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# Triple Column Pressure-Swing Distillation for Ternary Mixture of Methyl Ethyl Ketone /Isopropanol /Ethanol

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Methyl ethyl ketone (MEK), isopropanol (IPA), and ethanol (EtOH) are important chemical materials and widely used as intermediates solvent in many chemical processes. The boiling points of three pure components are very close and the maximum temperature difference is 3.74 K. Under atmospheric and high pressures, the MEK /IPA /EtOH mixture forms two binary pressure-sensitive azeotropes of MEK-IPA and MEK-EtOH and its residue curve maps (RCMs) present one distillation boundary. Under 0.1 atm, the azeotrope of MEK-IPA disappeared and the MEK /IPA /EtOH mixture forms one azeotrope of MEK-EtOH. According to the RCMs, two different separation sequences using triple column pressure-swing distillation (TCPSD) were available for the separation of this ternary mixture. Vapor-liquid equilibrium data from the literature were regressed to verify the reliability of the thermodynamic model used. Several operating parameters were optimized on the basis of minimum total annual cost (TAC) to study the effect of separation sequence and heat integration on the economy of TCPSD. The results show that the IPA-MEK-EtOH separation sequence is more economical and partial heat integration with this sequence has great economic advantage over full heat integration. The choice of separation sequence and heat integration should be considered for separating this type of mixture from the perspective of TAC.

## 1. Introduction

A ternary mixture of methyl ethyl ketone (MEK), isopropanol (IPA) and ethanol (EtOH) is generated in the Fischer Tropsch synthesis process, it is attractive and necessary for the effective separation and recovery of mixture to conserve resource and protect environment. However, conventional distillation cannot achieve the separation of three components effectively due to the close boiling points, the existence of different azeotropes and distillation boundaries. Pressure-swing distillation (Liang et al., 2016; Luyben, 2017) is based on the shift of the azeotropic composition by changing the operating pressures. Compared with extractive distillation (Ortega et al., 2013 and later (Wang et al., 2015) which is achieved by adding an appropriate entrainer to enhance the relative volatility of the components, pressure-swing distillation avoids introducing another component and has an advantage of a simple configuration. Modia et al. (2011) compared different column configurations for separating ternary mixture of chloroform-acetone-toluene and found that triple-column configuration was more economical. Li et al. (2016) investigated the residue curve maps (RCMs) of butanol-butyl acetate-methyl isobutyl ketone ternary mixture and found that methyl isobutyl ketone can be used as azeotropic agent for the separation. Triple column pressure-swing distillation (TCPSD) processes with four different separation sequences were investigated to separate the ternary mixture of acetonitrile-methanol-benzene using RCMs to confirm the feasibility of separation sequence by Zhu et al. (2016), and the results showed that the TCPSD process with acetonitrile-methanol-benzene separation sequence was the most economical column sequence.
According to the classifications of RCM, the ternary mixture of MEK /IPA /EtOH belongs to the Serafimov class 2.0-2b (Hegely and Lang, 2011). The commercial process simulator of Aspen Plus (version 7.2) was applied to simulate and optimize the separation process. The RCMs of the ternary mixture under different pressures were investigated to study the effect of separation sequence and heat integration on economics.

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## 2. Basis of design and analysis

### 2.1 Property method

The Aspen built-in binary interaction parameters cannot achieve satisfactory results for describing the phase behavior for the MEK-IPA binary system. Experimental data (Martínez et al., 2008) for the MEK-IPA system at 101.3 kPa were regressed to obtain binary interaction parameters. Figure 1 shows the comparison among the experimental data, the correlated results, and the default results at 101.3 kPa. The results show that the azeotropic compositions and temperatures calculated with the regressed binary interaction parameters are consistent with the experimental data. For the binary system of MEK-EtOH and IPA-EtOH, the NRTL model with the Aspen built-in binary interaction parameters fits the experimental data well. All parameters employed in this paper are listed in Table 1.

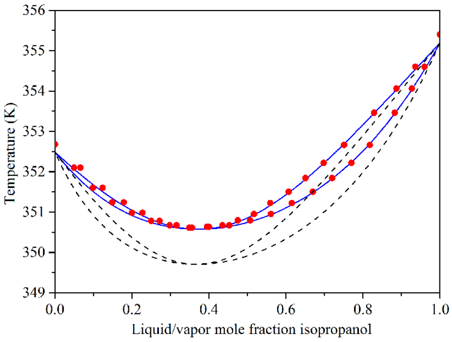

*Figure 1: T-x-y phase diagram of MEK-IPA at 101.3 kPa: ● experimental data; — correlated results; ---the default results.*

*Table 1: The binary interaction parameters of ternary system*

| | EtOH /IPA | EtOH /MEK | IPA /MEK |
|---|---|---|---|
| $A_{ij}$ | 0.1352 | -1.5609 | -0.3329 |
| $A_{ji}$ | 0.7014 | 0.7593 | -0.8619 |
| $B_{ij}$ | -215.7354 | 654.5550 | 280.7251 |
| $B_{ji}$ | -58.3840 | -132.9897 | 339.4895 |
| $C_{ij}$ | 0.30 | 0.30 | 0.47 |
| $D_{ij}$ | 0 | 0 | 0 |

### 2.2 Process analysis using RCMs

Triangular diagram is used to describe the properties of residue curves, distillation boundary and azeotropes. The RCMs of MEK /IPA /EtOH ternary mixture at 1 and 0.1 atm are obtained through Aspen Plus and shown in Figures 2a and b. Figure 2a illustrates that the boiling points of MEK, IPA, and EtOH are 352.49, 355.20, and 351.46 K. Under atmospheric pressure, the minimum-boiling have compositions of 64.90 wt% MEK between MEK and IPA with the boiling point at 350.26 K, and 60.99 wt% MEK between MEK and EtOH with the boiling point at 347.34 K. The azeotrope of MEK-IPA and vertex EtOH are saddles, vertices MEK and IPA are stable nodes, and the MEK-EtOH azeotrope is the unstable node, respectively. There is one distillation boundary moving from the MEK-EtOH azeotrope to the MEK-IPA azeotrope and the distillation boundary divides the diagram into two areas of Ⅰ and Ⅱ.

Figure 2b shows the RCMs of MEK /IPA /EtOH ternary mixture at 0.1 atm. The boiling points of MEK, IPA, and EtOH under 0.1 atm are 294.07, 307.37, and 302.47 K. Under atmospheric pressure MEK is the intermediate boiling component in the ternary mixture of MEK /IPA /EtOH. Compared with the boiling sequence of ternary mixture under atmospheric pressure, MEK is the minimum boiling component and vertices MEK changes from stable node at 1 atm to saddle at 0.1 atm. The azeotropic point of MEK-IPA disappeared when the pressure is set at 0.1 atm and the azeotropic composition of MEK-EtOH changes from 60.99 wt% MEK at 1 atm to 77.59 wt% MEK at 0.1 atm. There is no distillation boundary under 0.1 atm.

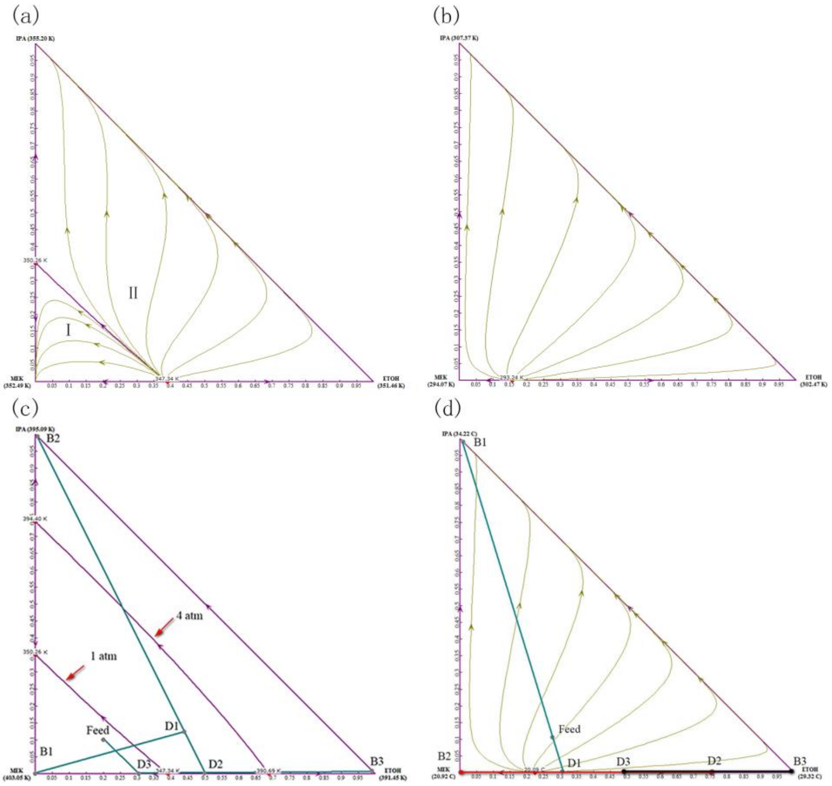

*Figure 2: Residue curve for* MEK /IPA /EtOH*: (a) 1 atm; (b) 0.1 atm; (c) material balance lines for MEK-IPA-EtOH separation sequence; (d) material balance lines for IPA-MEK-EtOH separation sequence.*

Two different TCPSD separation sequence are feasible to separate the ternary mixture with different pressure combinations. Figure 2c shows that the MEK /IPA /EtOH ternary system can be separated with the MEK-IPA-EtOH separation sequence. When the first column (C1) is operated at 4 atm, the point of fresh feed locates in the distillation region Ⅰ and MEK product can be obtained from the bottom of C1. The distillation boundaries can be shifted from the C1 operating pressure to the second column (C2) operating pressure to ensure D1 situate in region Ⅱ and the IPA from the bottom of C2 can be obtained. The stream of D2 is fed into the third column (C3). EtOH is obtained from the bottom of C2, and the distillation stream of D3 is recycled to the C1.

Figure 2d shows that the MEK /IPA /EtOH ternary mixture can be separated with the IPA-MEK-EtOH separation sequence. When the pressure of C1 is operated at 0.1 atm, the azeotrope of MEK-IPA disappeared. The efficient separation of IPA from the ternary mixture is achieved and IPA as the product leaves the C1 from the bottom. The top stream consists of the mixture of MEK-EtOH with a trace amount of IPA and enter the C2 for further distillation. The azeotropic point of MEK-IPA changes significantly with the increasing pressures. Two products of MEK and EtOH are obtained from the bottoms of C2 and C3, respectively. The distillation stream of D3 is recycled to the C2.

## 3. Process design and optimization

The flow rate of the feed stream is 1000 kg/h with a composition of 70 wt% MEK, 10 wt% IPA, and 20 wt% EtOH. The purity of MEK, IPA, and EtOH products are set as 99.9, 99.3, and 99.1 wt%. For the separation sequence of MEK-IPA-EtOH, the operating pressure of C1 is set at 4 atm to use the low-pressure steam (433 K, $7.78 per GJ) as heat source in the reboiler to reduce the energy costs. The C3 is operated at 0.4 atm, so the cooling water (305 K, 0.03$/1,000 gal) can be used with the condenser temperature is 323.55 K. The C2 pressure is determined by calculating the minimal TAC when C1 and C3 pressure are fixed at 4 and 0.4 atm, respectively. The operating pressure of C2 is fixed at 1 atm with the minimal TAC. For the separation sequence of IPA-MEK-EtOH, the pressure of the C1 is operated at 0.1 atm to destroy the azeotrope of MEK-IPA. The operating pressure of C3 is set at 0.4 atm with the consideration of using cooling water, and the optimum C2 pressure is 5.8 atm for this TCPSD process.

The TAC is taken into account as an objective function to optimize the TCPSD process. The definition of TAC is the sum of annual operating costs and capital costs. Annual operating costs comprise annual stream and cooling water cost. Annual capital costs refer to the cost of column vessels and heat exchangers with the investments of valves, reflux drums, pipes, and pumps are usually neglected. The capital investment is denoted as the total capital investment divided by a three-year period. The total heat transfer coefficients are 0.852 kW/(K·m$^2$) for condensers and 0.568 kW/(K·m$^2$) for reboilers. Software has been developed to optimize TCPSD process based on the sequential iterative optimization procedures which named as Pressure-Swing Distillation Optimization Software (PSDOS). The process parameters including the total stages of three columns (NT$_1$, NT$_2$, NT$_3$), the feed tray location (NF$_1$, NF$_2$, NF$_3$), the reflux ratios of three columns (RR$_1$, RR$_2$, and RR$_3$) and recycle location (NR$_{EC}$) are optimized to obtain a minimal TAC. The “Design Spec” and “Vary” functions are utilized to adjust the distillation flow rate to reach the requirements of the purity of products. The detailed information of calculating TAC method and optimization procedure has been described in our previous papers (Cao et al., 2016) and also by (Zhu et al., 2016).

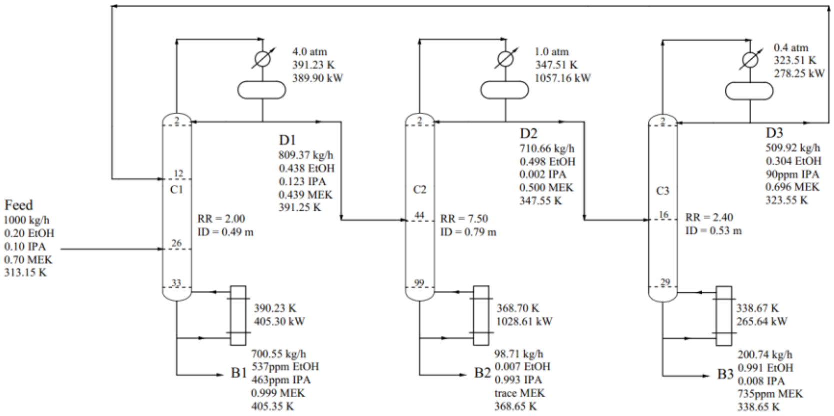

*Figure 3: Flowsheet of the optimal TCPSD process for MEK-IPA-EtOH separation sequence.*

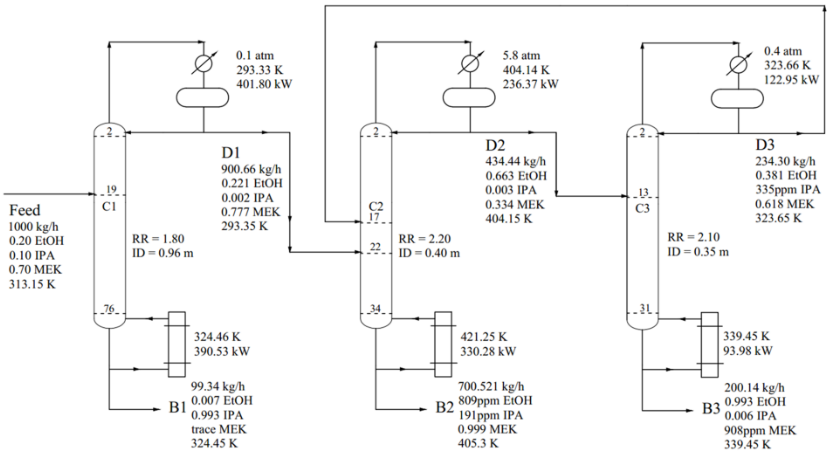

*Figure 4: Flowsheet of the optimal TCPSD process for IPA-MEK-EtOH separation sequence.*

Figure 3 shows the MEK-IPA-EtOH separation sequence with detailed stream information, equipment sizes, heat duties, and operating conditions. The optimization results show that the reboiler and condenser duties of TCPSD process are 1699.55 and 1725.31 kW. The minimal TAC of the optimized MEK-IPA-EtOH separation configuration process is $7.20\times10^5$ \$/y, annual operating cost is $4.04\times10^5$ \$/y, and total capital investment is $9.49\times10^5$ \$/y. The detailed information of the TCPSD process with IPA-MEK-EtOH separation sequence is shown in Figure 4. The optimization results show that the minimal TAC is $4.98\times10^5$ \$/y, annual operating cost is $2.33\times10^5$ \$/y, and total capital investment is $7.94\times10^5$ \$/y. The reboiler and condenser duties of TCPSD process are 877.00 and 832.57 kW.

Two different separation sequences were analysed and compared to separate the complex ternary mixture of 70 wt% MEK, 20 wt% IPA, and 10 wt% EtOH. The purity of 99.9 wt% MEK, 99.3wt% IPA, and 99.1 wt% EtOH product were achieved in different separation configurations. The TAC of the TCPSD process with IPA-MEK-EtOH sequence decreased by 30.83% compared with MEK-IPA-EtOH sequence process. The annual operating cost and total capital investment decreased by 42.33% and 16.33%. The TCPSD process with MEK-IPA-EtOH separation sequence needed more energy consumption because relative volatility of IPA and EtOH was smaller. The results showed that IPA-MEK-EtOH separation sequence was more economical.

## 4. Heat-integrated process design for the TCPSD process with IPA-MEK-EtOH separation sequence

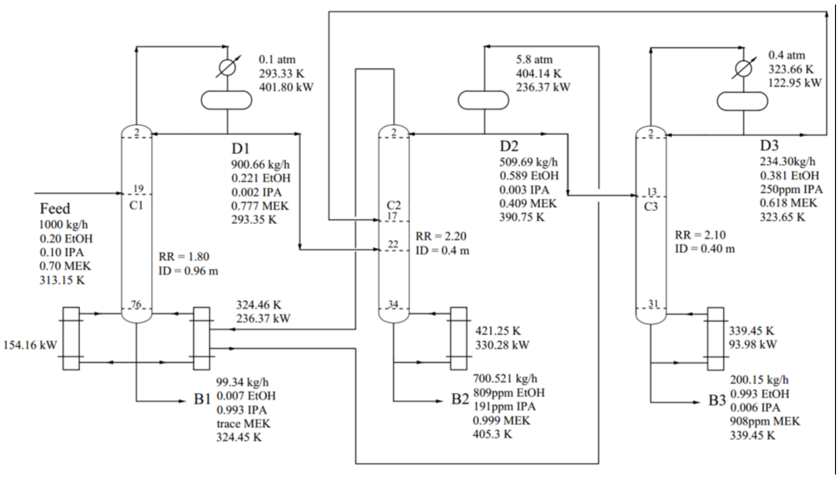

*Figure 5: Flowsheet of the optimal TCPSD with partial Heat Integration.*

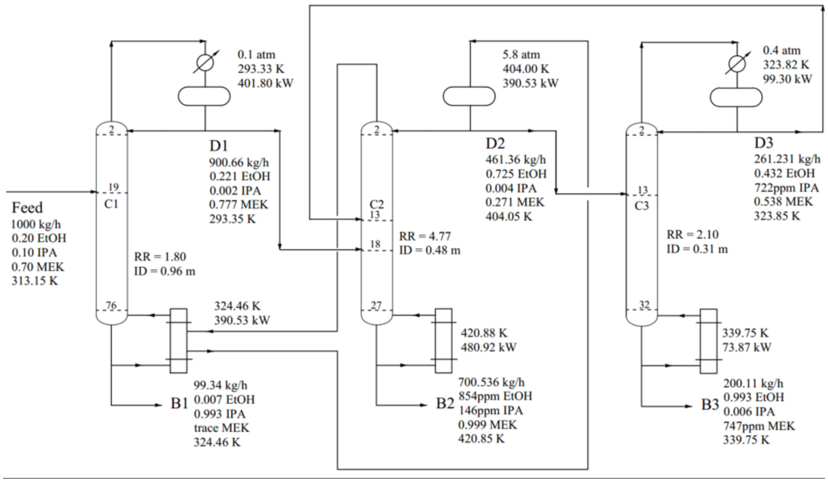

*Figure 6: Flowsheet of the optimal TCPSD with full Heat Integration.*

To make the distillation process more energy-efficient, the Heat Integration processes with the IPA-MEK-EtOH separation sequence were studied. The differential temperature between C2 condenser and C1 reboiler, C2 condenser and C3 reboiler are 79.68 K and 64.49 K. It is possible to make Heat Integration between the C1 and C2 or between C2 and C3. To achieve heat integration, the distillate of C2 can provide energy to the reboiler of C1 or C3. The heat duty difference between C2 and C1, C2 and C3 are 154.16 kW and 142.39 kW. The larger the heat duty difference, the more extra heat exchanger is needed. Considered the temperature and heat duty difference in the condenser/reboiler, the heat of the top of C2 served as the heat source for the bottom of C1 is better than the heat source for the bottom of C2.

For the partially heat-integrated TCPSD process, the heat of the condenser in C2 is transferred to the reboiler of C1, and the makeup heat is provided by an auxiliary reboiler. For the fully heat-integrated TCPSD process, the reflux ratio of C2 is adjusted to make the C1 condenser duty equal to the C2 reboiler duty. The detailed information of the optimized partially and fully heat-integrated TCPSD processes are shown in Figures 5 and 6. The TACs of the partially and fully heat-integrated TCPSD processes are $4.42 \times 10^5$ \$/y and $4.55 \times 10^5$ \$/y. The partially heat-integrated TCPSD process is better than the fully heat-integrated TCPSD process with the IPA-MEK-EtOH separation sequence.

## 5. Conclusion

Triple column pressure-swing distillation for the separation of MEK /IPA /EtOH was studied in this paper. The feasibility of TCPSD was analysed using RCMs and the process was optimized based on the TAC minimization. The TCPSD process with the MEK-IPA-EtOH separation sequence needed more stages and heat duty to reach the requirements of the purity of IPA product. The TAC of the TCPSD process with IPA-MEK-EtOH separation sequence decreased by 30.83% compared with MEK-IPA-EtOH separation sequence. The partially heat-integrated TCPSD process with the IPA-MEK-EtOH sequence was superior to the fully heat-integrated TCPSD process with the TAC decreasing 2.86%. These studies revealed that the partially heat-integrated TCPSD process with the IPA-MEK-EtOH separation sequence was worth regarding as an economic and feasible technological route for separating MEK /IPA /EtOH mixture.

### Acknowledgments

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