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Comparison of Conventional Extractive Distillation and Heat Integrated Extractive Distillation for Separating Tetrahydrofuran/Ethanol/Water

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The distillation is one of the most energy-intensive unit operations in the chemical and pharmaceutical processes. As to the separation of azeotropic mixtures, energy consumption is even more critical. Extractive distillation is an important technique to separate binary or multiple azeotropes. It is important for the extractive distillation processes to achieve the energy consumption reducing. In recent years, partially thermally coupled distillation columns have been applied in extractive distillation to decrease the energy consumption. In this paper, the mixture of tetrahydrofuran, ethanol and water is separated by conventional extractive distillation and partially thermally coupled extractive distillation. The economics of steady state design for the conventional extractive distillation and partially thermally coupled extractive distillation process are explored by calculating total annual costs (TAC). The result showed that more than 16.3 % energy savings and 6.3 % TAC savings can be achieved by the partially thermally coupled extractive distillation process when compared with the conventional extractive distillation process. Partially thermally coupled extractive distillation is an effective way to achieve energy-saving and gain the economic for the separation of ternary azeotropic mixtures.

1. Introduction

In some chemical and pharmaceutical processes, such as the production process of norgestrel, an effluent containing tetrahydrofuran (THF), ethanol, and water is usually produced. THF and ethanol are widely used solvents. Therefore, it is necessary to recovery THF and ethanol, which is also an essential issue to reduce environmental pollution and conserve resources. Three binary azeotropes exist in THF/ethanol/water ternary system at atmospheric pressure, in which the minimum azeotropes have compositions of 90.54 mol% (mole fraction) THF at 65.75 °C between THF and ethanol, 82.87 mol% THF at 63.43 ^{0}C between THF and water, and 89.52 mol% ethanol at 78.15 ^{0}C between ethanol and water.

Distillation is an important method used for separation of mixture, which consumes about 49 % of the total energy consumption in separation processes (Sholl and Lively, 2016). As to the separation of azeotropic mixtures, energy consumption is even more critical. Some special distillation methods such as azeotropic distillation (Luyben, 2012), pressure swing distillation (Liang et al., 2017), and extractive distillation (Wang et al., 2015) have been used to implement these separations. Extractive distillation is a broadly used technology for separating azeotropic mixture, which can reverse the relative volatility of the initial mixture azeotropic components by adding entrainer. Despite the fact that the extractive distillation is usually more energy efficiently in comparison with pressure-swing distillation (Muñoz et al., 2006) and azeotropic distillation (Ramos et al., 2016), the energy consumption reducing is an actual problem for the extractive distillation processes.

Recently, lots of energy-saving technologies such as heat-pump-assisted distillation (Luo et al., 2015), dividing-wall columns (Sun et al. 2014), heat-investigated distillation, and partially thermally coupled distillation columns (PTCDC) (Luyben, 2016) have been proposed to reduce the energy consumption of extractive distillation processes on the basis of process intensification. These technologies have been applied to extractive distillation for separating binary azeotropic mixtures. Sun et al. (2014) explored extractive dividing wall column (EDWC) for separating benzene/cyclohexane, and the result showed that the total reboiler duty could reduce 22 %. Li et al. (2016) combined heat-integrated technology and intermediate heat to enhance

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thermodynamic efficiency, which achieved large energy saving. All of the mentioned studies promoted the development of energy-saving technologies of extractive distillation.
The single EDWC cannot be applied for separating ternary mixture since three product streams must be produced (Luyben, 2016). Timoshenko et al. (2015) introduced many alternative extractive distillation configurations to separate ternary azeotropic mixtures and evaluated the applicability of the extractive distillation flowsheets with the PTCDCs for all types of vapor-liquid equilibrium diagram. In their work, a case study was presented for the ternary mixture containing single binary azeotrope in initial. However, there appears to be little published work separating ternary mixture with three binary azeotropes by extractive distillation flowsheets with the PTCDCs.
In this work, the mixture of THF/ethanol/water is separated by conventional extractive distillation (CED) and partially thermally coupled extractive distillation (PTCED). The economical evaluations of the CED and PTCED for separating THF/ethanol/water are carried out to estimate their feasibilities by calculating total annual costs (TAC).

2. Basis of design

2.1 Entrainer selection

Entrainers play an important role in extractive distillation processes, and the relative volatility is a criterion of its selection. A preliminary screening was carried out and the four solvents DMSO, EG, N,N-dimethylformamide (DMF), and dimethylacetamide (DMAC) were selected as candidate entrainers in accordance with the polarity of the solvents. Figure 1 shows the effect of different entrainers on VLE of THF/ethanol, THF/water and ethanol/water with an entrainer to feed mole ratio 1. DMSO can both greatly enhance the relative volatilities of THF/ethanol, THF/water, and ethanol/water.

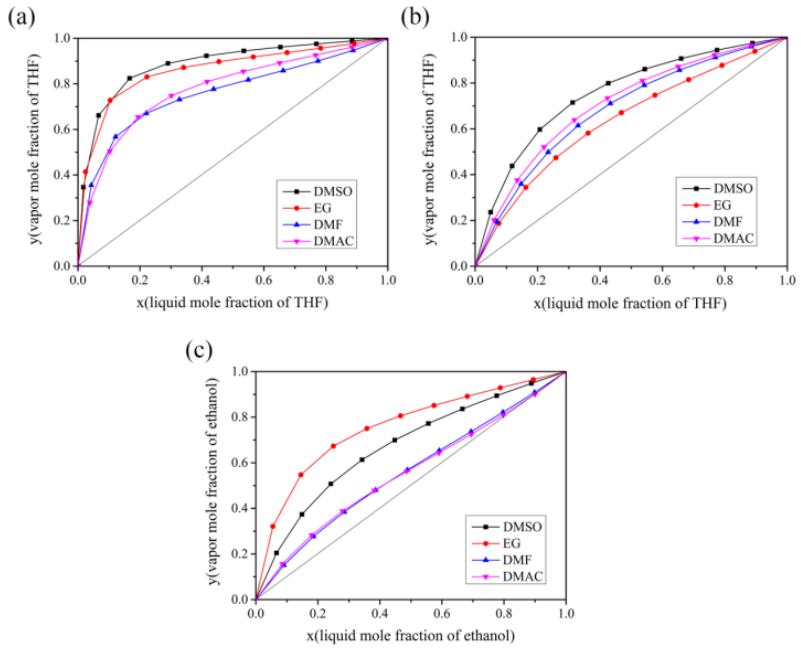

Figure 1: Effect of different entrainers on VLE of (a) THF/ethanol, (b) THF/water, and (c) ethanol/water

2.2 Thermodynamic model and feasibility analysis

In this study, the non-random two liquid (NRTL) model with built-in binary interaction parameters (in Table 1) was used to describe the phase behaviour of the system.
A residue curve map (RCM) can be used as a convenient tool to evaluate the feasibility of extractive distillation sequences. Four ternary RCMs are calculated by Aspen Plus at 1 atm based on NRTL (in Figure 2). It is observed that there is no additional azeotrope that formed with DMSO at 1 atm; the DMSO is the stable node; THF/ethanol, THF/water and ethanol/water three azeotropes are the unstable node; THF, ethanol and water are all the saddles. Moreover, there are no distillation boundaries for the three ternary systems with DMSO, so extractive distillation process will be an efficient method for the separation of THF/ethanol/water mixture.

Table 1: The interaction parameters of the NRTL model

Component i	Component j	Aij	Aji	Bij/K	Bji/K	αij
THF (1)	Ethanol (2)	2.323	-2.777	-524.909	905.739	0.300
THF (1)	Water (2)	1.214	4.760	157.781	-733.402	0.473
THF (1)	DMSO (2)	0	0	347.549	74.937	0.300
Ethanol (1)	Water (2)	-0.801	3.458	246.180	-586.081	0.300
Ethanol (1)	DMSO (2)	0	0	116.573	-393.319	0.300
Water (1)	DMSO (2)	-1.245	1.752	586.801	-1,130.216	0.300

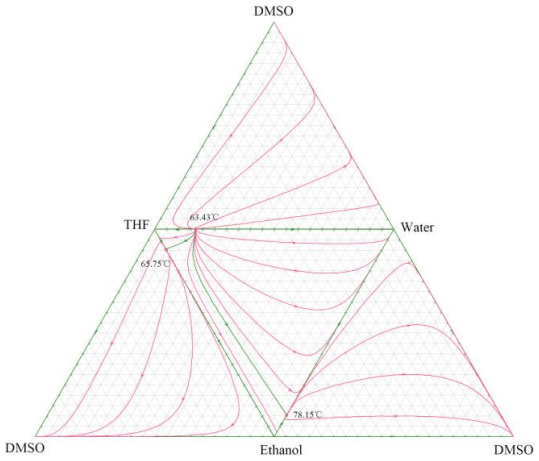

Figure 2: Four ternary residue curve maps (RCMS)

2.3 Economics

TAC, including annual investment costs and operating costs, is an economical evaluation criterion of process design. In this paper, investment cost mainly includes the costs of distillation column vessels and heat exchangers. Additional costs such as valves, pumps, and pipes are much lower than column vessels and heat exchangers and are ignored. The operating costs mainly consist of the cost of stream and cooling water. The differential temperature driving forces in the reboilers are the difference between the temperature of stream and the temperature of the column base. It should be noted that the temperature difference driving forces in the condensers are log-mean temperature difference that are calculated using cooling water inlet and outlet temperatures of 32 and 42 ˚C. The basis of the economics and equipment sizing (Luyben, 2011) were summarized in Table 2.

Table 2: Basis of economics and equipment sizing

Equipment	Cost calculation
column vessel	column diameter (D) = Aspen tray sizing column length (L) = N_T trays with 2 ft spacing plus 20 % extra length investment cost=1,7640$D^{1.066}L^{0.802}$ where D and L are in m
reboilers	heat transfer coefficient = 0.568 kW/(Km^2) differential temperature = stream temperature - column base temperature investment cost = 7,296$A^{0.65}$, where A is in m^2
condensers	heat transfer coefficient = 0.852 kW/(Km^2) differential temperature = log-mean temperature difference of inlet and outlet temperature differences investment cost = 7,296$A^{0.65}$, where A is in m^2
utility prices	low pressure steam (160 ^{0}C) = \$7.78/GJ medium pressure steam (184 ^{0}C) = \$8.22/GJ high pressure steam (254 ^{0}C) = \$9.88/GJ cooling water = \$0.354/GJ
TAC = (investment cost/payback period) + operating cost payback period = 3 y	

3. Process design and economic optimization

3.1 CED process

The CED process includes three distillation columns, in which the first two columns are extractive distillation columns (EDCs), and the other one is entrainer recovery column (ERC). The initial feed flow rate is 100 kmol/h with the composition of 30 mol% THF, 30 mol% ethanol, and 40 mol% water. The purities of three products are set at no less than 99.9 mol%, and the impurity of recycling entrainer is specified at 0.0001 mol% in the bottom of the ERC. The condenser pressure of the first EDC was set 1atm. The condenser pressures of the second EDC and the ERC were set at 0.4 and 0.15 atm to avoid using expensive high-pressure stream in reboilers. The sequential iterative optimization procedure of CED process (see Figure 3) is established to obtain the optimal design variables including total stages (NT1), fresh feed stage (NF1), entrainer feed stage (NFE1), and entrainer flow rate (EF1) of the first EDC, total stages (NT2), fresh feed stage (NF2), entrainer feed stage (NFE2), and entrainer flow rate (EF2) of the second EDC, total stages (NT3), and fresh feed stage (NF3). The optimal ternary CED flowsheet is given in Figure 4.

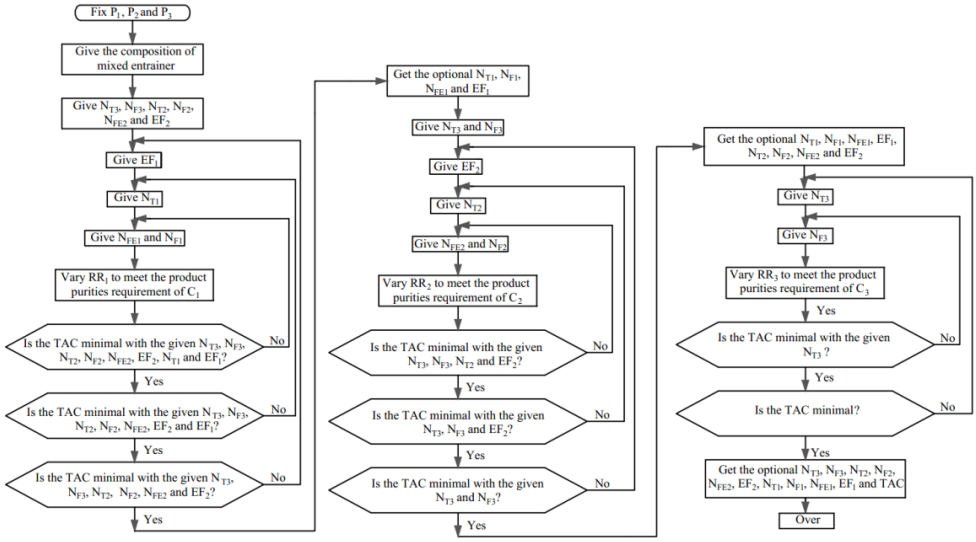

Figure 3: Sequential iterative optimization procedure of CED process

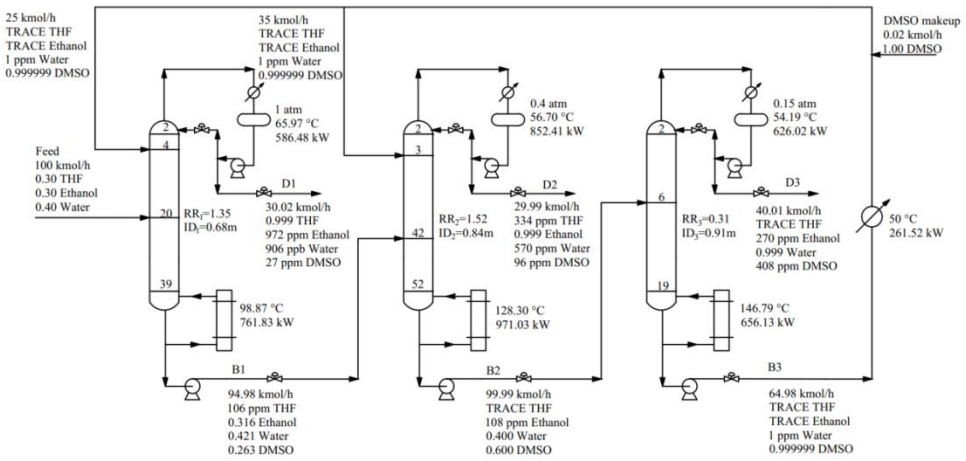

Figure 4: Optimal ternary CED flowsheet

3.2 PTCED process

PTCED process includes an EDC, a side rectifier and a ERC. It should be noticed that a vapor stream is removed from a stage of EDC and fed to the base of side rectifier. The distillate product of the EDC is the THF. The distillate product of the rectifier is the ethanol. The distillate product of the ERC is the water. The bottom from the ERC is the entrainer recycled back to the EDC and rectifier. The sequential iterative optimization

procedure of PTCED process (see Figure 5) is established to obtain the optimal design variables. The optimal ternary CED flowsheet is given in Figure 6.

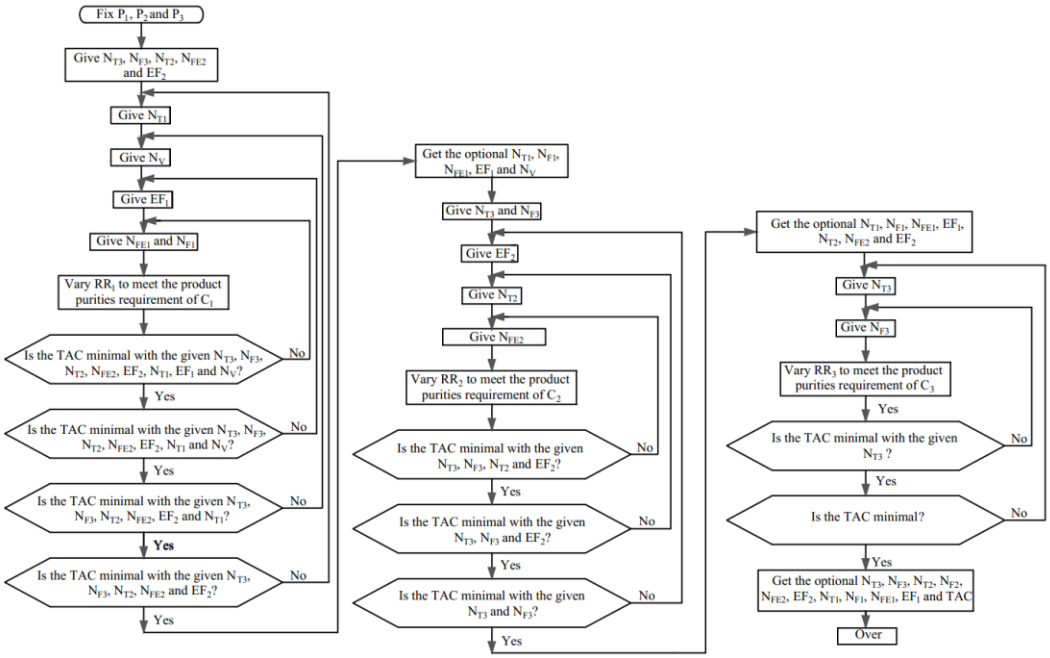

Figure 5: Sequential iterative optimization procedure of PTCED process

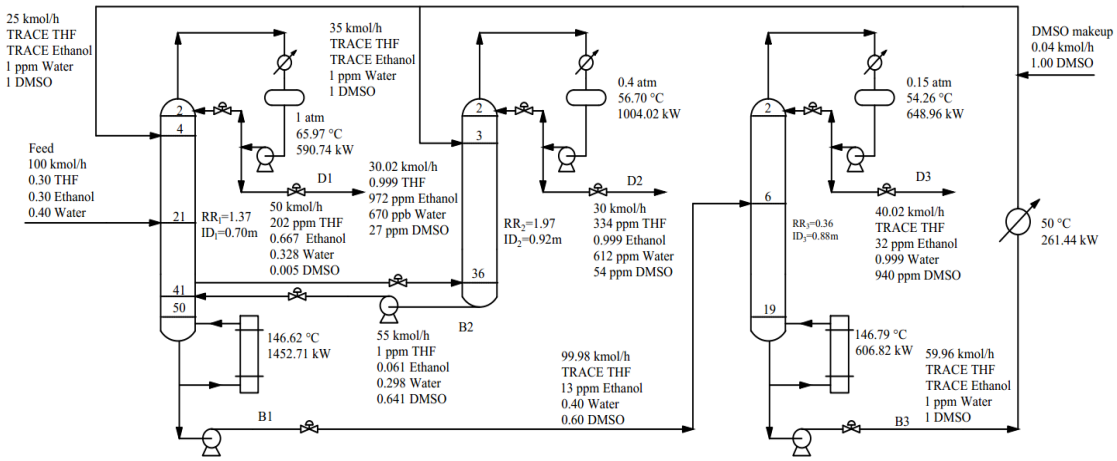

Figure 6: Optimal ternary PTCED flowsheet

4. Process comparison

In this section, a comparison was carried out for the CED and PTCED processes. The optimal configurations for the CED process have been obtained based on minimum TAC. Table 3 summarize the optimal design variables and minimized TAC results for the CED and the PTCED process. It is observed that the PTCED process can lead to reboiler duty savings of about 349.2 kW in terms of energy requirements. It is about 14.5 % savings in energy consumption compared with the CED process. It should be noting that the new process leads to a 9.4 % reduction in operating costs and a 1.4 % reduction in capital investment costs from the perspective of economics. A 6.3 % TAC savings can be obtained by the optimum PTCED compared with the conventional design.

Table 3: Comparison between optimum CED and PTCED

Parameters	CED			PTCED		
	EDC1	EDC2	ERC	EDC	Rectifier	ERC
N_T	40	50	20	51	36	20
RR	1.35	1.52	0.31	1.37	1.97	0.36
A_C (m^2)	24	52	44	24	61	45
A_R (m^2)	22	54	31	68	-	29
Q_C (kW)	586.5	852.4	626.0	590.7	1,004.0	649.0
Q_R (kW)	761.8	973.1	673.8	1,452.7	-	606.8
Total reboiler duty (kW)	2,408.7			2,059.5		
Capital investment costs (10^5 \$)	10.20			10.05		
Operating costs (10^5 \$/y)	5.42			4.91		
TAC (10^5 \$/y)	8.82			8.26		

5. Conclusions

In this work, the conventional extractive distillation (CED) and partially thermally coupled extractive distillation (PTCED) for separating the ternary mixture of THF/ethanol/water with DMSO were studied. On the basis of sequential iterative optimization procedure with total annual costs (TAC) as the objective function, the optional conditions of the CED process and PTCED process are obtained. The result showed that more than 16.3 % energy savings can be achieved by the PTCED process when compared with the CED process. It can be concluded that PTCED is an effective way to achieve energy-saving and gain the economic.

Acknowledgments

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