

# Extractive Distillation Process Combined with Decanter for Separating Ternary Azeotropic Mixture of Toluene-Methanol-Water

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The mixture of toluene-methanol-water is difficult to separate because of the formation of toluene-methanol and toluene-water azeotropes. Extractive distillation process with two-column decanter (EDTCD) was improved to separate the system. The process was optimized by the software named Extractive Distillation Optimization Software (EDOS) which based on the minimum total annual cost (TAC). A comparison of the EDTCD and the traditional extractive distillation with triple-column (TEDT) indicated that the former was much more economical. In this comparison, *n*-methyl-2-pyrrolidone (NMP) and diethylene glycol (DEG) was used as a heavy entrainer in EDTCD and TEDT. The choice of thermodynamic model was discussed in this paper, and the model of UNIQUAC was used in the two processes. The results show that high purity of toluene, methanol and water can be obtained from the process of EDTCD, and it can save 34 % TAC than the process of TEDT.

## 1. Introduction

Toluene and methanol are both widely used as solvents and raw materials in chemical industry, it is very important for the plant to reuse the two components in the mixture of toluene-methanol-water. However, it is difficult to implement because two kinds of azeotropes are formed in the mixtures (in a valid phase of vapor-liquid-liquid in Aspen Plus), which one of them was toluene-water heteroazeotrope with a composition of 52.30 - 56.41 mol % water at 357.25 - 358.15 K under 1 atm, the other was toluene-methanol homogenous azeotrope with a composition of 88.20-88.60 mol % methanol at 336.41 - 336.95K under 1 atm. All the provided azeotropic information obtained from the Azeotropic Data (Gmehling et al., 1994). The common methods are impossible to separate the mixture of toluene-methanol-water, and special distillation methods such as pressure-swing distillation (Zhu et al., 2016), azeotropic distillation (Arifin and Chien, 2007), extractive distillation (Luyben, 2013) are used to separate the azeotropic mixtures. A new extractive distillation process was designed to separate the mixture of toluene-ethanol-water (Zhao et al., 2017). On account of the advantages of the process and the similar physical property of the two systems, the process is used to separate the mixture of toluene-methanol-water. Differ from the process which separated toluene-ethanol-water, EDTCD added a heat exchanger before the decanter rather than reduce the operating pressure of the solvent recovery column, and high purity of toluene and water can be obtained after cooling the stream. This study aims to separate the ternary mixture and find the optimum configuration of the EDTCD process.

Aspen Plus is used in this paper for simulating the process. The accuracy of the thermodynamic model and the binary interaction parameters are the important elements which affect the results greatly. Accurate thermodynamic parameters are the basis to make the simulation result as close as possible to the actual industrial production. It will cause large equipment investment or energy cost or obtain impurity production due to using the inaccurate parameters. It is important to discuss the selection of thermodynamic model for the simulation. The azeotropic composition and azeotropic temperature calculated by the model of NRTL and UNIQUAC were compared with the experimental data in order to select the more accurate model for this system. A comparison of the EDTCD and the traditional extractive distillation with triple-column (TEDT) was made in order to prove the feasibility of EDTCD. Based on the total annual cost (TAC), the design of the two

processes was optimized in order to obtain more economical configuration. The entrainer of both process were selected according to the relative volatility, and the residue curve map of this system was made to analysis the process.

## 2. The process of EDTCD

### 2.1 Basis of the process

#### 2.1.1 The selection of thermodynamics model

In this paper, the mixture of toluene-methanol-water was separated by EDTCD which based on the traditional extractive distillation with two-column. The major difference with the traditional extractive distillation is the utility of decanter which plays an important role in EDTCD. Both the vapor-liquid equilibria (VLE) parameters and liquid-liquid equilibria parameters (LLE) are important for the results of simulation. And an accuracy result is also important for industrial use. The model of UNIQUAC was chosen as the thermodynamics model in this paper in view of the follow reasons.

For the VLE parameters, the data which calculated by the model of NRTL and UNIQUAC were compared with the experimental data published in Azeotropic Data (Gmehling et al., 1994). The azeotropic data were shown in Table 1. The data about toluene-water which calculated by the model of NRTL and UNIQUAC were both greatly satisfied with the data from experiment. However, for the azeotrope of toluene-methanol, the model of UNIQUAC was rigorously agreed with the experimental data compared with NRTL. Therefore, the model of UNIQUAC was chosen.

Table 1: The azeotropic information of toluene-water and toluene-methanol

Azeotrope	Toluene-water		Toluene-methanol	
	$X_{\text{water}}$ (mol)	Temperature (K)	$X_{\text{methanol}}$ (mol)	Temperature (K)
Experimental data	0.5230 - 0.5641	357.25 - 358.15	0.8820 - 0.8860	336.41 - 336.95
Calculated by NRTL	0.5597	357.68	0.8870	337.02
Calculated by UNIQUAC	0.5578	357.58	0.8843	336.91

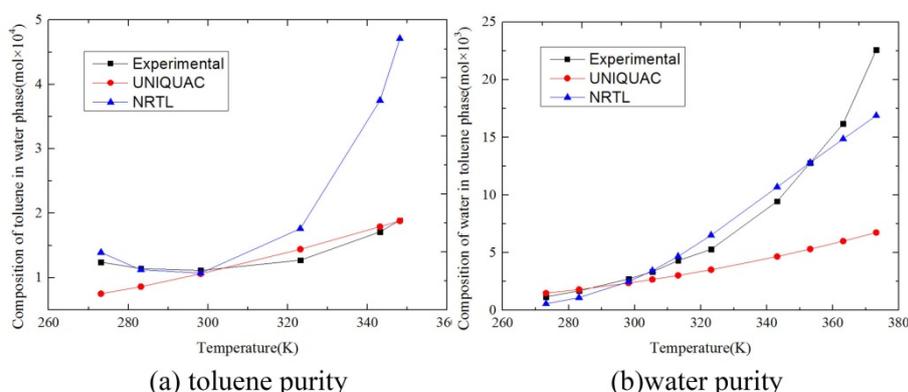


Figure 1: Effect of temperature for toluene and water on changing composition.

Because of the utility of the decanter in this process, the LLE parameters of toluene-water are also important for the results. Lots of parameters about LLE of toluene-water from the literatures were quoted to compare with the results which calculated by the model of NRTL and UNIQUAC. Jou and Mather (2003) measured the mutual solubility of toluene and water over the range of temperatures from (273 to 458) K; Valtz et al.(2007) and Neely et al.(2007) tested the composition of toluene phase and water phase over the range of temperatures from (297 to 392, 297 to 492) K; Chen and Wagner (1994) and Marche et al. (2006) reported the experimental value of solubility of water and toluene over the range of temperatures from (303 to 373, 303 to 453) K. The results are shown in Figure 1. When the temperature is lower than 298.15 K, the composition of toluene in water phase calculated by the model of NRTL is much more precise than that calculated by the model of UNIQUAC, and the composition of water in toluene phase calculated by the model of UNIQUAC is much more precise than that calculated by the model of NRTL. And when the temperature is higher than 298.15 K, the composition of toluene in water phase calculated by the model of UNIQUAC is much more

precise than that calculated by the model of NRTL, and the composition of water in toluene phase calculated by the model of NRTL is much more precise than that calculated by the model of UNIQUAC. The temperature of the distilled stream from the solvent recovery column is 357.55 K, while the composition of toluene is only 98.7 mol % in toluene phase when the stream out of the decanter in this state. In order to obtain toluene with much higher purity, the stream must be cooling. The purity of water is higher than 99.9 mol % no matter what thermodynamic model is chosen. The effect of thermodynamic model on the purity of water can be neglected. The experimental data indicate that the lower the temperature, the higher the purity of toluene. The purity of toluene was 99.8 mol % if the temperature is cooled to 283.15 K in the heat exchanger. Therefore, cooling water is needed in this process to cool the stream to 283.15 K in order to obtain higher purity of toluene. This temperature is lower than 298.15 K, the model of UNIQUAC is chosen for getting precise results compared with NRTL at 283.15 K.

### 2.1.2 Entrainer determination

The determination of entrainer is very important for extractive distillation process. The method of entrainer selection has been discussed in the paper (Guez-Donis et al., 2001). In order to find a useful solvent to separate the mixture of methanol and toluene, three different solvents n-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), n, n-dimethylformamide (DMF) were tested respectively. As shown in Figure 2, the VLE curve of methanol affected by NMP show the largest deviation from diagonal, that means the relative volatility between toluene and methanol is highest. The data were generated by a Flash 2 Aspen model. The pressure and vapor fraction of feed stream were set at 1 atm and 0. And the flash temperature and heat duty were set at 337.68 K and 0. Because NMP does not bring in further azeotrope in the system and shows a higher relative volatility (3.94) at the S/F ratio of 2, it is chosen as the entrainer in this paper.

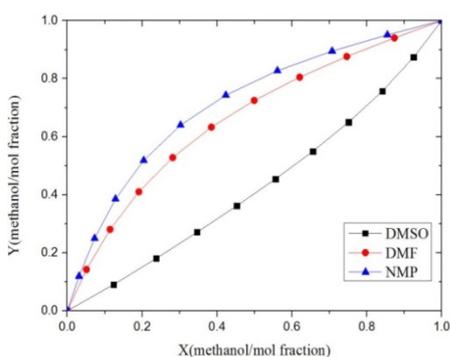


Figure 2: Effect on VLE with different solvents at fixed S/F of 2.

The relationship of the methanol purity with reflux ratio (RR1) in the extractive distillation column at different entrainer flowrates is shown in Figure 3. Wang et al. (2015) studied on the effect of solvent flow rates of extractive distillation. There is an optimum reflux ratio which corresponded to a maximum purity of methanol at each entrainer flowrate. And no matter what the value of RR1 is set, the purity of methanol could not achieve 99.9 mol % when the flow rate is set as 50 kmol, 60 kmol, 70 kmol. To achieve the desired purity of 99.9 mol % for methanol, the entrainer flow rate has to be set excess 80 kmol/h when the reflux ratio is set to about 2.

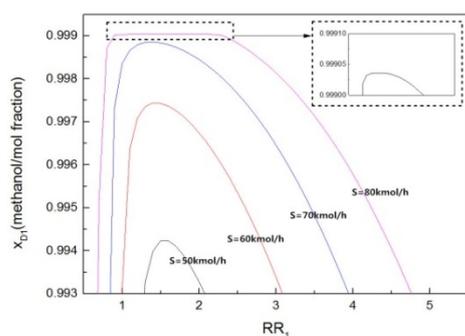


Figure 3: Effect of RR1 on methanol composition with different solvents flow rates.

### 2.1.3 The analysis of residue curve map

The residue curve map (RCM) (Gerbaud et al., 2006) of this system contains four components (toluene, methanol, water, NMP), and it is divided into two sections. The RCM of ternary system drawn by Aspen Plus using the UNIQUAC model is shown in Figure 4a and 4b. The blue line stands for the material balance line. The residue curves with arrows from the unstable node point to pure NMP point and no presence of the distillation boundary in the RCM. This is an ideal situation for this extractive distillation process.

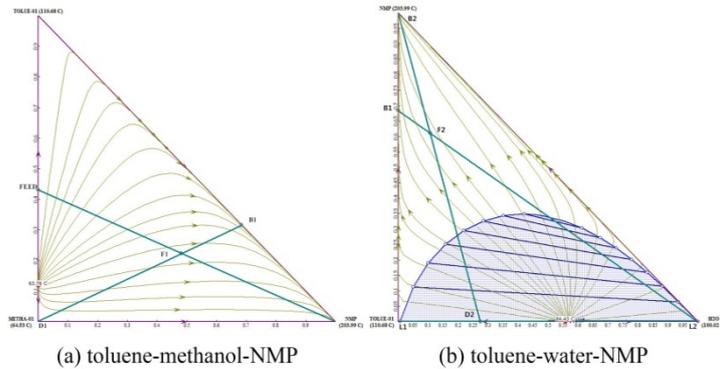


Figure 4: The residue curve map of ternary mixture.

For the first section, the behaviour of toluene-methanol-NMP (neglecting the third key component water) in the extractive distillation column is described. As shown in Figure 4a, we can see that both toluene and methanol are the saddles while NMP is the stable node, and the azeotropic point of toluene-methanol is the unstable node. In this column, toluene and methanol is one binary azeotrope mixture which is fed into the column as the state point of B1. It mixes with NMP from the solvent recovery column and form into another state as the state point of F1. The component of methanol gather in the top of the extractive distillation column and the high purity of methanol can be obtained in the distilled stream.

For the second section, the behaviour of toluene-water-NMP (neglecting the little component of methanol) in the solvent recovery column is described. As shown in Figure 4(b), both toluene and water are the saddles while NMP is the stable node, and the azeotropic point of toluene-water is the unstable node. The composition of stream which fed into the solvent recovery column is described as the point of F2. And it is divided into stream D2 and stream B2 in the top and bottom of the solvent recovery column. The mixture of toluene and methanol in stream D2 is the heterogeneous azeotrope, which can be divided by a decanter. And the composition of toluene phase and water phase are described as the state point of L1 and L2. High purity of water and toluene can be obtained in the two phases. NMP is recycled to the extractive distillation column and reused in the process.

## 2.2 Flowsheet simulation

A heat exchanger is added into the flowsheet because the distilled stream from the solvent recovery column needed to be cooling to 283.15 K. And the modified flowsheet with information of this process is described in Figure 5.

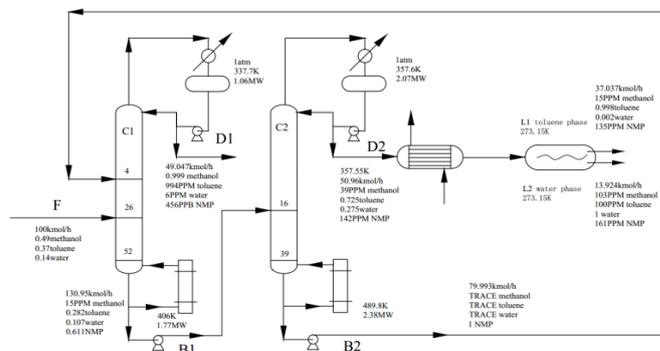


Figure 5: The flowsheet information of the EDTCD.

The feed flow of this simulation is set at 100 kmol/h with 49 mol % methanol, 37 mol % toluene and 14 mol % water. The optimized flowrate of entrainer in recycle stream is set at 80 kmol/h. The commercial software of Aspen Plus is used to simulate the process.

### 2.3 Flowsheet optimization

The optimization of chemical engineering is necessary due to the high energy cost and the high investment for the equipment. The TAC of this process is regarded as the objective function in this paper. In this paper, the temperature, pressure, flow rate and composition of the feed flow are specified. At the same time, the number of stages in the extractive distillation column and the solvent recovery column (NT1 and NT2), the feed locations (NF1 and NF2), the reflux ratio (RR1 and RR2) of the two columns are also needed to be optimized to make the TAC minimum. The optimization procedure is complicated for every simulation, and an efficient calculation software had been developed to solve this problem. This software named Extractive Distillation Optimization Software (EDOS) (QUST, 2015) by using software of Aspen Plus and Visual Basic. The stages of the extractive distillation column and the solvents recovery column are 52 and 39 with the reflux ratio are 2 and 2.5. The annual operating cost is 361,116.2 \$ and 339742.6 \$ of the two columns, while the total capital investment is 915,264.0 \$, and the TAC of EDTCD is 1,005,946.8 \$.

## 3. The process of TEDT

### 3.1 Basis of the simulation

Traditional extractive distillation process (TEDT) is established in order to make a comparison with the EDTCD. UNIQUAC model is also used as thermodynamics model of TEDT. Different with EDTCD, toluene is distilled from the system first as the corporate component of the two kinds of azeotropes (toluene-methanol, toluene-water). Diethylene glycol (DEG) is chosen as a heavy entrainer of this system for the TEDT after comparing with NMP, DMF, DMSO, and the flowrate of DEG is optimized to minimal the TAC.

### 3.2 Flowsheet simulation

The mixture of toluene-methanol-water is fed into the TEDT. The feed flow of this simulation is set at 100 kmol/h with 49 mol % methanol, 37 mol % toluene and 14 mol % water. It is same with the feed flow of the EDTCD. The entrainer which can break the two kinds of azeotropes is fed into the top of first column, and the key component of toluene is distilled from the system first. The other two components mixed with DEG are fed into the second column in which methanol is distilled from the top of the second column. And the third key component water is distilled from the third column while DEG is recycled to the first column and reused in the system. The purity of methanol and toluene and water are 99.9 mol %. The pressure of triple columns is set at 0.1 atm, 1 atm, and 1 atm. The configuration of TEDT is shown in Figure 6.

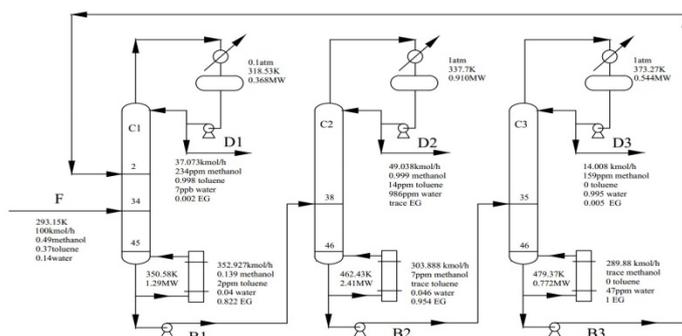


Figure 6: The configuration of TEDT.

### 3.3 Optimization and comparison

In order to reduce the equipment investment and energy cost, optimization is necessary for this process. TAC is regarded as the objective function in this optimization procedure, and the results showed that the optimal stages of the three columns are 45, 46 and 46, and the reflux ratio are 0.01, 0.9, and 2.1. The annual operating cost is 245,831.6 \$ and 687,133.5 \$ and 223,617.1 \$ of each column, while the total capital investment is 1,112,244.8 \$, and the TAC of TEDT is 1,527,330.6 \$. TEDT is better than EDTCD on the purity of toluene. On the other hand, the TAC of EDTCD is 1,005,946.8 \$, while the TAC of TEDT is 1,527,330.638

\$, and 34 % of TAC is saved. Considering the trade-off between TAC and the purity of toluene in both process (99.8 mol % in EDTCD and 99.9 mol % in TEDT), EDTCD is more attractive than TEDT.

#### 4. Conclusion

EDTCD which based on the traditional extractive distillation with two-column was improved for separating ternary azeotrope of toluene-methanol-water and high purity of toluene, methanol, water could be obtained, respectively. UNIQUAC model was chosen as the thermodynamics model because the predicted values fit well with the experimental values at 283.15 K and n-methyl-2-pyrrolidone (NMP) was selected as entrainer. The flowsheet of traditional triple-column extractive distillation process (TEDT) with diethylene glycol (DEG) as entrainer was established for comparison with EDTCD. The results indicated the purity of toluene from TEDT was slightly higher than the purity of toluene from EDTCD, while EDTCD saved 34 % total annual cost (TAC) than TEDT. Considering the trade-off, the purity of toluene and TAC, EDTCD is more attractive. Generally, EDTCD can be used for separating ternary mixture which contained heterogeneous azeotrope for its advantage in annual operating cost and equipment investment.

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#### References

- Arifin S., Chien I.L., 2007, Combined Preconcentrator/Recovery Column Design for Isopropyl Alcohol Dehydration Process, *Industrial & Engineering Chemistry Research*, 46, 2535-2543.
- Chen H., Wagner J., 1994, An efficient and reliable gas chromatographic method for measuring liquid-liquid mutual solubilities in alkylbenzene+ water mixtures: toluene+ water from 303 to 373 K, *Journal of Chemical and Engineering Data*, 39, 475-479.
- Gerbaud V., Xavier J., Ivonne R.-D., Olivier B., Olivier R., Alain V., Pierre C., 2006, Practical residue curve map analysis applied to solvent recovery in non-ideal binary mixtures by batch distillation processes, *Chemical Engineering and Processing: Process Intensification*, 45, 672-683.
- Gmehling J., Menke J., Krafczyk J., Fischer J., 1994, *Azeotropic Data*, Wiley-VCH, Weinheim, Germany.
- Guez-Donis I.R., Gerbaud V., Joulia X., 2001, Entrainer selection rules for the separation of azeotropic and close-boiling-temperature mixtures by homogeneous batch distillation process, *Industrial & Engineering Chemistry Research*, 40, 2729-2741.
- Jou F.-Y., Mather A.E., 2003, Liquid-liquid equilibria for binary mixtures of water+ benzene, water+ toluene, and water+ p-xylene from 273 K to 458 K, *Journal of Chemical & Engineering Data*, 48, 750-752.
- Luyben W.L., 2013, Comparison of extractive distillation and pressure-swing distillation for acetone/chloroform separation, *Computers & Chemical Engineering*, 50, 1-7.
- Marche C.I., Ferronato C., Hemptinne J.-C.D., Jose J., 2006, Apparatus for the Determination of Water Solubility in Hydrocarbon: Toluene and Alkylcyclohexanes (C6 to C8) from 30 C to 180 C, *Journal of Chemical & Engineering Data*, 51, 355-359.
- Neely B.J., Wagner J., Robinson R.L., Jr, Gasem K.A.M., 2007, Mutual solubility measurements of hydrocarbon-water systems containing benzene, toluene, and 3-methylpentane, *Journal of Chemical & Engineering Data*, 53, 167-174.
- Qingdao University of Science & Technology, *Extractive Distillation Optimization Software: porpoise V1.0*. NO.2015SR214466.
- Valtz A., Coquelet C., Richon D., 2007, Solubility data for toluene in various aqueous alkanolamine solutions, *The Journal of Chemical Thermodynamics*, 39, 426-432.
- Wang Y., Liang S., Bu G., Liu W., Zhang Z., Zhu Z., 2015b, Effect of Solvent Flow Rates on Controllability of Extractive Distillation for Separating Binary Azeotropic Mixture, *Industrial & Engineering Chemistry Research*, 54, 12908-12919.
- Zhao L., Lyu X., Wang W., Shan J., Qiu T., 2017, Comparison of heterogeneous azeotropic distillation and extractive distillation methods for ternary azeotrope ethanol/toluene/water separation, *Computers & Chemical Engineering*, 100, 27-37.
- Zhu Z., Xu D., Liu X., Zhang Z., Wang Y., 2016, Separation of acetonitrile/methanol/benzene ternary azeotrope via triple column pressure-swing distillation, *Separation and Purification Technology*, 169, 66-77.