

# Recovery of Acetonitrile from Pharmacy Factory Wastewater by Distillation Process

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## 1. Introduction

Acetonitrile is one of the important substances in the chemical industry and is widely used in the pharmaceutical industry as a solvent or reactant. Although it is industrially obtained as a by-product in the production of acrylonitrile, acetonitrile is demanded more than acrylonitrile, and recycle method of acetonitrile in the wastewater from pharmaceutical factory has attracted attention. However, acetonitrile and water form azeotropic mixture, and it is difficult to completely separate them in ordinary distillation. Then, pressure swing distillation[1] and extractive distillation[2] have been studied to separate acetonitrile and water.

This study aims to propose efficient separation of acetonitrile and water by pressure swing and extractive distillation processes. First, the vapor-liquid equilibrium (VLE) was estimated to examine the effects of the conditions on the azeotrope point. Then, the separation was computationally simulated and energy consumptions by both processes were compared.

## 2. Vapor-Liquid Equilibrium of Binary and Ternary Systems

### 2.1 Estimation of Vapor-Liquid Equilibrium

Table 1 shows the calculation conditions for the VLE estimations with binary system of acetonitrile and water, and ternary system of acetonitrile, water and dimethyl sulfoxide (DMSO). DMSO was selected as the third compound because it has been proved that is a suitable solvent[3]. The UNIFAC model was used to estimate the activity coefficients in the liquid phase, one of the thermodynamic estimation methods with interaction parameters between functional groups composing the molecular. Then, the effects of the pressure and DMSO on the VLE was studied.

Table 1 Conditions for VLE estimation

|                       |                           |        |
|-----------------------|---------------------------|--------|
| Binary system         | acetonitrile, water       |        |
| Pressure              | [kPa]                     | 10-500 |
| Ternary system        | acetonitrile, water, DMSO |        |
| Pressure              | [kPa]                     | 100    |
| Mole Fraction of DMSO | [-]                       | 1-30   |

### 2.2 Results and Discussion

Figure 1 shows vapor-liquid equilibrium of a binary system. It can be seen that the azeotropic composition changed when pressure is increasing. Figure 2 shows vapor-liquid equilibrium of a ternary system after adding the solvent. It can be seen that as the solvent concentration increases, the azeotropic composition increases. From Figure 3, the azeotropic composition changes rapidly when the pressure is around 10kPa to 100kPa and change lower and lower when the pressure is rising over 300kPa.

And from Figure 4, the minimum required mole fraction of solvent can be known.

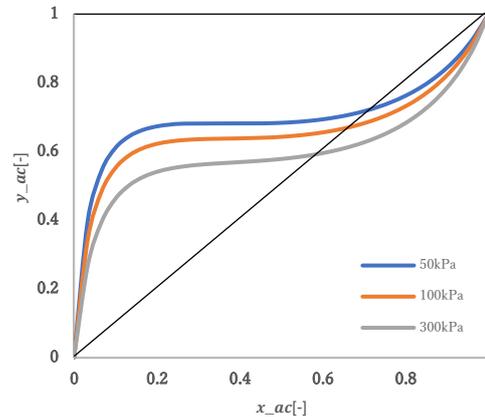


Figure 1 VLE diagram of binary system

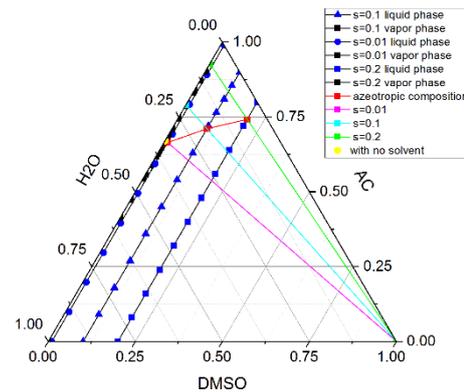


Figure 2 VLE diagram of ternary system

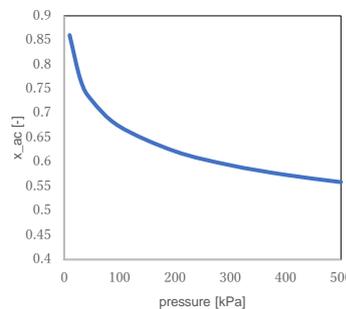


Figure 3 Azeotropic composition of acetonitrile with different pressure

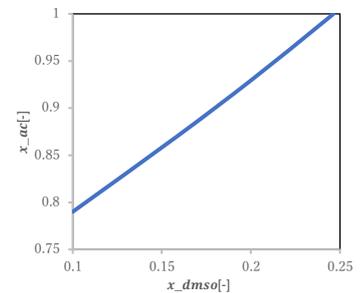


Figure 4 Azeotropic composition of acetonitrile with different mole fraction of solvent

## 3. Process Simulation

### 3.1 Process Description

Pressure swing distillation is a distillation method that relies on the phenomenon that the azeotropic composition changes with the change in pressure. The process of pressure swing distillation is shown in **Figure 5**, distillation column D1 and D2 are the low-pressure distillation column and the high-pressure distillation column respectively. And the process of extractive distillation is shown in **Figure 6**. It consisted of an extractive distillation columns(D3) and a solvent recovery column(D4). The process simulation was conducted with the general process simulator of PRO II.

### 3.2 Simulation Conditions

**Table 2** shows the calculation conditions of pressure swing and extractive distillations. The composition of the feed consisted of acetonitrile and water and the mole fraction of acetonitrile was 0.4 because actual factory wastewater has such a composition. The specification of the product was that the mole fraction and yield of acetonitrile was set as 0.999. In the case of pressure swing distillation, the operating pressure was set at 50kPa and 300kPa. The low-pressure column operated lower than 30kPa should be vacuum distillation and the energy consumption will increase rapidly. When the pressure of high pressure column is higher than 300kPa, the azeotrope point changed unremarkably. And from **Figure 4**, when the molar ratio of acetonitrile and water is 4:6, the minimum required amount of solvent can be known.

Table 2 Conditions of the simulation

| Feed and Product                         |          |         |
|--|----------|---------|
| Feed Mole Flow rate                      | [kmol/h] | 1000    |
| Temperature                              | [K]      | 298     |
| Mole Fraction of Acetonitrile in Feed    | [-]      | 40      |
| Yield                                    | [-]      | 0.999   |
| Mole Fraction of Acetonitrile in Product | [-]      | 0.999   |
| Pressure Swing Distillation              |          |         |
| Feed Stage (D1)                          | [-]      | 10-20   |
| Number of Stages (D1)                    | [-]      | 10-20   |
| Number of Stages (D2)                    | [-]      | 20-30   |
| Pressure (D1)                            | [kPa]    | 50      |
| Pressure (D2)                            | [kPa]    | 300     |
| Reflux Ratio (D1)                        | [-]      | 1.0-2.0 |
| Reflux Ratio (D2)                        | [-]      | 0-1.0   |
| Extractive Distillation                  |          |         |
| Pressure (D3 and D4)                     | [kPa]    | 100     |
| Number of Stages (D3)                    | [-]      | 1-100   |
| Number of Stages (D4)                    | [-]      | 1-20    |
| Feed Stage (D3)                          | [-]      | 1-100   |
| Solvent Stage (D3)                       | [-]      | 1-10    |
| Reflux Ratio (D3)                        | [-]      | 0.1-1.0 |
| Reflux Ratio (D4)                        | [-]      | 0.1-1.0 |

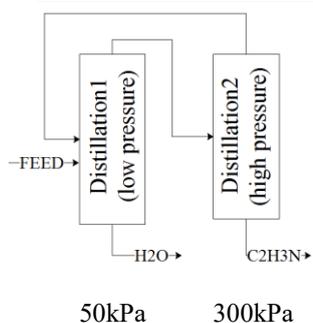


Figure 5 Process of pressure swing distillation

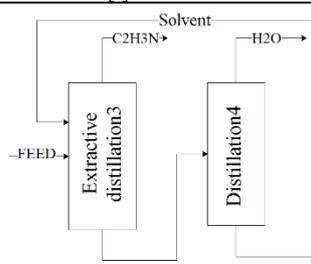


Figure 6 Process of extractive distillation

## 3.3 Results and discussion

### 3.3.1 Operating conditions and heat duty

Operating conditions and heat duty for pressure swing distillation and extractive distillation are shown in **Table 3**.

Table 3 Optimal condition and heat duty of distillation

| Distillation column | Pressure [kPa] | Stage number | Feed-in stage | Reflux ratio | Heat duty of reboiler[kJ/mol] |
|---------------------|----------------|--------------|---------------|--------------|-------------------------------|
| D1                  | 50             | 15           | 10            | 1.8          | 115.4                         |
| D2                  | 300            | 30           | 13            | 0.9          | 58.2                          |
| D3                  | 100            | 58           | 52            | 0.9          | 28.8                          |
| D4                  | 100            | 19           | 8             | 0.1          | 34.1                          |

### 3.3.2 Comparison of two types of distillation

The total energy consumption by the reboiler after two distillations is shown in **Table 3**. Therefore, extractive distillation is more efficient than pressure swing distillation in acetonitrile-water system. The reasons leading to such results were considered to be related to latent heat of water. With the data of the overall flow rate in the two processes, in the pressure swing distillation, the flow rate of mixture with water and acetonitrile refluxed is as high as 822kmol/h, so a large amount of heat is necessary to evaporate mixture which contains 42.7% of water again in distillation column D1. However, in the case of the extractive distillation, since there is no mixture except solvent is refluxed, less energy is required to evaporate mixture again. Otherwise, trace amounts of solvent may be contained in the product depending on the state of the distillation facility, so there is a risk of affecting quality while using extractive distillation.

## 4 Conclusion

1) By making a relationship diagram between mole fraction of solvent and azeotropic composition of acetonitrile, the minimum required mole fraction of dimethyl sulfoxide is 24.6% when the mole ratio of acetonitrile and water is 4: 6.

2) After running simulation and optimizing operating conditions, both pressure swing distillation and extractive distillation proved that can separate acetonitrile and water into target concentrations.

3) Extractive distillation is more efficient than pressure swing distillation by comparing energy consumption of two distillation processes.

## References

- [1]Zhou Jinbo, Cui Xianbao, et al. Separation of acetonitrile-water mixture by batch extractive distillation[J]. Chemical Industry and Engineering,26(6):482-486, (2009).
- [2]Repke J U, Klein A, et al. Pressure swing batch distillation for homogeneous azeotropic separation[J]. Chemical Engineering Research and Design,85(4):492-501, (2007).
- [3]Zhang Zhigang, Lv Ming, et al. Isobaric vapor-liquid equilibrium for the extractive distillation of acetonitrile-water mixtures using dimethyl sulfoxide at 101.3kPa[J]. Chem.Eng.Data,58,3364-3369(2013).