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Simulation of extractive distillation for separating Acetonitrile-Toluene using Butyl Propionate as entrainer

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ABSTRACT

Acetonitrile is known as a polar solvent that can dissolve in non-polar hydrocarbon liquids. As an example of a nonpolar solvent, toluene is one of the solvents that dissolves well in acetonitrile. If acetonitrile and toluene are mixed, a minimum boiling azeotrope will form. The maximum purity of acetonitrile when distilled is 89.5% mole at 81.19 °C under conventional distillation. To achieve high purity of acetonitrile, a new solvent should be added to this mixture. In this work, high purity of acetonitrile (99.9% mass) with extractive distillation method was simulated using Aspen Plus software. Based on the pseudo-binary analysis by Aspen Plus, butyl propionate can break the azeotrope mixture at concentration of 0.3 (mole fraction). The simulation results showed that, to get 99.9% mass of acetonitrile, a solvent to feed ratio of 1.5, reflux ratio of 1.5 a number of stages of 32 were required. After obtained the optimum parameters, economic evaluation was calculated using total annual cost (TAC) objective function method. From the economic evaluation, a feasible TAC of 1.225×10^6 \$/year was obtained.

ABSTRAK

Asetonitril dikenal sebagai pelarut polar yang dapat larut dalam cairan hidrokarbon non-polar. Sebagai contoh pelarut nonpolar, toluena merupakan salah satu pelarut yang larut dengan baik dalam asetonitril. Jika asetonitril dan toluena dicampur, azeotrop dengan titik didih minimum akan terbentuk. Kemurnian maksimum asetonitril saat disuling adalah 89,5% mol pada 81,19 °C pada distilasi konvensional. Untuk mencapai kemurnian asetonitril yang tinggi, pelarut baru harus ditambahkan ke dalam campuran ini. Dalam karya ini, asetonitril dengan kemurnian tinggi (99,9% massa) dengan metode distilasi ekstraktif disimulasikan menggunakan perangkat lunak Aspen Plus. Berdasarkan analisis pseudo-biner dengan Aspen Plus, butil propionat dapat memecah campuran azeotrop pada konsentrasi 0,3 (fraksi mol). Hasil simulasi menunjukkan bahwa untuk mendapatkan massa asetonitril 99,9%, rasio pelarut terhadap umpan 1,5, rasio refluks 1,5 diperlukan sejumlah tahapan sebanyak 32. Setelah diperoleh parameter optimum, dilakukan perhitungan evaluasi keekonomian dengan menggunakan metode fungsi tujuan total biaya tahunan (TAC). Dari evaluasi ekonomi, diperoleh TAC layak sebesar 1,225×106 \$/tahun

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1. Introduction

Acetonitrile is a polar solvent with large dipole moment which is widely used in the pharmaceutical industry to laboratory-scale experiments [1], [2]. Due to its low toxicity and good solvation ability, global demand for acetonitrile reaches up to 70% of the whole market [3]. Along with high global demand, acetonitrile liquid waste is also often found in wastewater treatment [4]. Acetonitrile is known to dissolve completely in polar liquids such as water, ethanol, to non-polar aromatic hydrocarbons. As an example of a nonpolar solvent, toluene is an aromatic compound that dissolves well with acetonitrile. If acetonitrile and toluene are mixed, a minimum boiling azeotrope will form in binary.

Pharmaceutical industry, electrochemistry, and polymer phase diagram study are the practical applications of the acetonitrile + toluene mixture [1]. The remaining mixture of acetonitrile and toluene in these chemical processes is difficult to separate through ordinary distillation [2]. If the mixture of acetonitrile and toluene is not separated, the concentration of these two compounds will increase in the wastewater. Based on this circumstance, the separation of acetonitrile and toluene needs to be studied further through various separation methods in chemical engineering.

Acetonitrile forms a ternary azeotrope with water and toluene [5]. Because the separation of acetonitrile from water has been widely studied [1], this research will investigate further the separation of binary mixtures of acetonitrile from toluene using the extractive distillation method. Minimum boiling azeotrope that occurs in acetonitrile and toluene is a common thing in chemical industries and waste treatment. This kind of azeotrope in binary mixtures hindered the separation method when distilled [6].When acetonitrile is mixed with toluene, the mixtures form an azeotropic mixture at 81.19 °C and the maximum purity of acetonitrile is 89.5% mole [7].To achieve 99.9% mass purity of acetonitrile from toluene, an entrainer should be added to increase the relative volatility of acetonitrile.

The previous study of extractive distillation of acetonitrile and toluene mixtures has been carried out [8]. The study involved three benzene-derived solvents such as 1,4-diethybenzene, 4-tert-butyltoluene, and Isopropylbenzene. Among them, 1,4-diethybenzene showed optimal conditions with acetonitrile purity reaching 99.7% mole. The study of acetonitrile-toluene binary mixture separation using butyl propionate has not been published before. Butyl propionate was chosen as a solvent because it has good mixing ability. This solvent is also considered an environmentally friendly solvent because of its low vapor pressure and the odor of this solvent is safe and tolerable [9].

In this study, the effect of reflux ratio, solvent to feed ratio (S/F ratio), number of stages, and feed stage position was analyzed. This study aims to obtain the highest acetonitrile purity by extractive distillation method. The entrainer used in this research is butyl propionate which has a higher boiling point than acetonitrile and toluene. Simulation of extractive distillation for separating acetonitrile-toluene using butyl propionate as entrainer was simulated using Aspen Plus software. The feed used is at equimolar concentrations, the thermodynamic model uses a complex model, namely UNIQUAC, and the economic evaluation used is the Total Annual Cost (TAC) where equipment costs are also taken into account in addition to utility costs. The purity of acetonitrile and toluene products is also maintained so that they meet ASTM specifications.

2. Method

The optimization procedure for separating acetonitrile and toluene using extractive distillation method provides in Figure 1. This diagram has been made by referring to some literature. Identifying the main compound is essential to select the fluid package in this simulation. Acetonitrile and toluene are hydrocarbon compounds which the VLE data have been correlated in the previous study [7][10]. Separating azeotropic mixtures by extractive distillation requires suitable solvent candidates to obtain optimal condition. The following are some steps of optimization procedure.

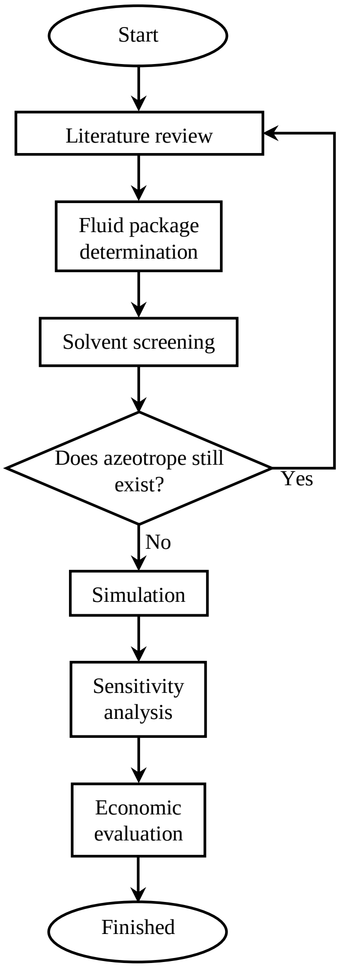

Figure 1. Optimization procedure of extractive distillation

The isothermal and isobaric vapor liquid equilibria of acetonitrile/toluene/butyl propionate was reviewed from the references [7], [10] respectively. The VLE data from Monfort have been correlated with Wilson, NRTL, and UNIQUAC equations. This updated reference demonstrates that the

UNIQUAC model is appropriate and comparable to that experimental data. In this study UNIQUAC thermodynamic model and butyl propionate chosen as an appropriate fluid package and solvent to simulate the extractive distillation. To check the capability of butyl propionate to remove toluene from acetonitrile, pseudo binary x-y diagram was attempt at 0.3 mole fraction of butyl propionate. Mole fraction of 0.3 was attempt in assumption that ternary mixture nearly equimolar condition (0.35 acetonitrile, 0.35 toluene, and 0.3 butyl propionate). At this concentration, butyl propionate has enough capabilities to break the azeotrope of acetonitrile and toluene as shown in Figure 2.

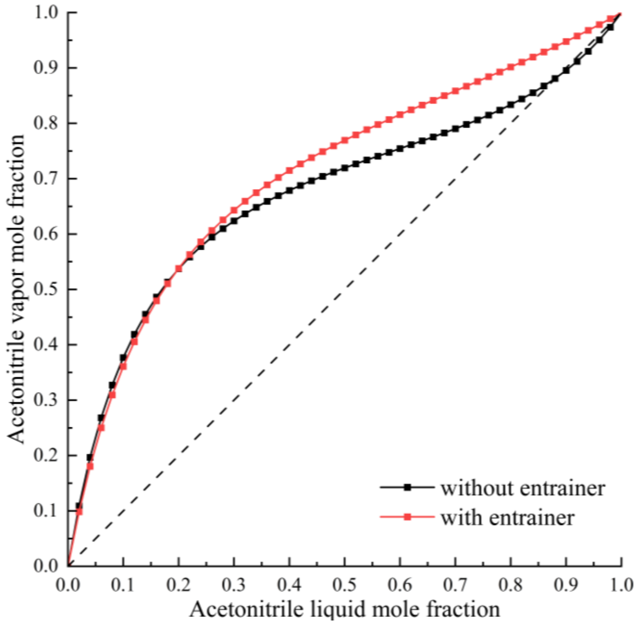

Figure 2. Pseudo-binary diagram for acetonitrile-toluene with butyl propionate 0.3 mole fraction at 101.325 kPa

Using UNIQUAC thermodynamic model, residue curve map with univolatility line was constructed using Aspen Plus distillation synthesis ternary maps. This residue curve map (Figure 3) was designed in a right-angled triangle with entrainer position at an angle of 90°. Acetonitrile and toluene were located at the ends of the hypotenuse. At 101.325 kPa, the azeotropic mixture of acetonitrile (boiling point 81.65 °C) and toluene (boiling point 110.68 °C) shows a minimum boiling point at 81.19 °C. From this optimal configuration of the residue curve map, it was observed that butyl propionate was a feasible entrainer for the acetonitrile-toluene separation.

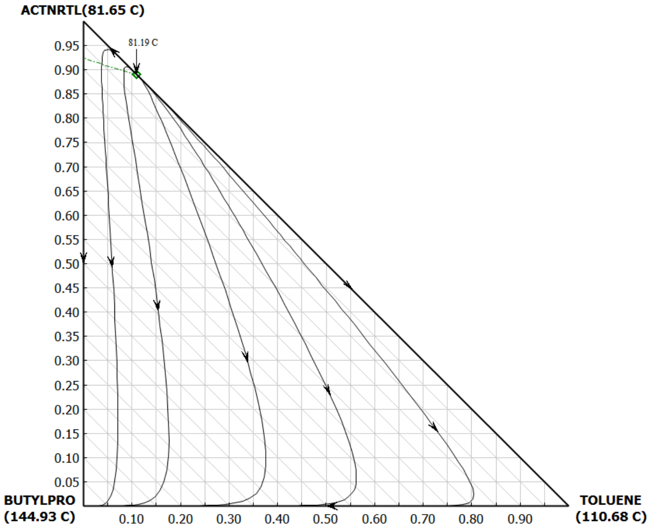

Figure 3. Residue curve map for acetonitrile/toluene/butyl propionate system at 101.325 kPa

In this study, the extractive distillation simulation was presented in Figure 4 as a process flow diagram which consist of two columns, one as an extractive distillation column (EDC) and the other as solvent recovery column (SRC). Simulation of the separation process was performed with Aspen Plus V14. Feed stream (binary azeotropic mixture) and solvent stream are fed to the first column at initial temperature of 25 °C. In EDC, acetonitrile will be evaporated as distillate product and toluene as heavy key component with butyl propionate will be separated in SRC.

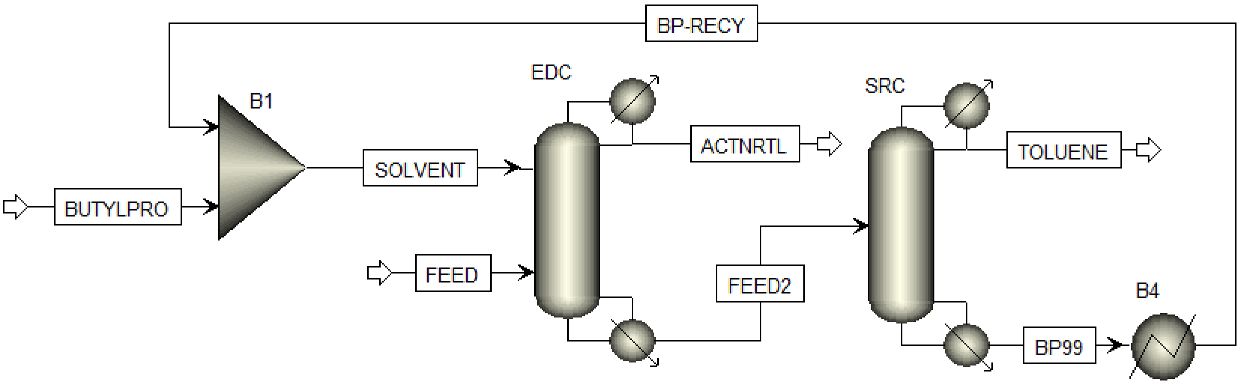

Figure 4. Aspen Plus PFD (process flow diagram) for the extractive distillation using butyl propionate as entrainer

Additional information from Figure 3:
BUTYLPRO = Makeup stream of butyl propionate
BP99 = Bottom product of butyl propionate from SRC with 99% purity (high temperature)
BP-RECY = Bottom product of butyl propionate from SRC with 99% purity (low temperature)

3. Results and Discussion

In this work, sensitivity analysis was operated for EDC to obtain the optimum configuration for the extractive distillation process. Number of stages, solvent to feed ratio, feed stage, and reflux ratio were analyzed in this work. Figure 5 depicts the number of stages effect to the acetonitrile purity based on variations in the value of reflux ratio from 0.6 to 1.5. A high reflux ratio value will increase the direct contact of solvent with heavy components so the relative volatility of acetonitrile also increases. The highest acetonitrile purity can be obtained at reflux ratio of 1.5. From this graph, the minimum number of stages to achieve acetonitrile with 99.9% purity was 32 as an optimal condition.

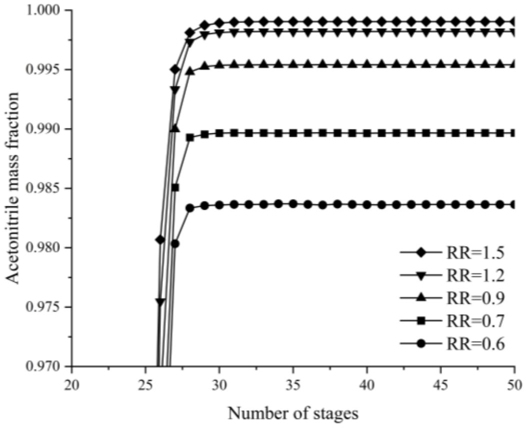

Figure 5. Effect of the number of stages determination and to acetonitrile distillate purity based on reflux ratio from 0.6 to 1.5.

To achieve 99.9% purity of acetonitrile, a sensitivity analysis of solvent stream effect was reported in Figure 6. The original data of this analysis is mole flow of butyl propionate in solvent stream. To obtain the S/F ratio, the value of butyl propionate mole flow as solvent was divided by absolute value of acetonitrile feed mole flow. From this data, the maximum purity of acetonitrile at distillate was achieved when S/F ratio was 1.5. As the S/F ratio increases, the acetonitrile purity will decrease to zero at the bottom product of EDC.

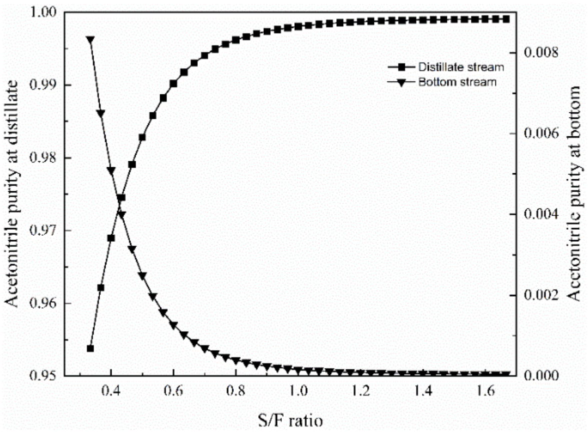

Figure 6. Effect of S/F ratio to acetonitrile purity at distillate and bottom section of EDC

After determine the number of stages, reflux ratio, and S/F ratio, the optimum feed stage of EDC was established. Figure 7 presented the effect of feed stage to acetone purity based on entrainer feed stage (EFS) configuration of 6, 12, 18, and 24. When the EFS was set at 6, the acetonitrile purity indicated the maximum purity of 98%. When entrainer feed stage attempt at 18 and 24, the maximum acetonitrile purity was 99.7% and 97.5% respectively. It is confirmed that the maximum acetonitrile purity of 99.9% was achieved at EFS configuration of 12 and feed stage of 24.

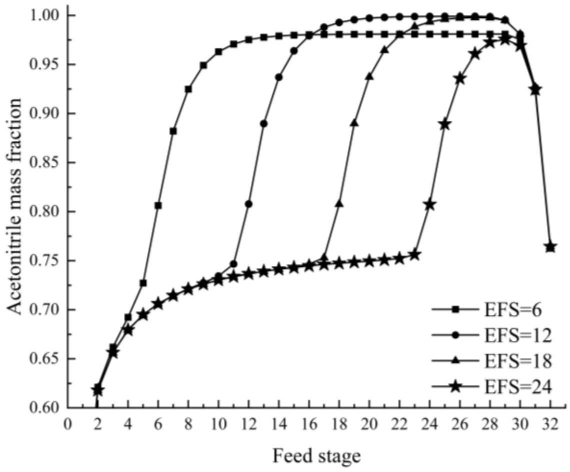

Figure 7. Effect of feed stage determination to acetonitrile purity based on entrainer feed stage from 6 to 24

The effect of mole reflux ratio to the condenser and reboiler duty were analyzed in Figure 8. The maximum acetonitrile purity was achieved at reflux ratio of 1.5. As the reflux ratio increases, the purity of acetonitrile decreases. It shows that the large reflux ratio will increase the mixing (dilution) of acetonitrile with butyl propionate [11]. The change of reflux ratio indicated a significant effect to condenser and reboiler duty in EDC. From this graph, the minimum condenser and reboiler duty were 0.64 MW and 1.13 MW to achieve acetonitrile purity of 99.9% respectively.

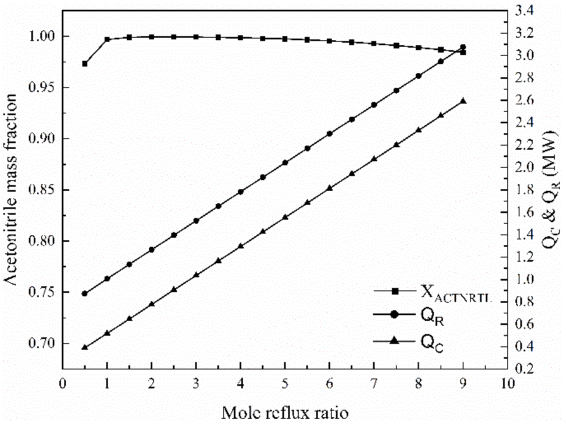

Figure 8. Effect of reflux ratio determination to acetonitrile purity and duty of condenser and reboiler of EDC

Figure 9 represents the vapor and liquid mole fraction profiles in EDC. At stage 12 where the entrainer was fed to EDC, the acetonitrile liquid and vapor concentration increased at range 12 to 1. From stage 12 to 32 the vapor and liquid concentration of acetonitrile was decreased but at stage 24, there was an increase. This increase was indicated that at stage 24, binary feed stage was fed. From this graph, relative volatility profile in EDC can be calculated using equation 1 [12].

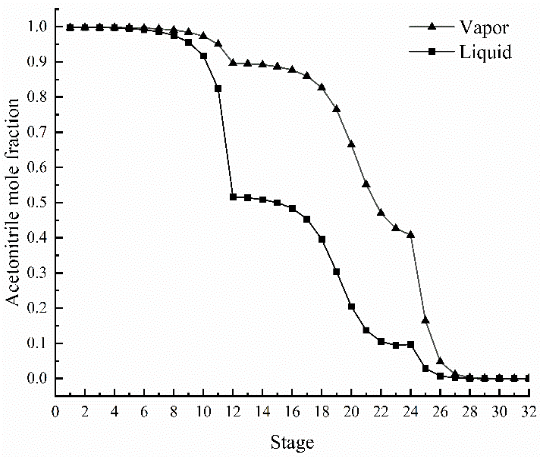

Figure 9. Acetonitrile vapor and liquid concentration profile of EDC from stage 1 to 32

$$\alpha_{12} = \frac{y_1/x_1}{y_2/x_2} \quad (1)$$

To simplified the calculation of relative volatility, Figure 10 shows the K value of each component. Relative volatility of acetonitrile will be written as,

$$\alpha_{12} = \frac{K_1}{K_2} \quad (2)$$

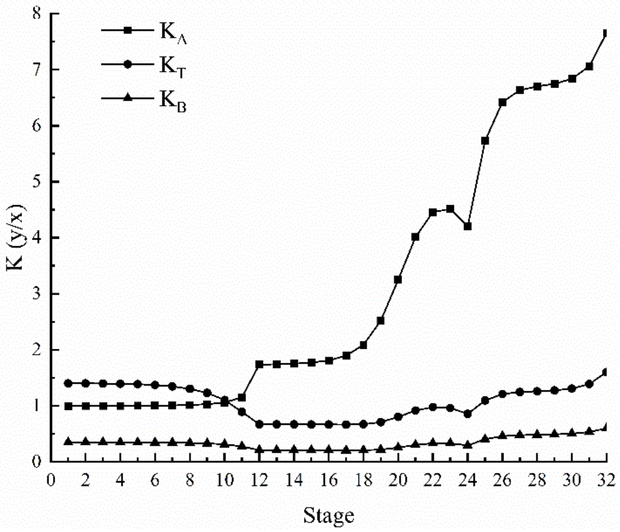

Figure 10. K-value profile of EDC from stage 1 to 32

From equation 1 and 2, relative volatility can be obtained from K1 and K2. Both of them are vapor concentration to liquid concentration ratio. In this work, an increase of acetonitrile relative volatility is expected. Figure 11 represents the relative volatility profile per stages of acetonitrile in EDC. As can be viewed, relative volatility of acetonitrile increases at stage of 12. At this stage, butyl propionate enters as solvent for toluene and directs it to the bottom. Due to its good mixing ability [9], butyl propionate is able to extract toluene from acetonitrile and increase the relative volatility of acetonitrile.

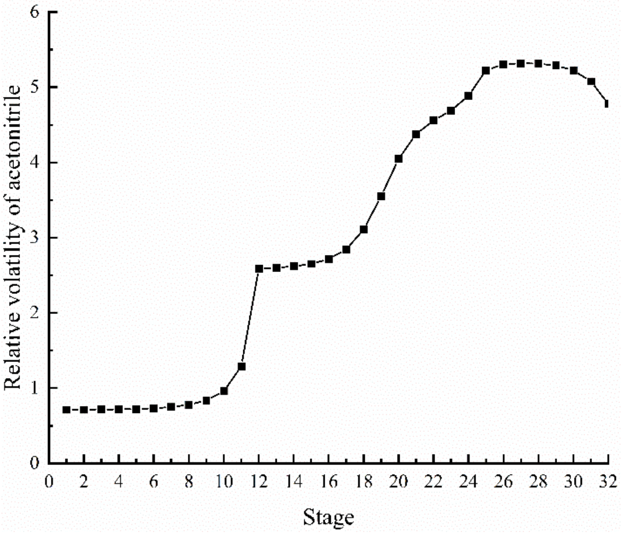

Figure 11. Acetonitrile relative volatility profile of EDC from stage 1 to 32

The EDC column's configuration and operating condition based on sensitivity analysis results are given in Table 1. To obtain high purity of acetonitrile, the solvent is fed above the feed mixture [11]. It was shown that the distillate rate of acetonitrile and toluene was 30 and 20 kmol/hr and both obtained purity was 0.999 mass fraction. At the bottom of the SRC, the recovered butyl propionate was 0.999 mass fraction. Similar proposed design for separating azeotrope mixtures with a minimum boiling point have been published in the literature [13], [14].

Table 1. Process design parameters of extractive and recovery column

Parameter	EDC	SRC
Reflux ratio	1.5	5.1
Number of theoretical plates	32	29
Feed stage	24	10
Entrainer feed stage	12	-
Pressure (kPa)	101.325	101.325

Parameter	**EDC**	**SRC**
Feed & entrainer temperature	25	-
Distillate rate (kmol/hr)	30	20
Distillate purity (mass fraction)	0.999 (Acetonitrile)	0.999 (Toluene)

After obtained the optimum parameters, economic evaluation should be considered when separating acetonitrile and toluene azeotropic mixture by extractive distillation. Total annual cost (TAC) is a common economic objective function to evaluate the economic feasibility of the process. TAC calculation method was taken from [15] which implemented based on nonlinear programming (NLP) approach [11]. In this economic evaluation, design variables such as the tray numbers, column diameter, condenser and reboiler duty are optimized through the equations below.

$$TAC = operational\ cost + \frac{capital\ cost}{3} \tag{3}$$

Table 2. Total annual cost calculation

Parameter	**EDC**	**SRC**
Number of stages	32	29
Column diameter (m)	1.82	1.37
$Q_{Condenser}$ (kW)	647.35	1145.08
$A_{Condenser}$ (m2)	54.66	96.69
$Q_{Reboiler}$ (kW)	1544.75	1196.32
$A_{Reboiler}$ (m2)	78.15	60.52
Heat exchanger cost (106 $)	0.222	0.247
Column shell cost (106 $)	0.398	0.270
Total capital (106 $)	1.137	
Energy cost (106 $/year)	0.846	
TAC (106 $/year)	**1.225**	

4. Conclusion

Butyl propionate was chosen to break the azeotropic point of acetonitrile and toluene binary mixture. The feasibility of the process was confirmed via pseudo binary diagram of acetonitrile/toluene with 0.3 mole fraction of butyl propionate using UNIQUAC thermodynamic model. Only with a low solvent ratio, butyl propionate can separate acetonitrile/toluene binary mixture efficiently. Sensitivity analysis and EDC profile per stages were conducted to obtain the best condition and configuration for all unit operation. The simulation showed the optimal condition to achieve the 99.9% of acetonitrile and 99.9% toluene by extractive distillation.

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