CHEMICAL ENGINEERING TRANSACTIONS
VOL. 61, 2017

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Petar S Varbanov, Rongxin Su, Hon Loong Lam, Xia Liu, Jiří J Klemeš

ISBN 978-88-95608-51-8; **ISSN** 2283-9216
DOI: 10.3303/CET1761235

Comparison of Extractive and Pressure-Swing Distillation for Separation of Tetrahydrofuran-Water Mixture

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Tetrahydrofuran (THF) is widely used in many processes as solvent or chemical intermediate. It is necessary to separate mixture of THF-water, because in most commercial production processes, THF is produced from its water mixture. However, the above mixture cannot be separated with ordinary distillation, since THF and water can form azeotrope. Instead, extractive distillation (ED) and pressure-swing distillation (PSD) have been widely applied for commercial separation of mixture of THF-water. In this paper, Aspen Plus simulator is used to simulate extractive distillation and pressure-swing distillation process for separation of mixture of THF-water. Economic analysis is carried out by Aspen Process Economic Analyzer (APEA) for the two processes. The conclusion obtained based on the above process simulation and analysis is that the total annualized cost of the extractive distillation is slightly lower than that of pressure-swing distillation. The results obtained provide useful references for commercial separation of mixture of THF and water.

1. Introduction

THF is an excellent organic solvent and also a chemical intermediate for preparation of poly-tetramethylene glycol (PTMEG) and other chemicals. Therefore, the demand of tetrahydrofuran (THF) has increased all over the world. In commercial production, THF is often prepared as its water mixture. However, the mixture of THF and water is difficult to separate via ordinary distillation. The reason is that THF and water can form minimum-boiling azeotrope. To date, there are many methods to separate azeotropic mixtures, such as extractive distillation (Xu and Wang, 2006), pressure-swing distillation (Lee et al., 2011), pervaporation (Kuila and Ray, 2012), adsorption (Rao et al., 2007), etc. Compared to other methods, extractive distillation (ED) and pressure-swing distillation (PSD) have been widely used for the above separation commercially.

In extractive distillation, entrainer is utilized as separating agent. The entrainer can change relative volatility of the azeotropic mixture and this makes the separation easily. At present, commercial extractive agent, such as ethylene glycol (EG), 1, 2-Propanediol, dimethyl sulfoxide (DMSO), etc. have been widely used for extractive distillation for mixture of THF and water.

PSD is used to separate azeotropic mixture as well. The principle of PSD is that the components of THF-water azeotropes vary with pressure changing. The azeotropic composition of THF-water is affected prominently by pressure, as shown in Figure 1. From Figure 1, it can be seen that at 1 bar, the concentration of THF in the azeotrope is 82.9 mole %, while it becomes 65.5 mole % at 8 bar. Hence, it is feasible to separate THF-water azeotrope via PSD.

There have been a few reports on the comparison of extractive distillation and pressure-swing distillation. Lladosa et al. (2011) investigated separation of the azeotropic mixture of di-n-propyl ether and n-propyl alcohol. They concluded that PSD is more economic than extractive distillation for separation of the above mixture. The separation of THF and ethanol was studied via extractive distillation and PSD by Wang et al. (2014). In their study, minimum total annualized cost (TAC) was calculated. Their results showed that the TAC of PSD is lower than that of extractive distillation. Pravin et al. (2017) investigated both extractive and pressure swing distillation for separation of mixture of THF-water. They arbitrarily took the feed composition as equimolar which is different from the commercial value, and obtained the conclusion that the TAC of extractive

Please cite this article as: Liu X.-Y., Shang D.-J., Liu Z.-Y., 2017, Comparison of extractive and pressure-swing distillation for separation of tetrahydrofuran-water mixture, Chemical Engineering Transactions, 61, 1423-1428 DOI:10.3303/CET1761235

distillation is lower than that of PSD. Ma et al. (2017) addressed that the feed composition and feed flow rates have important influence on the design and operation of distillation systems. In addition, in the work of Wang et al. (2014) and Pravin et al. (2017), many factors, such as electricity and cooling water were not considered in calculation of utility cost, and in calculation of capital cost, the factors, such as piping, steel, electrical and insulation were not considered. The purpose of this article is to compare economic difference of the commercial separation processes of THF-water mixture via extractive distillation and pressure-swing distillation based on practical data, and to provide useful reference for industrial practice.

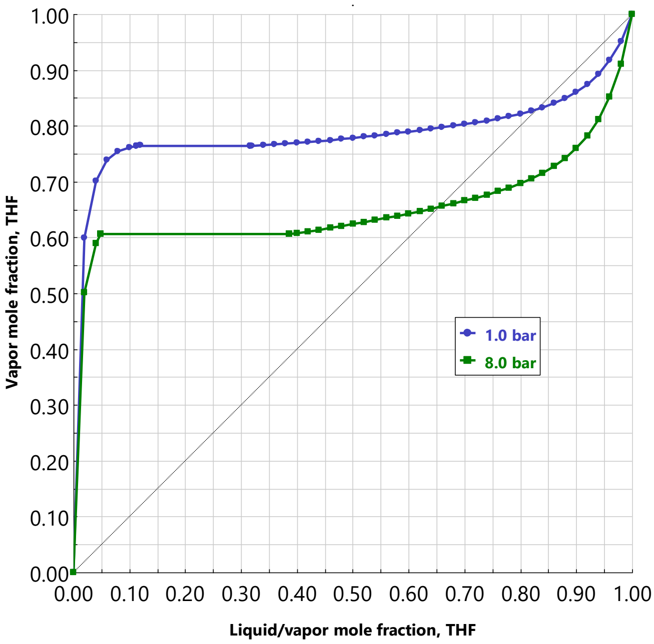

Figure 1: X-Y diagram of THF-water azeotrope at 1 bar and 8 bars

2. Method

In this paper, the authors consider the factors, which are missed by Wang et al. (2014) and more recently byPravin et al. (2017), in economic analysis. Aspen Plus is used to simulate the processes of both extractive distillation and PSD. It is necessary in the simulation to choose proper thermodynamic model. For the pressure-swing distillation, the most properly thermodynamic model is NRTL for the binary system of tetrahydrofuran and water (Gómez and Gil, 2009). In extractive distillation, the entrainer plays an important role. Zhang et al. (2014) and Deorukhkar et al. (2016) investigated the property of DMSO. Their study showed that DMSO is a very effective entrainer to separate THF-water mixture. Therefore, DMSO is taken as the entrainer for extractive distillation in this work. For the ternary system of tetrahydrofuran-water-DMSO, the comparison of the results of NRTL and UNIFAC, Wilson are shown in Figure 2 (Huang et al., 2015). It can be seen, from Figure 2, that the NRTL equation is better than the other ones. Consequently NRTL model is used to calculate activity coefficients for both of the two processes.

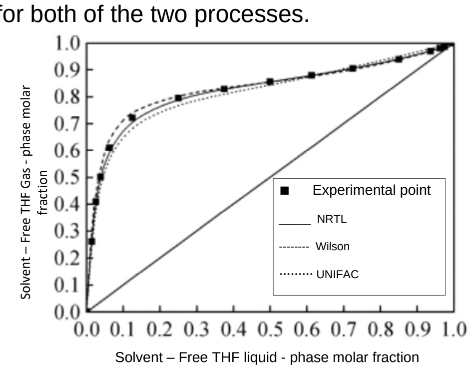

Figure 2: Experiments and thermodynamic model predictions of ternary VLE containing 20 % (mass fraction) DMSO

Table 1 lists the parameters of the columns in the two distillation processes to be determined by built-in module of sensitivity analysis in Aspen Plus simulator. All the optimal values of the parameters are obtained under the following conditions: the reboiler heat load is taken as the objective function, and THF purity as the constraint.

Table 1: Requires optimized parameters for extractive distillation and pressure-swing distillation

Parameters of ED	Parameters of PSD
Reflux ratio	Reflux ratio
Number of ideal stages	Number of ideal stages
Feed-stage	Feed-stage
DMSO-feed-stage	
Amount of entrainer (kg/h)	

The capital cost and utility cost are calculated by Aspen Process Economic Analyzer. The TAC is calculated by Eq(1) (Luyben, 2013). In capital cost, there are a few factors to be considered, including purchased equipment, equipment setting, instrumentation, piping, civil, steel, electrical, insulation, contingencies, general and administrative overheads (G and A overheads) and contract fee. In utility cost, there are three factors to be considered, including electricity, cooling water and steam. In order to compare with the results of Ghuge et al. (2017), who used the same calculation procedure as Luyben (2013), we also use the same procedure and choose 3 y as payback period. The relative difference between the TAC of extractive distillation and that of pressure-swing distillation is calculated with Eq(2).

$$TAC = \frac{\text{captialcost}}{\text{paybackperiod}} + \text{utilitycost} \tag{1}$$

$$\text{RelativeDifference(RD)} = \frac{\text{The value for ED - The value for PSD}}{\text{The value for PSD}} * 100\% \tag{2}$$

3. Simulation and analysis

In this part, a case study will be investigated. The feed flowrate of separation system is taken as 22,500 t/y of THF-water mixture based on the production of most of China's THF plants. The feed composition THF is taken as 79.8 % (mass fraction) and 20.2 % (mass fraction) of water. The feed composition is taken from Yusuke et al. (2014).

3.1 Extractive distillation

For extractive distillation, there are a few factors to be considered: the amount of entrainer, reflux ratio (RR) and number of ideal stages. Figure 3 shows the flowsheet of extractive distillation. The feed exchanges heat with entrainer recovered in column T2, then the feed is added in the middle of column T1. The recovered entrainer is added in the top of column T1. High purity THF can be obtained from the top of column T1, and the mixture of water and entrainer is obtained from the bottom of T1.

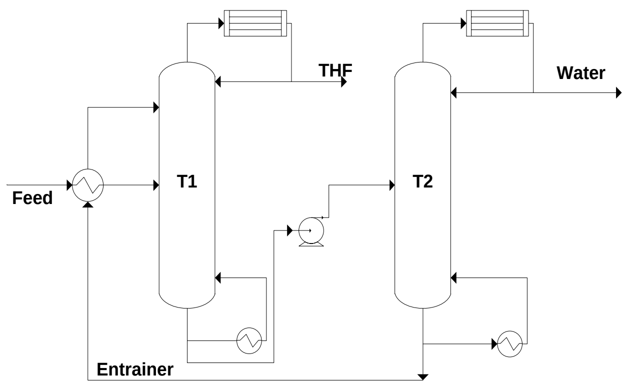

Figure 3: The flowsheet of extractive distillation

The mixture is sent to entrainer recovery column T2, in which dehydrated entrainer is obtained from its bottom. The entrainer is recycled to the extraction column. The parameters of the columns are optimized by using sensitivity analysis in Aspen Plus. Taking the extractive distillation column T2 as an example, when determining the reflux ratio, THF purity requirement (99.96 % mass fraction) is taken as constraint and the minimum heat load of the reboiler is taken as the objective function. The results are shown in Figure 4. In Figure 4, it is noted that when the reflux ratio is 0.5, the product purity is 99.96 % (mass fraction). Other parameters of extractive distillation are also optimized similarly and the results are shown in Table 2.

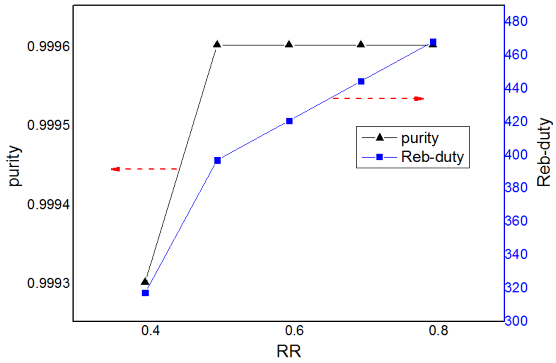

Figure 4: Effect of reflux ratio on heat load of reboiler

Table 2: The results of parameters column of extractive distillation

Parameters	Before optimization		Optimized	
	T1	T2	T1	T2
Reflux ratio	1.0	1.0	0.5	0.5
Number of ideal stages	25	15	15	10
Feed-stage	13	5	12	4
DMSO-feed-stage	4	-	3	-
Amount of entrainer (kg/h)	770	-	890	-

3.2 Pressure-swing distillation

There are two distillation columns in pressure-swing distillation, an atmospheric column, and a pressurizing column, as shown in Figure 5. The amounts of feed and feed composition are the same as that in the extractive distillation. Column T1 is operating at 1 bar. Most of water is removed in the bottom of column T1, because the bubble point of water is higher than that of the azeotropic mixture. The overhead product of column T1 is pumped to column T2.

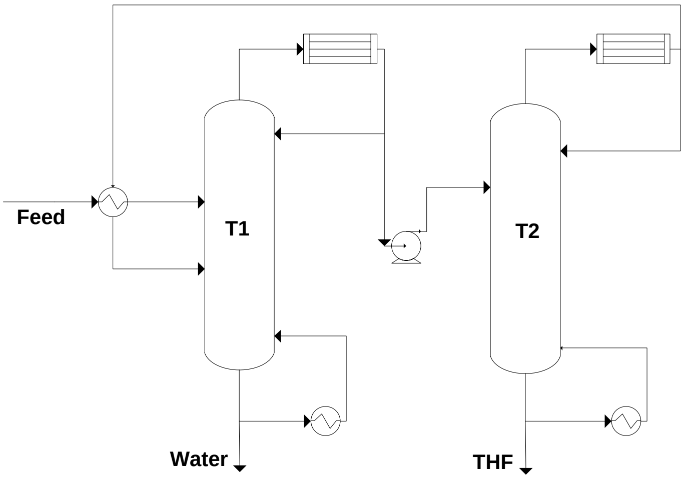

Figure 5: The flowsheet of pressure-swing distillation

The operating pressure of column T2 is 8 bars. THF product can be obtained from the bottom of column T2. The overhead product of T2 returns to T1 to be refined again (Li and Liu, 2013). The parameters of the columns such as the number of ideal stages, reflux ratio and feed-stage, can be determined by using the built-in sensitivity analysis module in Aspen simulator. The optimal results of PSD are shown in Table 3.

Table 3: The results of parameters column of pressure-swing distillation

Parameters	Before optimization		optimized	
	T1	T2	T1	T2
Reflux ratio	2.0	1.0	0.25	0.2
Number of ideal stages	15	13	13	10
Feed-stage	7	3	8	5

3.3 Economic evaluation of ED and PSD

Economic evaluation is carried out by Aspen Process Economic Analyzer. The calculation results of capital cost are shown in Table 4. The results of utility cost are shown in Table 5. It can be seen, from the data in Table 4, that the capital costs are almost the same for both of two processes. However, there is a difference in the cost of utilities for the two processes as shown in Table 5. The utility cost of PSD is 5.6 % higher than that of ED.TAC values for the two processes can be obtained with capital cost and utility cost with Eq(1) and are shown in Table 6. It can be seen that the TAC of extractive distillation is 1.69 % lower than that of pressure-swing distillation.

Table 4: Capital cost results of extractive distillation and PSD

Capital cost [$]	ED	PSD	RD
Purchased Equipment	239,630	242,200	
Equipment Setting	9,625.2	9,934.3	
Piping	303,455	314,284	
Instrumentation	69,901.4	72,030.7	
Civil	24,795	22,894	
Steel	674,276	655,447	
Electrical	503,416	506,533	
Insulation	80,616.5	74,295.6	
Contingencies	801,139	808,485	
G and A Overheads	81,708.3	81,884.9	
Contract Fee	248,053	250,801	
Total cost [$]	3,036,615.4	3,038,789.5	-0.07 %

Table 5: Utility cost results of extractive distillation and PSD

Utility cost [$]	ED	PSD	RD
Electricity	36,473	40,359	
Cooling Water	18,197	24,398	
Steam 6.9 bar	97,165	354,623	
Steam 27.6 bar	244,066	0	
Total cost [$]	395,901	419,380	-5.6 %

Table 6: TAC results of extractive distillation and PSD

Items	ED	PSD	RD
Capital cost [$]	3,036,615.4	3,038,789.5	
Utility cost [$/y]	395,901	419,380	
Payback period [y]	3	3	
TAC [$]	1,408,106	1,432,310	-0.69 %

4. Conclusion

Extractive distillation and pressure-swing distillation can be used in commercial separation of the mixture of THF-water. In this work, commercial separation processes of mixture of THF-water are investigated with Aspen simulator. In the simulation, the parameters of columns are determined by the function of sensitivity analysis built-in module in Aspen Plus simulator. Both of two processes are analysed by Aspen Process Economic Analyzer. TAC values can be calculated based on capital cost and utility cost. Compared to the literature, in the calculation of capital cost, we consider more aspects. In the calculation of utility cost, we consider electricity and cooling water costs, which were not considered before. Through comparative analysis, it is noted that TAC of extraction distillation is slightly lower than that of pressure-swing distillation for the same scale of production and the same product purity. However, in extractive distillation, the introducing of entrainer might bring additional impurity in the product. Therefore, there are a few tradeoff factors to be considered in choosing the suitable separation process for the mixture of THF and water. The results of this paper can be useful for industrial separation of THF-water mixture.

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