of entrainers, such as N-methyl acetamide (NMA), N-methyl-2- pyrrolidone (NMP), sulfolane, p-xylene and so on [4]. NMA and NMP were verified the better entrainers for the dehydration of acetic acid solution based on the experimental data as the two candidates has much better performances on both relative volatility and entrainer selection. However, to the best of our knowledge, very few publications focus on the design and optimization of extractive distillation for the dehydration of acetic acid. The main reason is probably that there is another tangent pinch point between the AA and entrainer, which will result in that it is impossible to save energy and capital cost or even worse compared with the conventional distillation process.

Based on the thermodynamic analysis, herein a counter-intuitive concept: low purity recycling entrainer for the extractive distillation is firstly proposed for class 0.0-1 (no univolatility line exists) as far as we know. The steady-state process is optimized while keeping high purity AA distillate at the regeneration column with the low purity recycling entrainer (NMA) as the bottom liquid. The sequence iterative optimization method is used for optimizing the operating variables. Moreover, the effects of main variables on the process performances are investigated as well.

2 Process simulation and objective functions

2.1 Extractive process simulation
The candidate entrainer NMA was investigated for AA dehydration process in extractive distillation. The NRTL activity coefficient model was used for the liquid phase, and the Hayden-O'Connell equation of state was employed for the vapor phase. The model could reliably predict the salvation of polar compounds and dimerization in the vapor phase that occurs with mixture containing carboxylic acids [1]. The default binary parameters of AA-water and NMA-water were verified by experimental data and the binary parameters of AA-NMA were taken from Chang et al., [5]. The T-xy maps at 1 atm are shown in Figure 1.
Figure 1. T-xy experiment and predicted map of water—AA—NMA system at 1 atm.

From Figure 1, the estimated data agree well with the experimental data. It demonstrates that the used binary parameters are able to describe well the system of water-AA-NMA. We also notice that there is a tangent point between AA and NMA at NMA rich part. It may contribute the rare designs of extractive distillation using NMA as entrainer for separating water-AA although NMA is reported as a suitable entrainer with high relative volatility and selection.

2.2 Objective functions
The first objective function (OF) is energy cost per unit product. It is used under given column tray number ($N_i$ and $N_e$) and specified NMA content in recycling entrainer stream.
\[
\min \ OF = \frac{M \cdot Q_{r1} + m \cdot Q_{c1} + M \cdot Q_{r2} + m \cdot Q_{c2}}{D_2}
\]

subject to: 
\[
\begin{align*}
x_{\text{water}, D1} & \geq 0.999 \\
x_{\text{water}, W1} & \leq 0.0001 \\
x_{\text{AA}, D2} & \geq 0.999 \\
x_{\text{NMA}, W2} & \geq \text{variable}
\end{align*}
\] (1)

Since \( D_1 \) product is water, no need treating it at denominator. Constraint 1 concerns the product (water) purity. It is necessary for reducing the entrainer NMA losses and AA purity following the interrelationship among distillates [6]. Constraint 2 in bottom \( W_1 \) \((F_2)\) aims at keeping high the product (water) recovery. Constraint 3 serves the product (AA) purity in \( D_2 \). Constraint 4 focuses on the recycling entrainer purity, which should be specified in advance, \( Q_{r1} \) and \( Q_{c1} \): extractive column reboiler and condenser duty, \( Q_{r2} \) and \( Q_{c2} \): entrainer regeneration column reboiler and condenser duty, \( D_1 \) and \( D_2 \) extractive column and entrainer regeneration column distillate flow rate, \( m = 0.036 \): energy price difference factor for condenser (cooling water) vs reboiler (low pressure steam). \( M \) may equal to 1, 1.065 or 1.280 when low, middle or high pressure steams are used, respectively.

TAC is also calculated for the comparison of the different designs. TAC includes capital cost per year and operating costs as shown in the following formula:

\[
\text{TAC} = \frac{\text{capital cost}}{\text{payback period}} + \text{operating costs}
\] (2)

The column shell, tray and heat exchanger cost constitute the capital cost and a three-year payback period are used. The operating cost contains the energy cost in reboiler and condenser. The heat exchanger for cooling the recycling entrainer is taken into account in order to emphasize its effect on the process. Other costs such as the liquid delivery pumps, pipes, valves are neglected at the conceptual design stage.

3 Results and discussions

3.1 Thermodynamic analysis of AA dehydration with NMA

For water—AA with NMA system, the ternary map belongs to class 0.0-1 and no univolatility line exists. Hence, water will be the top product of the extractive column, and the mixture of AA and NMA with little water impurity enters the entrainer regeneration column. AA will be the top product of regeneration column and high purity NMA seems to be the bottom product and recycle back to the extractive column. Unfortunately, there is a tangent point between AA and NMA at NMA rich region, which will cause the dramatically increase of reflux ratio and thus the reboiler duty for achieving the high purity NMA. This may counteract the energy saving potential of the extractive distillation compared with conventional distillation process, which goes against our intuition.

From the view of thermodynamic insight [7], when a high purity recycling entrainer NMA reenters into the extractive column, it is a point locating very close to the stable node of extractive section \((\text{SN}_{\text{ext}, A})\) in ternary map and interacting a residue curve reaching the vertex A (water). While a low recycling entrainer stream with impurity AA reenters into the extractive column, it is a point which is a little higher than the \( \text{SN}_{\text{ext}, A} \), and then interacts another residue curve reaching the vertex A (water). Of course, the penalty of increasing trays in rectifying section or reflux ratio in the extractive column is inevitable as low purity recycling entrainer with AA impurity is recycled back, but the process is still feasible to achieve high purity product A (water). This phenomenon for class 0.0-1 is totally different from that for class 1.0-1a, in which low purity recycling entrainer will prevent the high purity product.
A being distilled. The reason is that the distillate product is extractive stable node in class 0.0-1 instead of extractive saddle node in class 1.0-1a, in which the rectifying section profile will apart from and turn off at the saddle node following residue curve [7]. This will prevent achieving high purity distillate product. In summary, the low recycling entrainer purity strategy is feasible from theory analysis for separating mixtures of class 0.0-1. And the low recycling entrainer purity (x_{NMA,W2}) is specified as 0.99 instead of the common value of 0.9999.

3.2 Choice of D1 and D2
Since the effect of D1 and D2 on the product purity is strongly non-linear, D1 and D2 were varied with a discrete step of 0.1 kmol/h from 250 kmol/h to 250.2 kmol/h. The sequence quadratic program optimization was run for F_E, R1 and R2 with the initial design from literature [8]: N_1=30, N_2=20, N_{FE}=3, N_{FF}=8, N_{F2}=7. Notice that the tray number is counted from top to bottom of the column, and condenser and reboiler are considered as the first and last tray. The results are shown in Figure 2.

From Figure 2, we observe that (1) there is the effect of D1 on OF even there is no D1 in the denominator part of OF. It proved the ability of OF for optimizing the two columns together. Furthermore, the better OF value is found at D1=250.1 kmol/h, instead of the lower value of 250 kmol/h or the higher value 250.2 kmol/h at given D2. (2) It seem that OF will decrease following the increasing direction of D2 since D2 is the sole denominator in OF expression. However, OF decreases from Figure 2 following the decrease of D2 when D1 is fixed. It demonstrates that it is difficult to separate AA and NMA, evidencing the existence of pinch point between them. As we will optimize other variables in the subsequent steps, we select the pair of D1=250.1 kmol/h and D2=250 kmol/h, corresponding to a product recovery high enough but not too high so as to make the flow sheet convergence difficult. The related OF value is 246521.2 kJ/kmol, with F_E=182.4 kmol/h, R1=2.107 and R2=1.300.

![Figure 2](image_url)

**Figure 2.** Effects of D1 and D2 on OF with D1, D2, FE, R1 and R2 as variables.

3.3 Optimization of the three feed locations
The sensitivity analysis over the three feed locations with ranges [2; 25] for N_{FE}, [>N_{FE}; 29] for N_{FF}, [3; 15] for N_{F2} was made by using experimental planning procedure so as to avoid the local minimum. For each set of values, F_E, R1, R2 are optimized while D1 and D2 are fixed. The results are shown in Table 3.

| No. | N_{FE} | N_{FF} | N_{F2} | F_E   | R1    | R2   | OF       |
|-----|--------|--------|--------|-------|-------|-------|----------|
| 1   | 3      | 8      | 7      | 187.5 | 2.02  | 1.38  | 244603   |
NMA system while keeping the entrainer flow rate, reflux ratio, column diameters and heat exchanger areas in the two columns. Although the NMA purity in the recycling entrainer stream (0.99) is a little high, the difference reaches two orders of magnitude compared with the normal specification (0.9999) of the recycling entrainer purity.

From Table 3, we can conclude that (1) the suitable feed locations allow decreasing the energy cost per unit product OF, as seen by comparing design No. 1 in literature with all others. The three feed locations and three continuous variables ($F_E$, $R_1$ and $R_2$) affect each other and it demonstrates the necessary for optimizing the three feed locations together. (2) The reflux ratio of entrainer moves one tray down the column from design No.1 to No.7 for the lowest OF design, it agrees with the proverbial fact that increasing the number of trays in the rectifying section allows decreasing the reflux ratio $R_1$. (3) The minimum value of OF is found in design No.7 with four extra number of trays in the extractive section than design No.1. The four more trays have a positive significance on the process and contribute a better efficiency of the extractive section. (4) A lower $F_E$ and a higher $R_1$ in design 3, 4, 5 and 6 than that in design No.7 contribute a higher OF, meanwhile a higher $F_E$ and a lower $R_1$ in design 9 and 10 than that in design No.7 lead also a higher OF. This proves quantitatively that there is a balance between entrainer usage and energy cost. (5) Comparing design No. 7 and 8, we found that only one tray increase for $N_{F_E}$ affect the energy cost OF and three continuous variables. It indicates that OF can account the two columns’ variables together. (6) The lowest energy cost for per unit product OF is 182292.3 kJ/kmol. It represents a 25% decrease compared to literature design No.1 see Table 3.

### 3.4 Comparison

Our design with the low recycling entrainer purity strategy ($X_{\text{NMA,w2}}$ as 0.99) is compared with the reference design with common strategy ($X_{\text{NMA,w2}}$ as 0.9999). The design result is shown in Table 2.

**Table 2.** The design result of comparing with the low recycling entrainer purity strategy

| $N_{F_E}$ | $N_{F_F}$ | $N_{F_2}$ | $F_E$ | $R_1$ | $R_2$ | $D_1$ | $D_2$ | OF /kJ/kmol | TAC 10^5$/y$
|-----------|-----------|-----------|-------|-------|-------|-------|-------|-------------|-------------|
| Ref.      | 3         | 8         | 7     | 427.3 | 3.00  | 2.00  |       |             |             |
| our       | 4         | 13        | 6     | 166.4 | 0.90  | 1.05  |       |             |             |
|           | 250.0     | 250.0     | 368820|       |       |       |       | 6.753       |             |
| our       | 250.1     | 250.0     | 182292|       |       |       |       | 3.235       |             |

Compared with reference design, (1) the entrainer flow rate decreased drastically from 427.3 kmol/h in case Ref to 166.4 kmol/h. It demonstrates that too much entrainer contributes a worse design instead of a better one. (2) The reflux ratios are greatly reduced and the energy consumption showing through OF value is saved by 50.6%. (3) TAC is reduced by 52.1%. It is mainly due to the decrease of entrainer flow rate, reflux ratio, column diameters and heat exchanger areas in the two columns. (4) Four more trays are used in the extractive section. This point proves the statement that there should be enough trays in the extractive section in order to achieve the stable node of the extractive section. Most importantly, Table 4 shows that the proposed strategy low recycling entrainer purity could successfully improve the extractive distillation process for water—AA—NMA system while keeping the same number of trays in the extractive and regeneration columns. Although the NMA purity in the recycling entrainer stream (0.99) is a little high, the difference reaches two orders of magnitude compared with the normal specification (0.9999) of the recycling entrainer purity.
4 Conclusion
A novel strategy: low recycling entrainer purity is proposed for the acetic acid dehydration extractive distillation with N-methyl acetamide as entrainer. The strategy could reduce the amount of entrainer in extractive column and save energy cost in regeneration column by avoiding the approach of the pinch point between AA and NMA.

We have run sequence iterative optimization method for optimizing the extractive distillation process following the proposed novel strategy. The process is conducted with the aim of minimizing the total energy consumption per product unit OF at given tray number of columns and purity of recycling entrainer obtained through thermodynamic insight. Thanks to the novel strategy, significant cost savings are achieved: energy consumption OF by 50.6%, TAC by 52.1% compared with the design in literature. In addition, a suitable shift of the feed tray locations improves the efficiency of the separation, even when less entrainer is used.

References
[1] Long et al. 2010. Design and optimization of a dividing wall column for debottlenecking of the acetic acid purification process. Chem. Eng. Process. 49:825-835.
[2] Küürüm, S. & Fonyo, Z. 1996. Comparative study of recovering acetic acid with energy integrated schemes. Appl. Therm. Eng. 16:487-495.
[3] Chien et al., 2004. Design and control of acetic acid dehydration system via heterogeneous azeotropic distillation. Chem. Eng. Sci. 59:4547-4567.
[4] Pirola et al. 2014. Simulation and related experimental validation of acetic acid/water distillation using p-xylene as entrainer. Ind. Eng. Chem. Res. 53(46): 18063-18070.
[5] Chang et al. 2006. Isobaric vapor–liquid equilibria for water+ acetic acid+ ( N-methyl pyrrolidone or N-methyl acetamide). Fluid Phase Equilib. 242:204-209.
[6] You et al., 2016. Low pressure design for reducing energy cost of extractive distillation for separating diisopropyl ether and isopropyl alcohol. Chem. Eng. Res. Des. 109:540-552.
[7] Rodriguez-Donis et al., 2009. Thermodynamic insights on the feasibility of homogeneous batch extractive distillation, 2. Low-relative-volatility binary mixtures with a heavy entrainer. Ind. Eng. Chem. Res. 48(7): 3560-3572.
[8] Denglei et al., 2010. Concept design and optimization by Aspen Plus for extractive distillation. Comp. Appl. Chem. 6: 019.
[9] Chien, I. & Kuo, C.L. 2006. Investigating the need of a pre-concentrator column for acetic acid dehydration system via heterogeneous azeotropic distillation. Chem. Eng. Sci. 61:569-585.