

# Comparative Optimal Design and Control of Two Alternative Approaches for Separating Heterogeneous Mixtures Isopropyl Alcohol-Isopropyl Acetate-Water with Four Azeotropes

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**Abstract:** The separation of ternary mixtures with homogeneous or heterogeneous multi-azeotropes has received increasing attention. In this work, a systematic design, optimization and control procedure is proposed for extractive distillation of heterogeneous mixtures with four azeotropes. Herein, the ternary system isopropyl alcohol/isopropyl acetate/water is taken as a case study. The suitable entrainer is first obtained through a proposed approach combining the vapor-liquid equilibrium (VLE) curves and infinite dilution activity coefficient ratios. Conceptual design of two alternative separation sequences involving double-column extractive distillation with a pre-concentrator (DEDP) and triple-column extractive distillation (TED) are then investigated based on thermodynamic insights. With the method of sequential iterative optimization while taking total annual cost (TAC) as the objective function, the two processes are optimized. The optimal results indicate that the DEDP process with dimethyl sulfoxide as entrainer can save 6.43% TAC than that of TED. Finally, a new control structure combining reflux flowrate-to-feed (R/F) and adjustable reboiler duty-to-feed ( $Q_R/F$ ) with “HiLoSelect” strategy is proposed to better handle three product purities than that of the basic control structure while feed flowrate and composition disturbances are introduced in the studied DEDP process.

**Keywords:** Conceptual design; Multi-azeotropes; Triple-column extractive distillation; Dynamic control

## 1. Introduction

Isopropyl alcohol (IPA) and isopropyl acetate (IPAC), as important raw materials and solvents, have been widely used in pesticide, medicine, electronics and fuel additives industries [1-3]. IPA, IPAC and water are produced in the esterification reaction of IPA and acetic acid [4, 5]. Even though the processes for separating binary mixture IPA/IPAC or IPA/water have been well explored [6, 7], to the best of our knowledge, few efforts were found on separating ternary system IPA/IPAC/water with four azeotropes produced in the esterification reaction. It is noteworthy that the recovery of IPA and IPAC from water is very attractive from the view of sustainable development and environmental protection. However, there is a minimum heterogeneous ternary azeotrope (*i.e.*, IPA/IPAC/water azeotrope) and three binary azeotropes (*e.g.*, IPA/water azeotrope) formed in IPA/IPAC/water at atmospheric pressure, leading to the difficulty in separating such non-ideal systems.

Unconventional distillation approaches including pressure-swing distillation [8-11], azeotrope distillation [12-14] are generally applied in separating azeotropic mixtures. Besides, extractive distillation (ED) is one of the most promising approaches in the separation of azeotropic or close-boiling mixtures in chemical industries. For instance, You *et al.* [15] studied the ED design and optimization case for the separation of acetone-methanol with entrainer water. Luyben [16] made a comparison between ED process and pressure-swing distillation of acetone/chloroform separation and demonstrated that the ED process is much more attractive in both lower capital investment and energy consumption. Lang *et al.* [17] investigated a modified operational policy of batch ED for the recovery of tetrahydrofuran from industrial waste solvent mixture. An energy-efficient ED system with or without heat integration for the separation of tetrahydrofuran/water azeotropic mixture was also explored [18]. Lo and Chien [19] explored the separation of *tert*-butanol/water azeotropic mixtures by ED process.

Recently, the exploration of binary azeotropic mixture separation was extended to multi-component mixtures with multi-azeotropes extremely increasing the complexity

and difficulty. Wang *et al.* [20] introduced two methods involving triple-column ED and double-column ED with an additional decanter to separate the ternary azeotropic mixture toluene-methanol-water. Zhao *et al.* [21] made a comparison of heterogeneous azeotropic distillation and ED methods for ethanol/toluene/water separation. An application of ED with partially thermally coupled columns for the separation of ternary azeotropic mixtures with the different type of vapor-liquid equilibrium diagrams was studied by Timoshenko *et al.* [22].

To break distillation boundaries and azeotropes, a suitable entrainer altering the relative volatilities of the different components in the mixture is required for ED system. Entrainer selection is one of the most important factors determining the efficiency of an ED [23-25], as it will straightforwardly influence the energy consumptions. Raeva *et al.* [26] investigated the physical-chemical and selective properties of entrainer in the separation of ternary systems. A simple procedure was proposed by Hsu *et al.* [27] for the quick comparison of alternative entrainer candidates for the separation of dimethyl carbonate-methanol. Shen *et al.* developed a systematic approach in designing extractive distillation of azeotropes using heavy [28, 29] or light entrainer [30, 31] and these studies provided a comprehensive foundation in ranking entrainer and providing evaluation.

In order to confirm the operational feasibility of the ED process, the dynamic performance needs to be further considered. Luyben [32] explored an average temperature and solvent-to-feed (S/F) ratio control structures for the investigation of heat-integrated ED process. Another important control strategy is focused on fixing reflux-to-feed flowrate (R/F) ratio [33]. Li *et al.* [34] have discussed different control structures of ED processes for separating 2-methoxyethanol/toluene and found that the control loop with reboiler duty-to-feed ratio ( $Q_R/F$ ) is more efficient in holding product purities. Yang *et al.* [35] applied an effective control strategy with fixed  $Q_R/F$  and temperature proportion cascade to handle the product purities of methanol, toluene and water through the heat-integrated extractive dividing wall column. And the controllability of extractive dividing-wall column based on temperature differences was evaluated by Feng *et al.* [36], the dynamic results showed that the

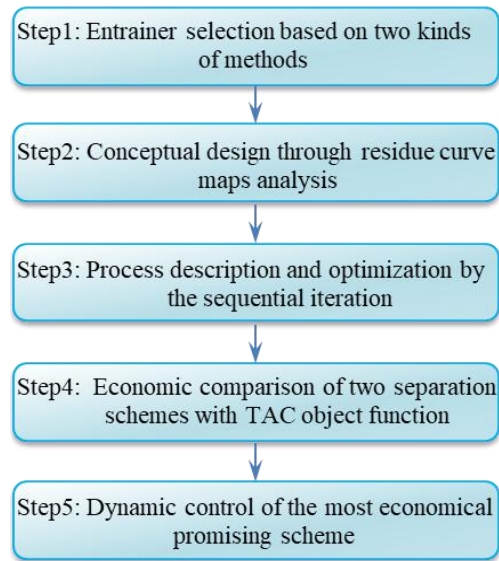
system with improved cascade structure can effectively maintain stable operation and handle large feed upsets. Inspired by above dynamic studies, an improved control strategy is proposed by adding a “HiLoSelect” block in aspen dynamics to achieve the function of  $Q_R/F$  controlling to be activated or deactivated depending on flow disturbances.

In this research, we propose a systematic procedure to design, optimize and control for the separation of ternary mixtures IPA/IPAC/water based on two approaches involving double-column extractive distillation with a pre-concentrator (DEDP) and triple-column extractive distillation (TED). The entrainer evaluation and screening *via* a short-cut procedure considering two criteria (*e.g.*, the infinite dilution activity coefficient ratio) and thermodynamic feasibility insight *via* residue curve maps (RCMs) are conducted. The sequential iterative optimization is then carried out by minimizing total annual cost (TAC) as the objective function. Finally, an improved control scheme focusing on optional reboiler duty-to-feed ( $Q_R/F$ ) strategy is proposed based on the basic control structures of the most economic DEDP process. The capability of rejecting disturbance in fresh feed flowrate and composition for the three control structures is evaluated in terms of the offset and transient deviation.

## 2. Methodology

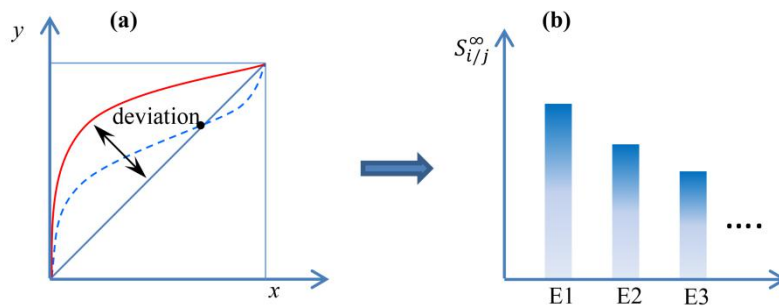
The proposed systematic method for separating heterogeneous mixtures IPA/IPAC/water with four azeotropes is carried out in five steps. As shown in **Fig.1**, **Step 1** is focused on determine suitable entrainers, the evaluation criteria involve the infinite dilution activity coefficient ratio and binary VLE curves. **Step 2** mainly focuses on the conceptual design *via* the residue curve maps (RCMs) using the selected entrainer. In **Step 3**, the proposed processes simulation and optimization are performed using sequential iteration optimization method with TAC as objective function. **Step 4** provides an economic comparison of two optimal separation processes. Eventually, the most economical scheme is further extended to the investigation of the dynamic controllability. In **Step 5**, an effective dynamic control strategy is proposed to ensure the system to be well controlled at (or close to) the set

points within a desired time under different disturbances.



**Fig.1.** The proposed procedure for optimal design and control of IPA/IPAC/water separation

## 2.1 Entrainer selection



**Fig.2.** The proposed short-cut procedure for screening entrainer

In general, entrainers are evaluated with different methods including experiment, database querying, computer aided molecular design (CMAD) [37, 38]. In this research, we adopt a short-cut procedure (see **Fig.2**) for entrainer determination involving the selectivity at infinite dilution and VLE curves [39]. As shown in **Fig.2 (a)**, there will be an intersection point in the diagonal of binary VLE diagram when binary mixture azeotrope exists. However, the intersection point will disappear and the binary VLE curve will deviate from the diagonal line if add entrainers into the azeotropic mixture. Generally, the larger deviation caused by introducing a special entrainer, the more efficient of the entrainer is.

The comparison of the selectivity at infinite dilution under different entrainers

(i.e., E1, E2 and E3) is illustrates **Fig.2 (b)**. For the ED, the selectivity always can be adopted as the standard to evaluate the suitability of solvent, which is defined in **eq. (1)** by the ratio of the activity coefficients in the presence of the entrainers in the mixture.

$$S_{i/j} = \frac{k_{i,s}}{k_{j,s}} \quad (1)$$

where  $k_{i,s}$  and  $k_{j,s}$  are activity coefficients of different components (i.e.,  $i$  and  $j$ ) in the entrainer, respectively. However, the activity coefficient increases with the concentration of the mixture increases [40-41]. The usual approach is to consider using the selectivity at infinite dilution  $S_{i/j}^{\infty}$  to evaluate the effect of different entrainers, which is defined by **eq. (2)**.

$$S_{i/j}^{\infty} = \frac{k_{i,s}^{\infty}}{k_{j,s}^{\infty}} \quad (2)$$

where  $k_{i,s}^{\infty}$  and  $k_{j,s}^{\infty}$  are the infinite dilution activity coefficients for trace component  $i$  and  $j$  in the entrainer, respectively.

Four promising components involving dimethyl sulfoxide (DMSO), ethylene glycol (EG), diethylene glycol (DEG) and triethylene glycol (TEG) are selected as candidate entrainers in accordance with the polarity of the solvents, which are frequently used in the separation of multi-azeotrope [20, 24, 42-44].

## 2.2 Conceptual design based on RCMs

The residue curve maps (RCMs) are important graphical techniques that are often used to assist conceptual design, as well as other separation operations where triangular composition diagrams are used. Distillation curve maps and mass balances are graphically represented by lines or curves connecting the corresponding compositions. Global flow rates are found through the application of the lever rule. Mass balance lines of the distillation have two restrictions: (1) bottom compositions, distillate, and feed shall be always on the same straight line; (2) with a very close approximation, bottom compositions and distillate are on the same residue curve. As

residue curves do not cross a distillation limit, the bottom compositions and distillate are on the same distillation region, and the intrinsic mass balance and line to the residue line are in both sites [45].

### 2.3 Process description

The separation is presented with the composition of 65.0/18.5/16.5 wt% IPA/IPAC/water based on the research of Xu *et al* [46]. The feed flowrate is set as 1600 kg·h<sup>-1</sup> under the pressure of 101.3 kPa. The purities of three products IPA, IPAC and water are specified as 99.5 wt%, 98.5 wt% and 99.5 wt%, respectively. The tray pressure drop of each column is set as 0.005 atm according to Luyben [47].

### 2.4 Process optimization and economic evaluation

For the determination of the minimum energy consumption of the heterogeneous extractive distillation process, the following variables need to be dealt with in the optimization process are entrainers flowrate, total number of stages of all columns, reflux ratio, feed locations, *etc.* These operating variables interact with each other raising a requirement of the suitable objective function to consider all the operational parameters in the meantime. Following the suggestions of Douglas [48], the minimization of an economical objective function TAC (see **eq. (3)**) is performed by considering both annualized capital and operational costs. TAC is calculated in Aspen Plus with FORTRAN functions as shown on **Table.S1**.

$$TAC = \frac{\text{total capital cost}}{\text{payback period}} + \text{total operating cost} \quad (3)$$

The equipment materials are stainless steel and the investment recovery period is set as three years, with the annual working time of 8000 hours [49, 50]. The major capital costs of equipment are column vessels and heat exchangers (reboiler and condenser). The capital cost is the sum of the heat exchanger cost (*hx*) and the column vessel capital cost (*shell*), calculated *via* **eq. (4)**.

$$\text{total capital cost} = \text{shell} + \text{hx} \quad (4)$$

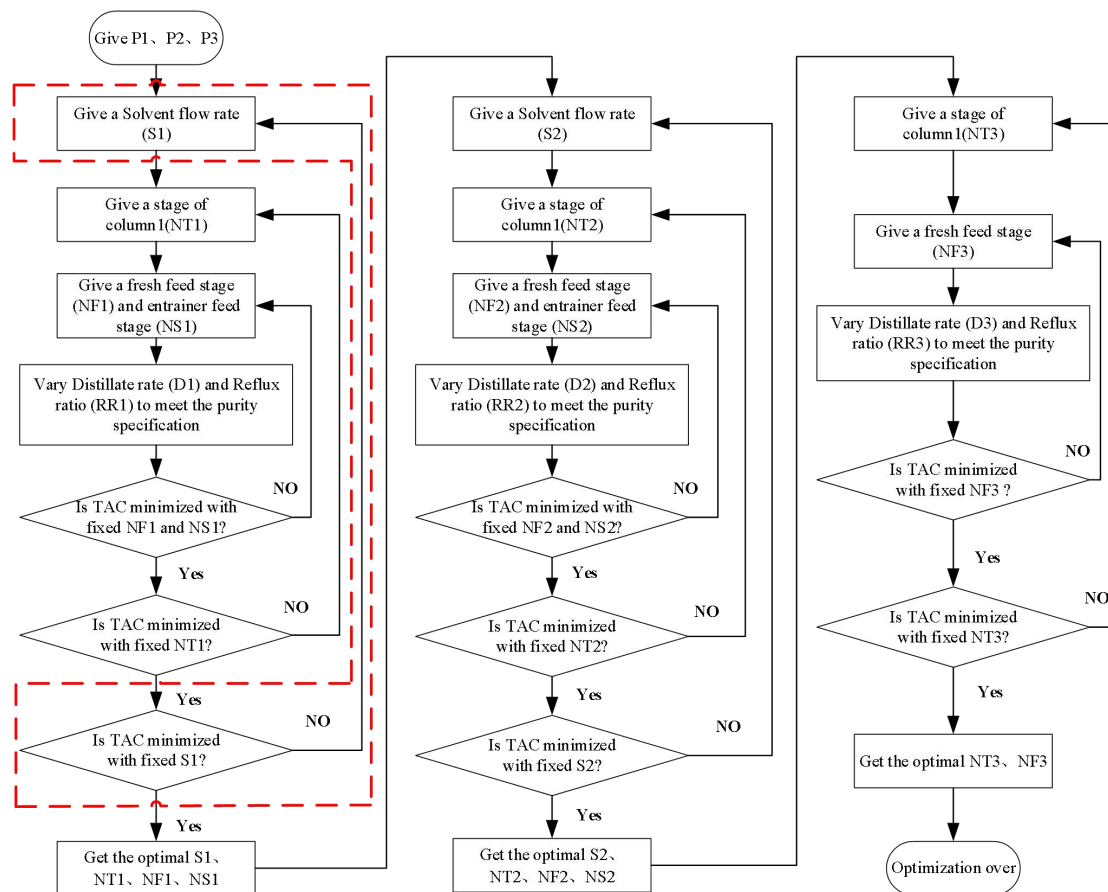
The total operation cost usually consists of two parts, represented by hot steam and cooling water consumption utilized in reboiler and condenser. The size of each

column is determined by the “*Tray Sizing*” function in Aspen Plus and a sieve plate is selected. The heat exchange areas of reboiler and condenser are calculated according to the following formula (*i.e.*, eq. (5) and eq. (6)).

$$A_R = \frac{Q_R}{U_R \cdot \Delta T_R} \quad (5)$$

$$A_C = \frac{Q_C}{U_C \cdot \Delta T_C} \quad (6)$$

where  $Q_R$  and  $Q_C$  are the reboiler duty and condenser duty of columns,  $\Delta T_R$  and  $\Delta T_C$  represent the differential temperatures for the reboiler and condenser, and  $U_R$  and  $U_C$  are the overall heat transfer coefficients for reboiler and condenser, respectively.



**Fig.3.** Sequential iterative optimization procedure

An economic calculation sequence is set up to optimize the process when the system has so many variables. Herein, sequential iterative procedure exhibited in **Fig.3** is utilized to achieve the optimization with the aid of “*Sensitivity Analysis*” tool in Aspen Plus [51]. For the first scheme with single recycled entrainer stream (not



including the steps in the red dashed line), feed locations (NF1, NF2 and NF3) and recycled solvent feed location (NS) are optimized as the inner iteration loop while other variables are optimized at the external loop to achieve the objective function. Differently, for another scheme with double recycled entrainer stream (including the steps in red dashed line), the optimization procedure is more complicated for two recycled solvent feed flow rates (S1 and S2) have to be optimized at the external optimization loop. The “Design Spec” and “Vary” functions of each column are utilized to adjust the distillate flow rate (D1, D2 and D3) and reflux ratio (RR1, RR2 and RR3) to obtain specified products purities, and three columns are optimized step by step [52, 53, 54].

## 2.5 Dynamic control

The disturbances of flow rate and feed composition often occur in the practical production process, and it will greatly affect the quality of products and benefits of factories. Instead of using costly composition on-line analyzers, temperature control can be good choice to obtain the composition requirement due to the corresponding linear relation between the temperature and the quality of the product [55]. In this research, temperature measuring control points are selected based on the “*slope criterion*” [56]. Furthermore, relay-feedback tests are run on the temperature controllers to obtain several ultimate gains ( $K_U$ ) and periods ( $P_U$ ). Then the Tyreus–Luyben tuning method built in Aspen Dynamics is used in all temperature controllers with the dead time of 1 min to obtain the  $K_C$  and  $\tau_1$  (see **eq.(7)** and **eq.(8)**).

$$K_C = K_U/3.2 \quad (7)$$

$$\tau_1 = 2.2P_U \quad (8)$$

Following the suggestion of Luyben [57], the feed flow rate can be controlled within a few seconds and 0.3 min is thus chosen as the integral time ( $\tau_1$ ) for flow controllers, and the gain ( $K_C$ ) is set as 0.5 to reduce the relative error of products. Proportional and integral (PI) settings of pressure control loops are set as  $K_C = 12$  and  $\tau_1 = 20$  min, all liquid level PI controllers are applied with  $K_C = 2$  and  $\tau_1 = 9999$  min.

### 3. Results and discussion

#### 3.1 Determination of the suitable entrainer

As commented in Section 2.1, four promising solvents DMSO, EG, DEG and TEG are selected as candidate entrainers. To determine the best entrainer, the effects of different solvents on vapor–liquid equilibrium (VLE) of IPA/IPAC, IPA/water, and IPAC/water systems are supposed to be studied. Fig.4 shows the pseudo-binary  $x$ - $y$  diagram of IPA/IPAC/water mixtures under the same ratio of solvent to feed flow. DMSO can significantly enhance the relative volatilities of IPA/water, IPA/IPAC, and IPAC/water. Moreover, to have a direct numerical comparison for the selectivity of different entrainers, the ratio of infinite dilution activity coefficient (*i.e.*,  $S_{ij}^\infty$ ) at atmospheric pressure in the IPA/IPAC/water system is demonstrated in Fig.5.

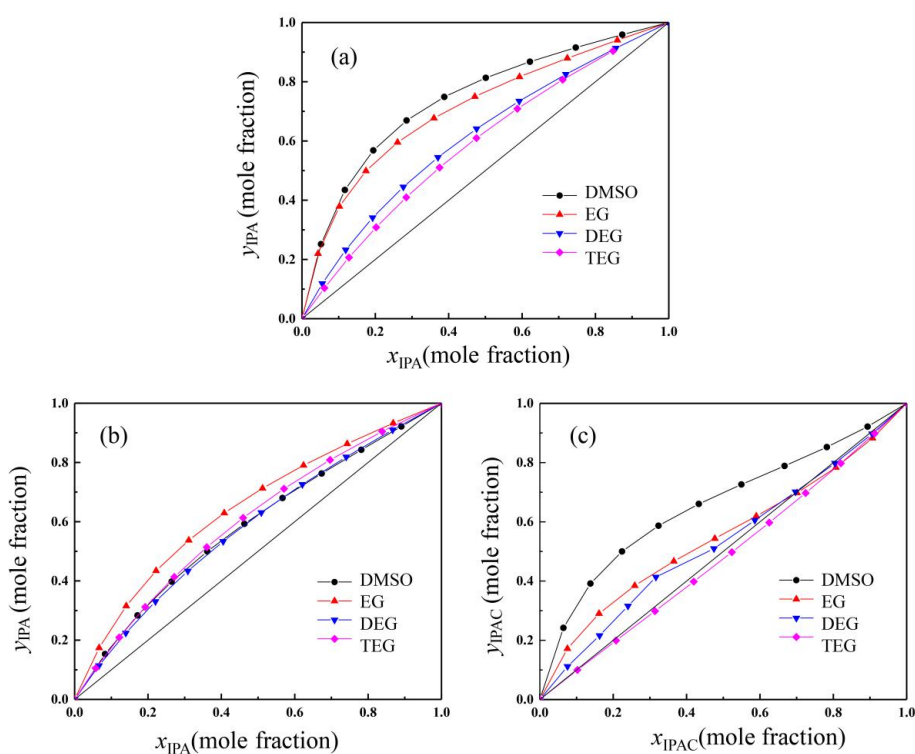
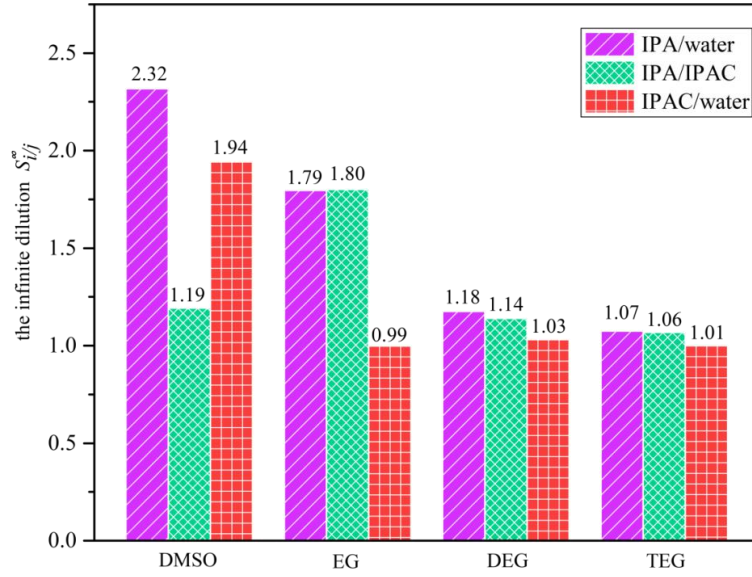


Fig.4. VLE curves with the addition of different entrainers for (a) IPA-water, (b) IPA-IPAC and (c) IPAC-water system



**Fig.5.** The infinite dilution  $S_{ij}^{\infty}$  for IPA/IPAC/water system

DMSO solvent exhibits much higher  $S_{ij}^{\infty}$  values compared with those of EG, DEG and TEG. Comparably, EG is not suitable for the IPAC/water system because it seems no able to break the azeotrope of IPAC/water. In summary, the entrainer DMSO is best for the separation of IPA/IPAC, IPAC/water and IPA/water simultaneously.

### 3.2 Conceptual process design

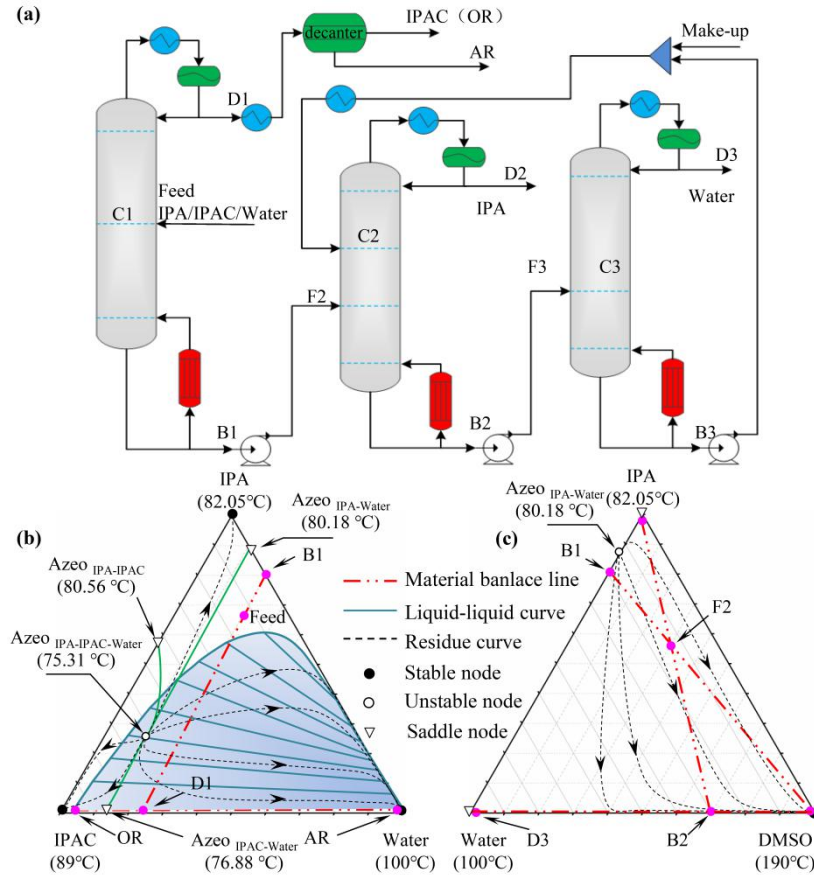
For the quaternary component system consisting of IPA/IPAC/water and an additional entrainer, the non-random two liquid (NRTL) model is used to describe the vapor–liquid–liquid phase equilibrium behaviors. The NRTL binary interaction parameters of IPA/IPAC/DMSO are provided in **Table.1**.

**Table.1** The parameters of NRTL model for IPA/ IPAC/water system

Component i	IPA	IPAC	IPA	IPA	IPAC	water
Component j	IPAC	water	water	DMSO	DMSO	DMSO
Property units	°C	°C	°C	°C	°C	°C
Sources	USER <sup>[6]</sup>	APV-LLE	APV-VLE	USER <sup>[6]</sup>	USER <sup>[6]</sup>	APV-VLE
$a_{ij}$	-6.3761	-3.0010	-1.3115	3.3041	-1.0165	-1.2449
$a_{ji}$	4.3534	10.3564	6.8284	-5.422	-0.7025	1.7524
$b_{ij}$	2374.47	1166.25	426.398	-1680.18	587.7175	586.801
$b_{ji}$	-1447.04	-1715.39	-1483.46	2473.13	541.8242	-1130.2155

The topologic and thermodynamic features of IPA/IPAC/water system at 1 atm are presented in the **Table.S2**. The normal boiling points of four components IPA, IPAC, water and DMSO are 82, 89, 100 and 190 °C, respectively. Besides, there is a

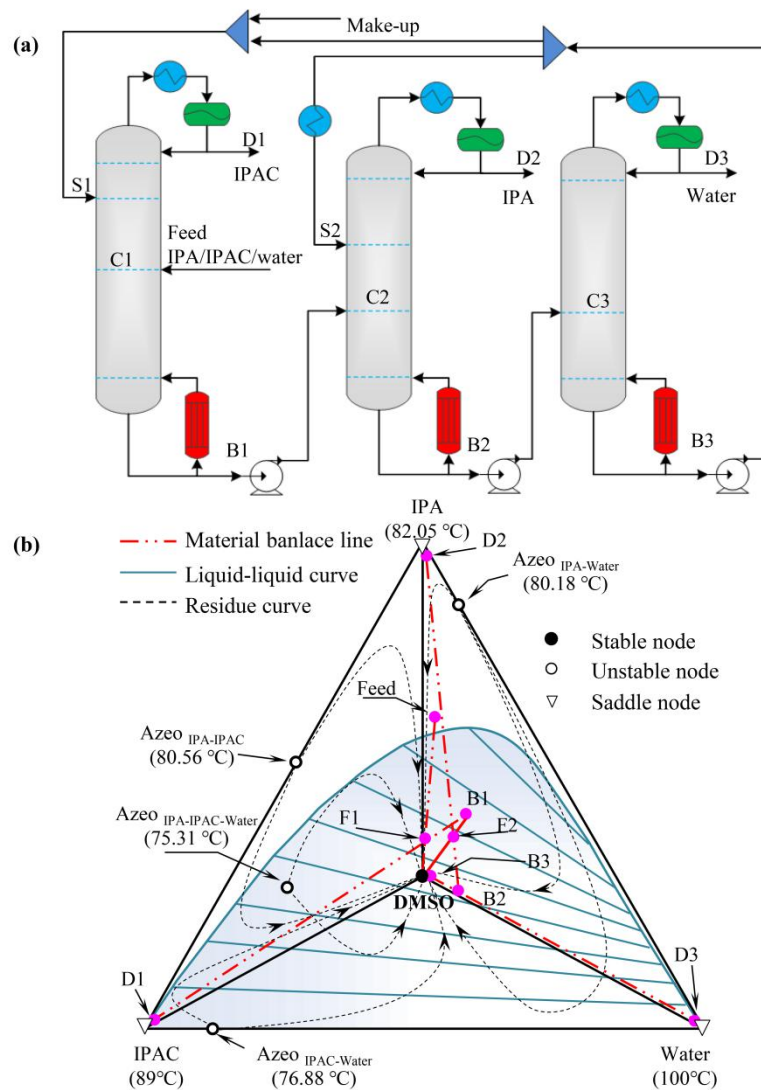
IPA/water azeotrope ( $x_{\text{azeo,IPA}} = 67.28 \text{ mol } \%$ ), a IPA/IPAC azeotrope ( $x_{\text{azeo,IPA}} = 67.75 \text{ mol } \%$ ), a IPAC/water azeotrope ( $x_{\text{azeo,IPAC}} = 58.96 \text{ mol } \%$ ) and a ternary heterogeneous IPA/IPAC/water azeotrope ( $x_{\text{azeo,IPA}} = 22.67 \text{ mol } \%$ ,  $x_{\text{azeo,IPAC}} = 40.08 \text{ mol } \%$ ).



**Fig.7. (a) Conceptual design flowsheet for DEDP process; (b) residue curve maps of IPA/IPAC/water system; (c) residue curve maps of IPA/water/DMSO system**

The conceptual design for the separation of the mixture IPA/IPAC/water by DEDP process with DMSO as the entrainer is presented in **Fig.7 (a)**, which consists of one decanter and three columns. **Fig.7 (b)-(c)** demonstrate the RCMs and material balance lines (represented by red lines) for the ternary system IPA/IPAC/water and IPA/water/DMSO, respectively. The total fresh feed donated as *Feed* point is fed into the column C-1 and separated into distillate mixture denoted as *D1* and bottom stream *B1* along the material balance line according to “lever rule”. Based on the component balance line of the liquid-liquid equilibrium, stream *D1* is fed to the decanter to obtain IPAC with 99.85 wt% at organic phase stream *OR*. While IPA and

water mixture (*B1* point) needs to be further separated by adding entrainer DMSO and **Fig.7 (c)** gives the demonstration of the material balance lines.



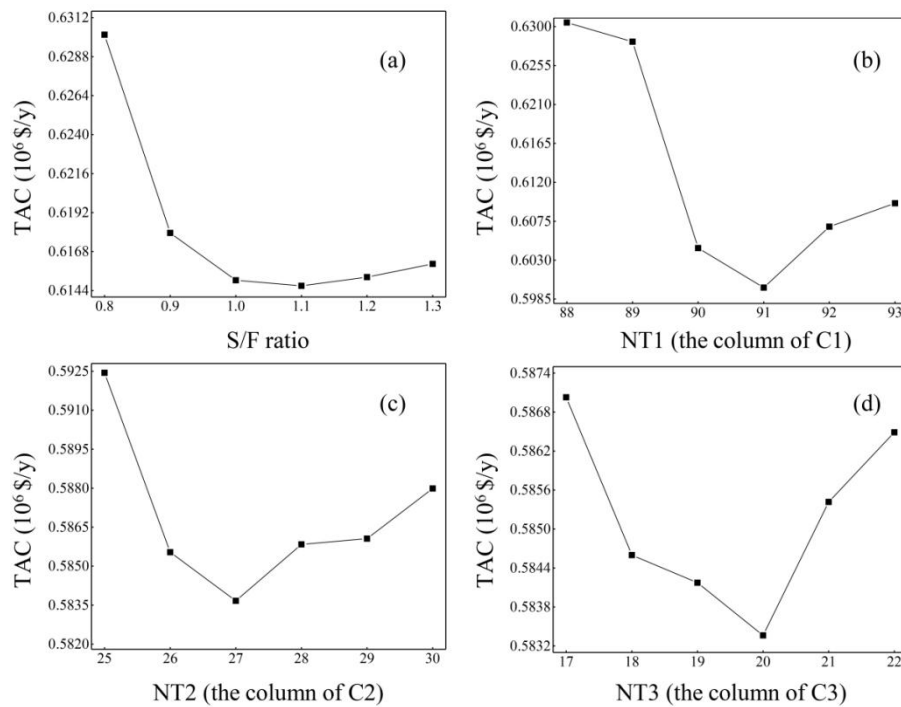
**Fig.8. (a)** Conceptual design flowsheet for triple-column extractive distillation (TED) process. **(b)** Material balance lines for separating azeotropic system IPA/IPAC/water using TED.

Similarly, the conceptual design flowsheet for TED process consist of double ED columns and a recovery column are described in **Fig.8 (a)**. A three-dimensional simplified demonstration map in **Fig.8 (b)** gives the material balance lines of the TED process which actually have four components of IPA/IPAC/water/DMSO. The fresh feed denoted as *Feed* component point is mixed with the entrainer DMSO as an input operation node (*i.e.*, *F1*) for the ED column C-1. As a consequence, the input stream is separated into an overhead product stream *D1* with 98.5 wt% IPAC and a

downstream *B1* composition point based on the material balance lines. After that, the non-product stream *B1* (IPA, water and DMSO) is introduced to the distillation column C-2 to obtain IPA with 99.5 wt% at overhead *D2* stream and bottom mixture component *B2* (DMSO and water). The mixture *B2* is then sent to the recovery column C-3, the high purity of DMSO is obtained at the bottom and recycled to the columns C-1 and C-2.

### 3.3 Optimal design of the two proposed process

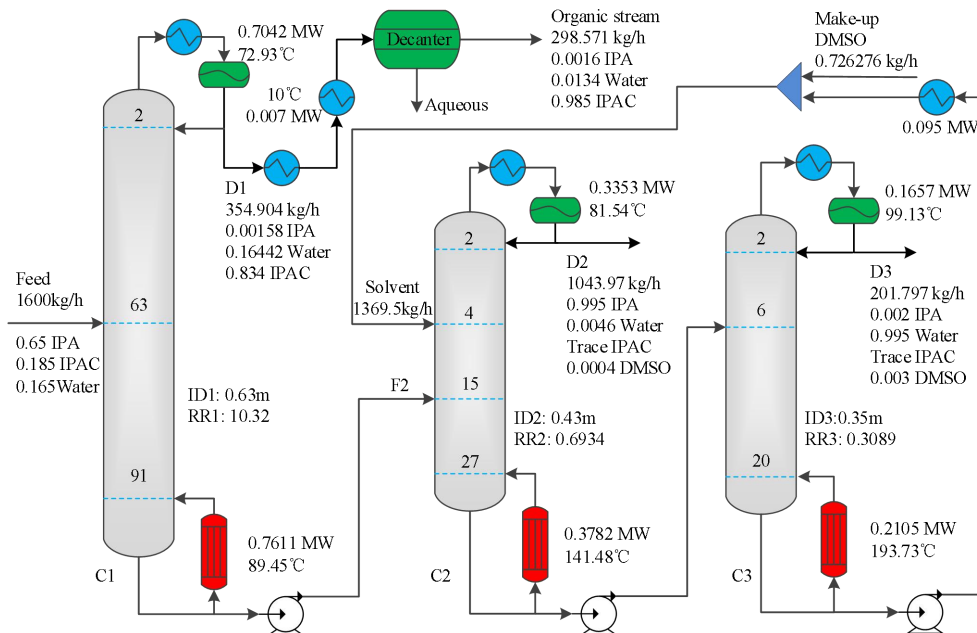
#### 3.3.1 Double-column ED with a Pre-concentrator (DEDP) process



**Fig.9.** The effect of S/F ratio (a), NT1 (b), NT2 (c) and NT3 (d) on TAC

Optimization results of the proposed DEDP process are obtained via the sequential iterative optimization procedure in **Section 2.4**. Eventually, the effect of the recycled solvent and three numbers of column stages on TAC is demonstrated in **Fig.9**. The optimal total numbers of stage for the three columns are 91, 27 and 20, respectively. Besides, the proposed optimal DEDP process for the separation of ternary azeotropic system IPA/IPAC/water is presented in **Fig.10**. The fresh feed is introduced to 63th stages of the pre-concentrator column C-1. And the overhead mixture with 83.4 wt% IPAC in pre-concentrator C-1 is then cooled to 10 °C and high-purity IPAC can be obtained. Moreover, the demonstration of selecting the

special temperature 10 °C is shown on **Fig.S1**. Then, the bottom stream from C-1 and recycled entrainer are respectively fed to 15th and 4th stages of the C-2 to obtain the overhead IPA of 99.5 wt%. Most of water with 99.5 wt% is distilled from the recovery column C-3. It is noteworthy that the temperature of the stream solvent is set at 70 °C in order to remain a relatively large difference of heat transfer temperature with the corresponding feed stage. More important reason to make the assumption is that the suggestion by **Knight and Doherty [58]** indicating the temperature of recycled entrainer should be 5-15 °C less than the boiling temperature of the distillate stream leaving the extractive column.

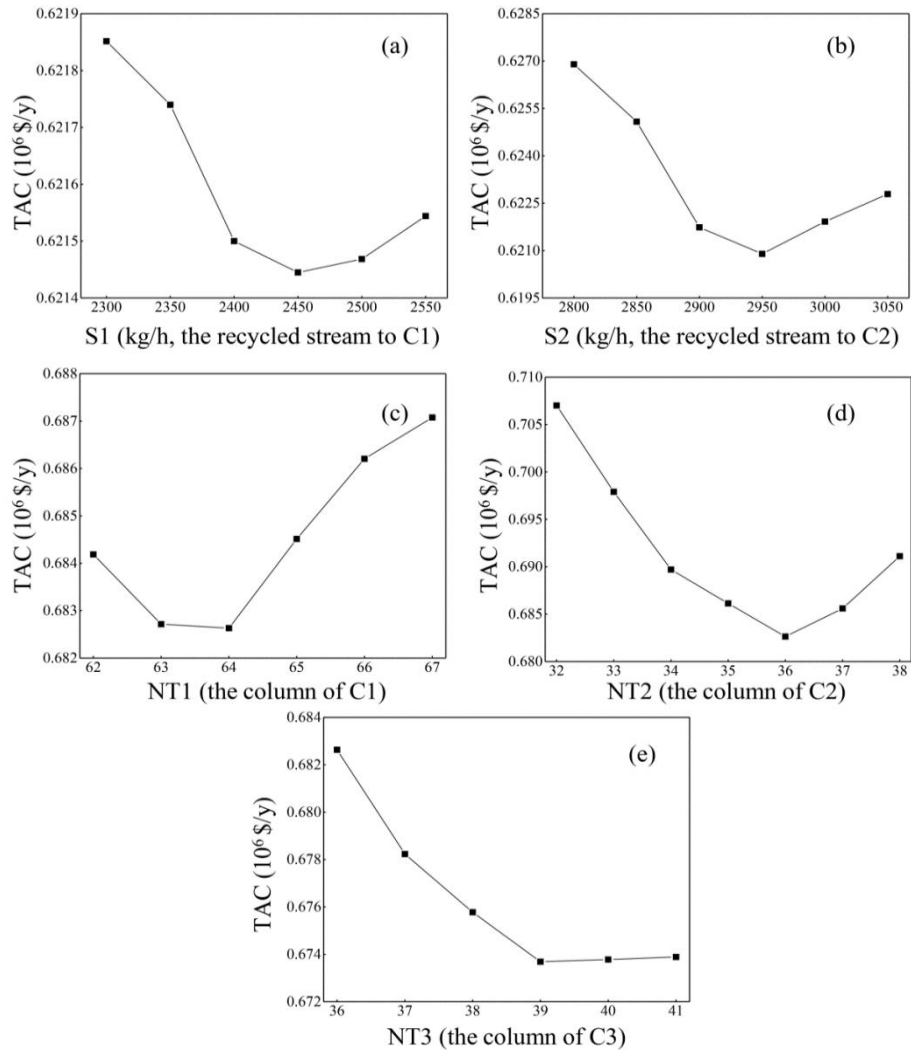


**Fig.10.** Proposed flowsheet of DEDP process with detailed optimal parameters

### 3.3.2 Triple-column extractive distillation (TED) process

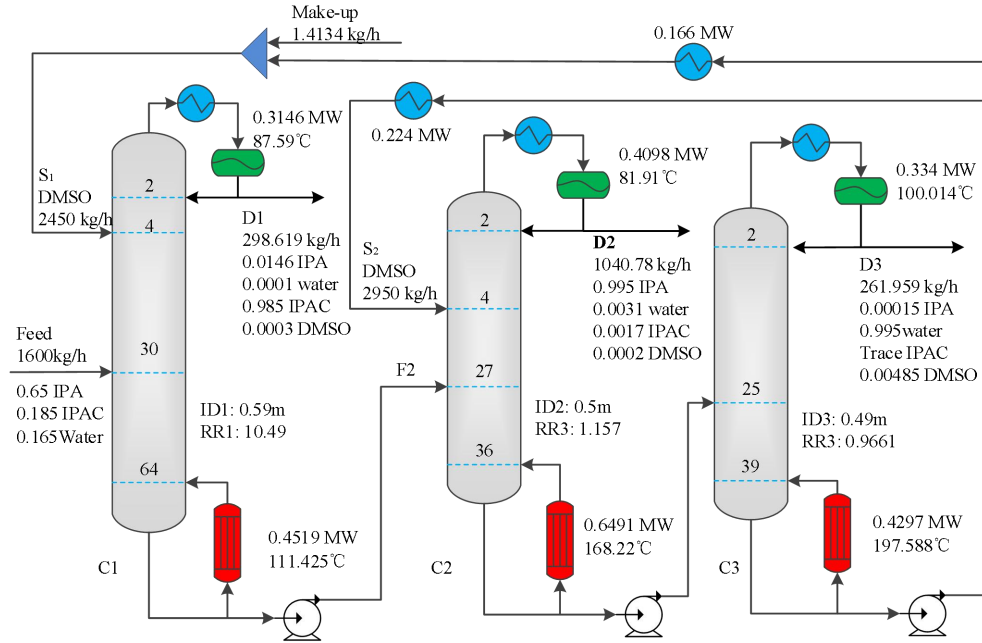
The existence of the two ED columns further increases the degree of freedom and brings more parameters need to be optimized. Therefore, two recycled solvents flowrate (*i.e.*,  $S1$  and  $S2$ ) need to be taken into consideration. The variables are optimized with the sequential iterative optimization procedure, which has been illustrated in **Fig.2** from **Section 2.4**. Furthermore, **Fig.11** summarizes the effect of design variables such as recycled entrainer flowrate and three numbers of column stages on TAC. The solvent flowrate recycled into two columns are 2450 kg/h and 2950 kg/h, respectively. Optimal flowsheet for TED process is described in **Fig.12**.

The fresh feed (*F1*) and entrainer (*S1*) stream are respectively fed to 30th and 4th stages in the ED column. The IPAC production with high purity 98.5 wt% is obtained at the top of the C-1. The bottom stream *F2* and entrainer *S2* are then introduced to 27th and 4th stages of the C-2 and IPA of 99.5 wt% is distilled. Finally, the bottom flowrate from C-2 is then fed to 25th stage in the recovery column C-3 to distillate the 99.5 wt% water and recover 99.99 wt% DMSO.



**Fig.11.** The effect of S1 (a), S2 (b), NT1 (c), NT2 (d) and NT3 (e) on TAC





**Fig.12.** Proposed flowsheet of TED process with detailed optimal parameters

### 3.3.3 Comparison of economic evaluation

**Table 1** Economic evaluation comparison between two processes

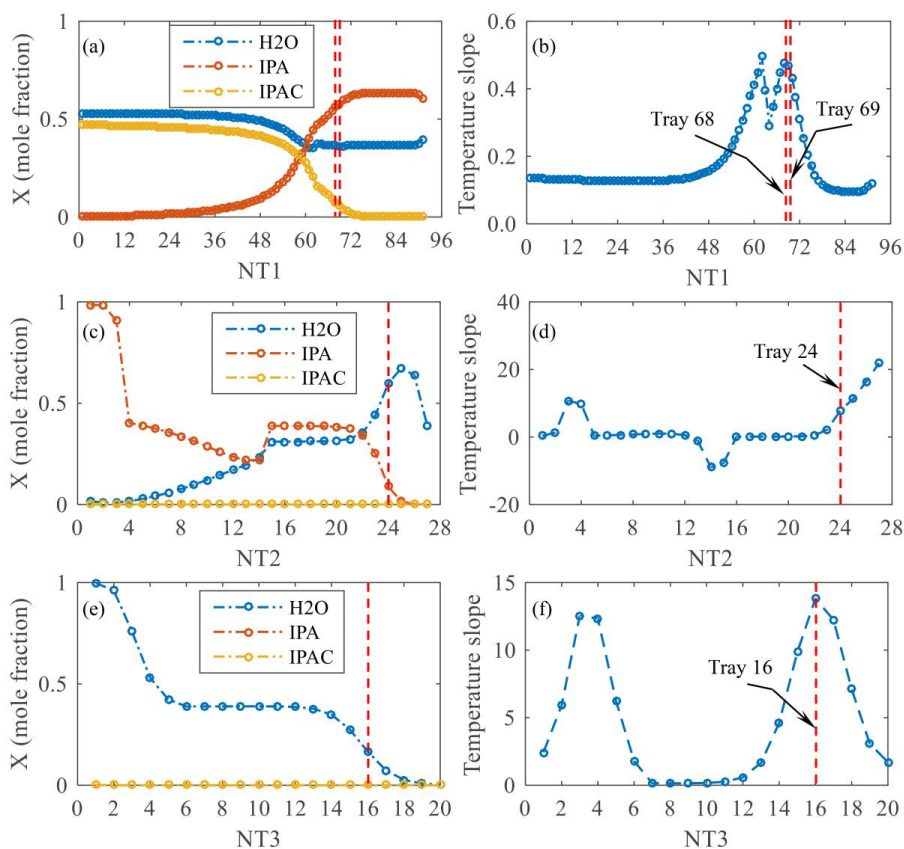
Scheme	Column	NT	NF	NS	RR	S(kg/h)	TAC(10 <sup>6</sup> \$/y)	TAC(10 <sup>6</sup> \$/y)
DEDP	C-1	91	63	-	10.32	-	0.338583	
	C-2	27	15	4	0.69	1369.5	0.148398	0.583363
	C-3	20	6	-	0.31	-	0.096381	
TED	C-1	64	30	4	10.51	2450.0	0.212504	
	C-2	36	27	4	1.20	2950.0	0.233789	0.620668
	C-3	39	25	-	1.50	-	0.174375	

In this section, optimal DEDP and TED processes are economically evaluated. **Table 1** compared the optimal TAC of two processes and show that the cost of DEDP separation process is mainly rested on the C-1 tower. It can be analyzed that the separation in column C-1 is difficult without the additional entrainer and this is why the number of trays and reflux ratio of DEDP process is larger than those of C-1 column in TED process. However, additional much more solvents applied in TED also increase the total capital cost and energy consumption. Above all, the DEDP process has reduced TAC by 6.43% compared with that of TED process.

## 4. Control strategy

### 4.1 Determination of tray temperature control points

The control strategy of DEDP process is investigated due to its economical superiority. **Fig.13** illustrates the composition profiles and temperature slope analysis in the three columns. It can be clearly seen from **Fig.13 (b)** that trays 68 and 69 of column C-1 are selected for the temperature control because maximum temperature variations occur in these two stages. The reason why stage 63 cannot be selected is that stage 63 is exactly the feed location, whose temperature is easily be disturbed. Then, the temperature at stage 24 is controlled by manipulating the corresponding reboiler heat input. Besides, compositions of IPA and water at stage 24 exhibit sharp changes as shown in **Fig.13(c)**. Similarly, it can be obviously observed from **Fig.13 (f)** that the temperature of stage 16 is controlled by manipulating the reboiler duty in the recovery column of DEDP.



**Fig.13** The composition profiles and temperature slopes of three columns for the DEDP process

## 4.2 Basis control structure with fixed reflux ratio (CS1)

Before converting the steady-state simulation to the dynamic one, it is indispensable to calculate the sizes of distillation columns. In this study, the “heuristic algorithm” [47] is used to determine the volumes of reflux drums and reboiler sumps to provide 10 min of holdup. Besides, the surge volume of a decanter is a 10 min holdup when half full. And the pressure drop in valves is set at 3 bar so that flowrates can be changed over a range of values and valve saturation does not occur. Two types of disturbances are used to test the proposed control structure performance, namely 10% changes in fresh feed flowrate and feed composition of IPAC. The magnitude of the disturbances in the feed is similar to the reported literature value [35].

The basic control structure (CS1) with fixed reflux ratios for the DEDP process is shown on **Fig.14**. And there are some basic inventory control structures applied to ensure safety.

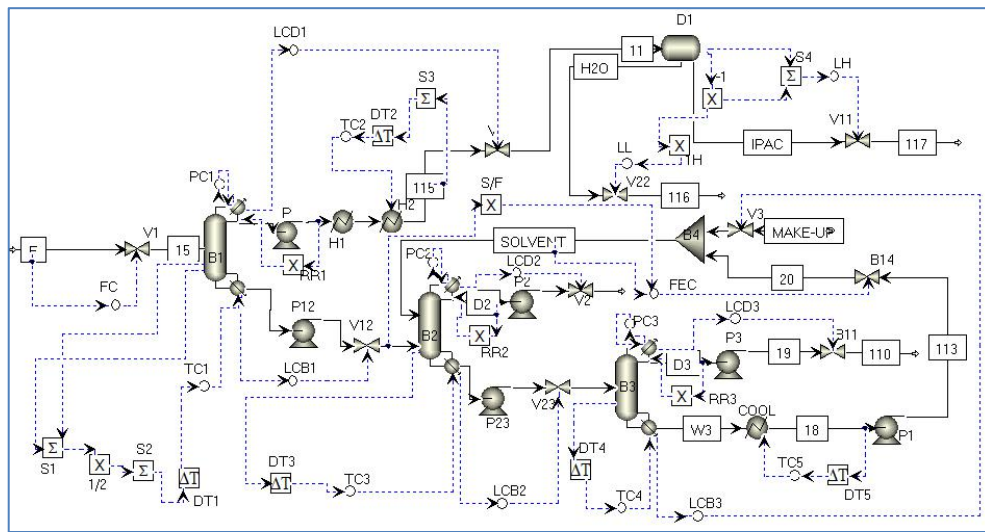
- (1) The fresh feed flow is controlled by throughput valve (reverse acting).
- (2) The recycled solvent flow rate is in proportion to the total feed flow rate from the bottom of pre-concentrator C-1.
- (3) The operating pressures in three columns are controlled by manipulating the condenser duties of three columns (reverse acting).
- (4) The distillate flow rates are manipulated to control the reflux tank levels in three columns (direct acting).
- (5) The bottom rate of pre-concentrator and extractive distillation column are manipulated to hold the sump level of two columns (direct acting).
- (6) The makeup DMSO flow rate is manipulated to hold the sump level of the recovery column C3 (reverse acting).
- (7) The cooler heat duty is manipulated to control the temperature of recycling solvent (reverse acting).
- (8) The heat removal in the heat exchanger is manipulated to control the stream temperature fed into decanter (reverse acting).
- (9) The organic flow rate of decanter is manipulated to control the difference of

upper lever to lower lever (direct acting).

(10) The aqueous flow rate of decanter is manipulated to control the lower lever (direct acting).

With disturbances occurring, reflux flow rate of three columns will be adapted to hold the reflux ratio at a constant value. It is noted that an average temperature control structure is applied to manipulate the reboiler duty of C-1. For the fixed solvent-to-feed ratio (S/F) controller, the first input signal is the mass flow rate of the fresh feed ( $FW$ ) from the bottom of pre-concentrator C-1, the output signal is the mass flow rate of the solvent ( $SW$ ), and the setpoint of solvent-to-feed ratio can be calculated by eq.(9). It is worth mention that heat duty is in  $GJ \cdot h^{-1}$  and temperature is in centigrade following the Aspen Dynamics notation.

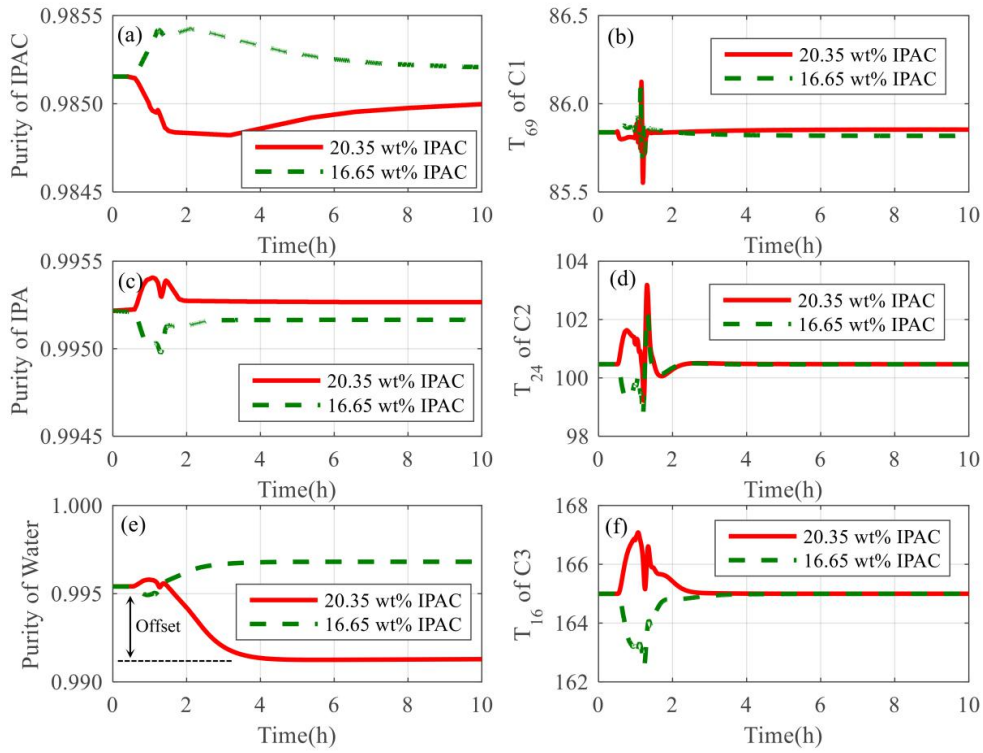
$$\frac{S}{F} = \frac{SW}{FW} = \frac{1370.23 \text{ kg / h}}{1245.1 \text{ kg / h}} = 1.1005 \quad (9)$$



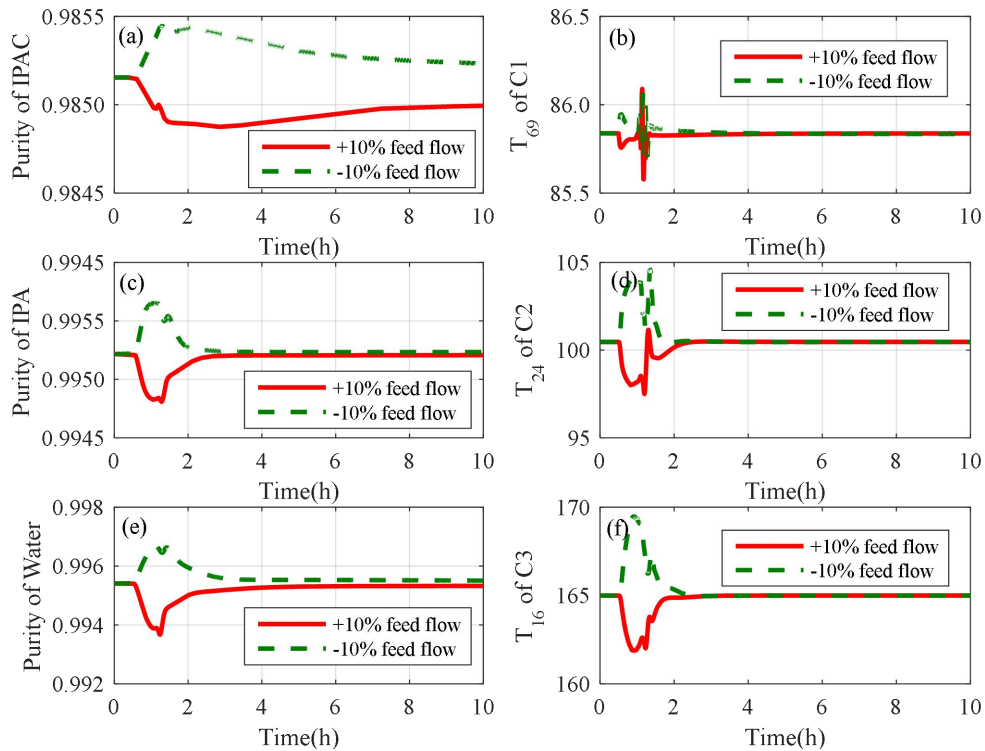
**Fig.14.** Basic control structure (CS1) for DEDP process

The dynamic responses under the feed composition and flow rate disturbances introduced at 0.5 h are illustrated in **Fig.15** and **Fig.16**, respectively. With the disturbances of IPAC feed composition, product purities of IPA and water are held quite close to their specifications. However, an increase in the IPAC feed composition from 18 to 20.35 wt% results in a large drop in the purity of the water product produced as distillate in the recovery column C-3 (bottom left graph in **Fig.15** (e)). With the changes in the fresh feed flowrate (see **Fig.16**), it can be concluded that the

purities of three products are almost controlled back to the setpoint within 4 hours.



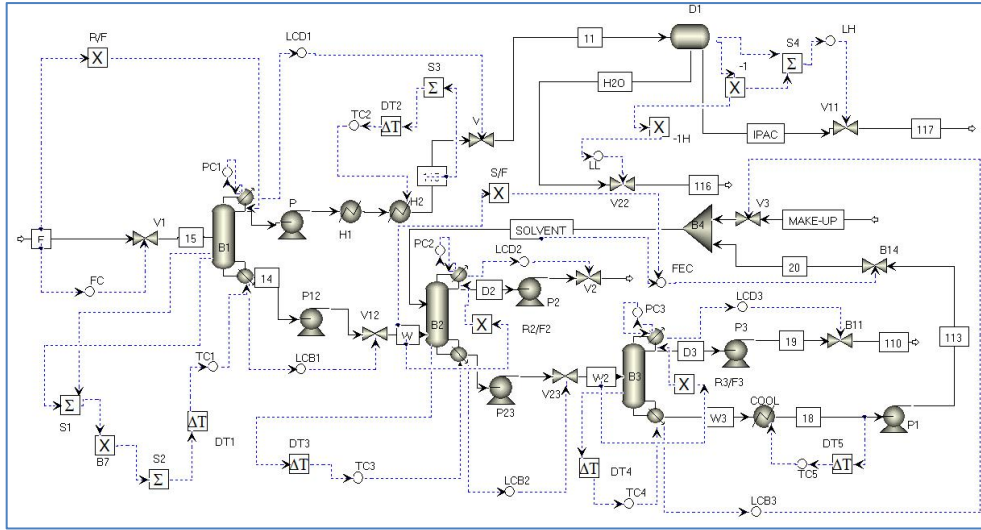
**Fig.15.** Dynamic responses to feed disturbances for the control system:  $\pm 10\%$  in IPAC feed composition



**Fig.16.** Dynamic responses to feed disturbances for the control system:  $\pm 10\%$  in fresh feed flow

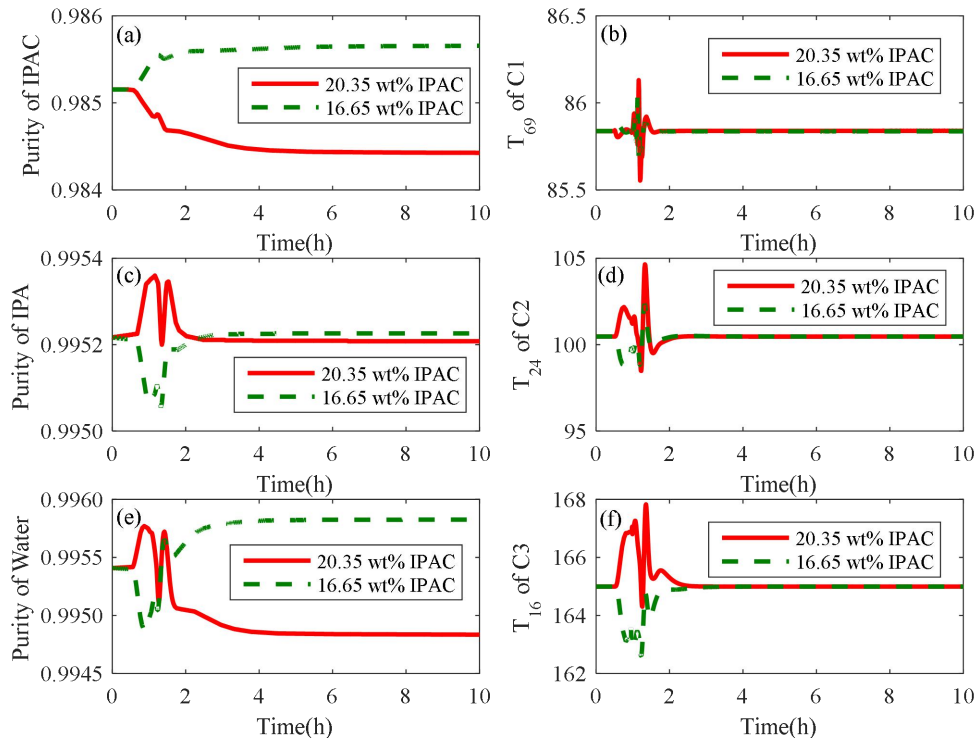
feed flow rate

### 4.3 Improved control structure with fixed reflux-to-feed ratio (CS2)

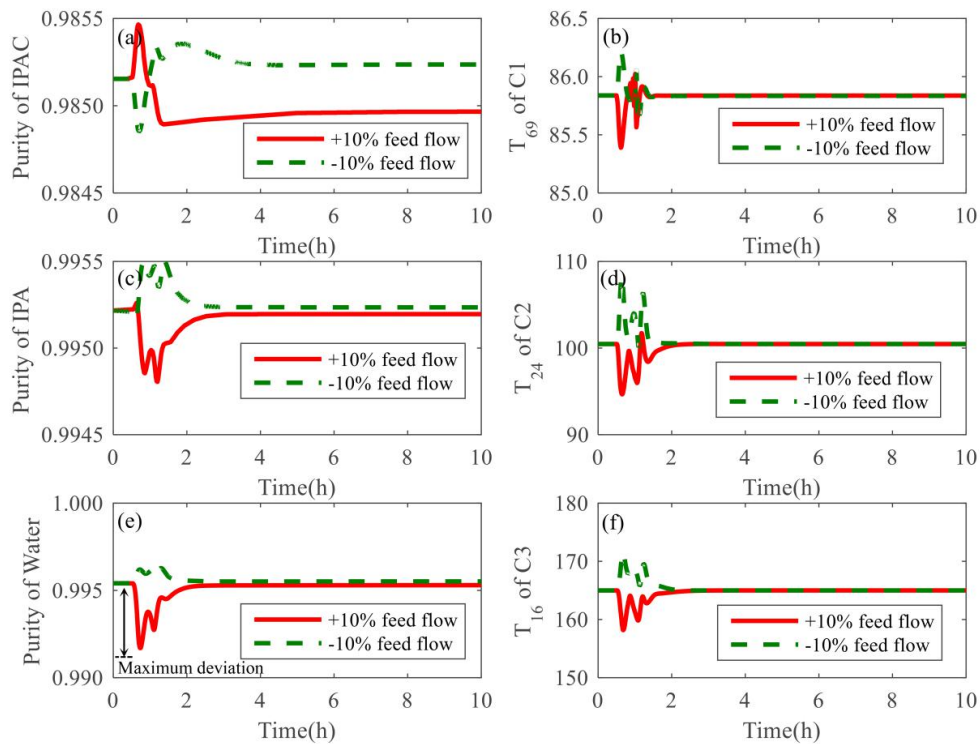


**Fig.17.** Control structure of CS2 for DEDP process

In order to reduce the large offset in the CS1, the control structure CS2 with fixed reflux-to-feed ratio ( $R/F$ ) is further investigated (see **Fig.17**). “Multiplier” blocks are used to fix the ratio of feed flowrate to reflux flowrate, and this control loop can manipulate the reflux flowrate value to handle the disturbances timely in fresh flow rate. The dynamic performances with  $\pm 10\%$  disturbances in IPAC composition are shown in **Fig.18**. The purities of three products are all returned back to new steady values which are very close to the initial setpoints. At the new steady-state, the purities of IPAC, IPA and water are 98.4426, 99.5208 and 99.4835 wt%, respectively, corresponding to the 10% IPAC composition increase in fresh feed. However, when the disturbance of decreased 10% IPAC composition happened at 0.5h, the purities of IPAC, IPA and water become 98.5656, 99.5256, and 99.5826 wt% in new steady state, respectively. **Fig.19** gives the dynamic performances with  $\pm 10\%$  disturbances in fresh feed flow rate. Although the large offsets in the product purities has been improved of CS2. It can be obviously seen from **Fig.19 (e)** that the existing large transient variation problems for the purity of water. Therefore, a more robust control strategy CS3 with heat duty of reboiler to feed ratio ( $Q_R/F$ ) is investigated in the following section.

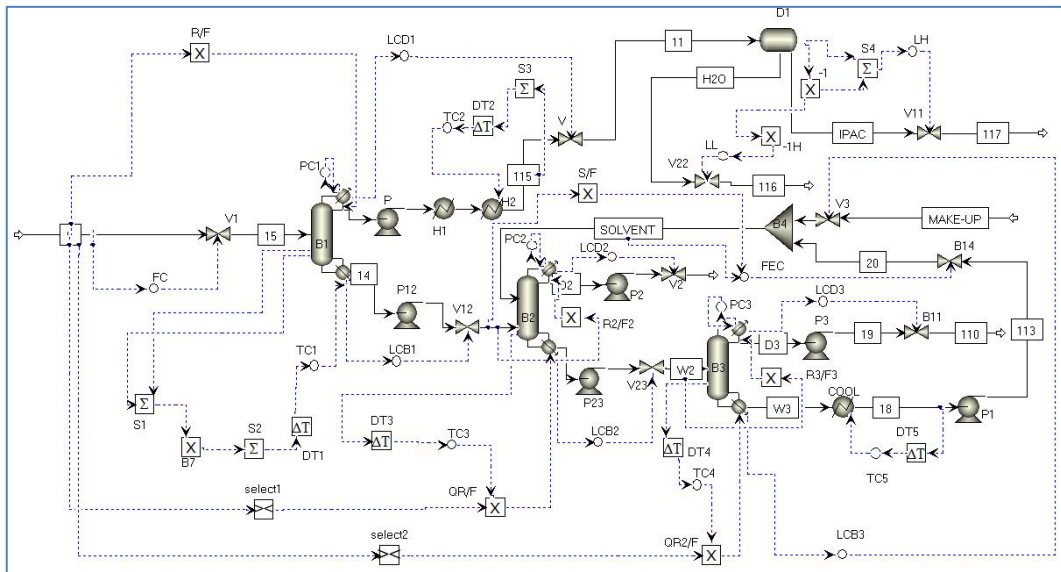


**Fig. 18** Dynamic responses to feed disturbances for the control system:  $\pm 10\%$  in IPAC feed composition



**Fig.19.** Dynamic responses to feed disturbances for the control system:  $\pm 10\%$  in fresh feed flow rate

#### 4.4 Improved control structure with optional reboiler duty-to-feed ratio (CS3)

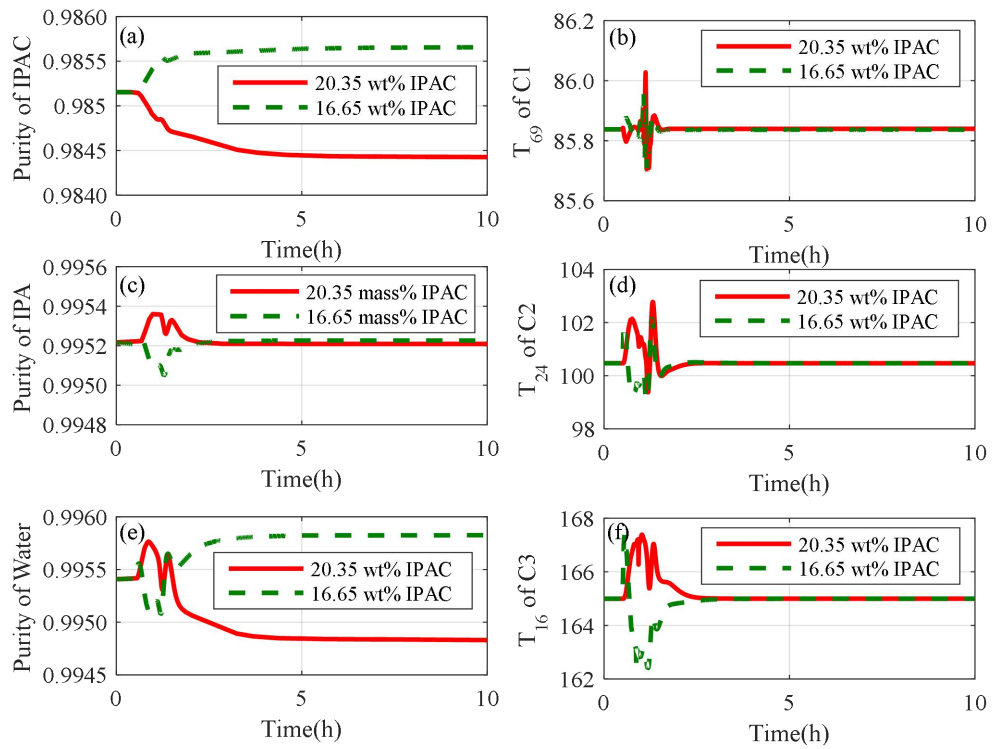


**Fig.20.** Control structure of CS3 for DEDP process

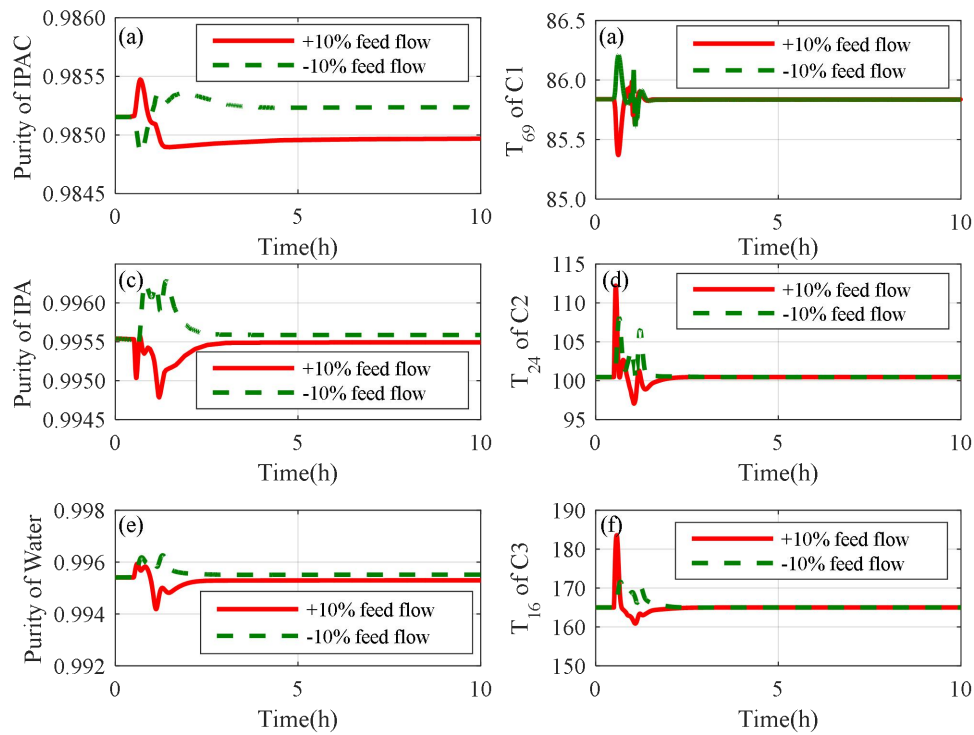
A more promising control strategy CS3 introducing two “HiLoSelect” blocks with optional reboiler duty to feed ratio ( $Q_R/F$ ) is proposed as shown in **Fig.20**. It is noticed that the control strategy with fixed  $Q_R/F$  can only handle the disturbance with positive increased flowrate but not the decreased changes effectively. Therefore, “HiLoSelect” module is applied to overcome the problem. The control loops can make a decision on whether the disturbance should be handled by  $Q_R/F$  ratio strategy. For instance, if there is a disturbance with +10% fresh feed flowrate, instantaneously, reboiler duty of distillation column will also be adjusted to maintain the  $Q_R/F$ . When the disturbance with -10% fresh feed flowrate happened, the reboiler duty of column will not be adjusted instead. The effectiveness of this control structure with  $\pm 10\%$  IPAC changes of feed composition and fresh feed flow rate disturbances are demonstrated in **Fig.21** and **22**, respectively. The new purities of three products under both disturbances are almost controlled back to initial value for IPA, and the offsets for IPAC and water are acceptable. It can be clearly observed that the control strategy CS3 exhibits small offsets and transient deviations of the purities for IPA and water compared with CS1 and CS2. In summary, the improved control strategy CS3 with optional  $Q_R/F$  can effectively handle the feed flow rates and compositions



disturbances at acceptable values than control structures CS1 and CS2.



**Fig.21.** Dynamic responses to feed disturbances for the control system:  $\pm 10\%$  in IPAC feed composition



**Fig.22.** Dynamic responses to feed disturbances for the control system:  $\pm 10\%$  in fresh feed flow rate

## 5. Conclusion

In this study, a systematic approach for optimal design and robust control of IPA/IPAC/water system separation is proposed. Two schemes of double-column extractive distillation with pre-concentrator (DEDP) and triple-column extractive distillation (TED) process for the separation are investigated. First, the thermodynamic conceptual design based on RCMs and univolatility curves indicates the operation feasibility and helps to propose two separation schemes. Then, two processes are optimized to obtain their optimal key design parameters and the results show that DEDP process can reduce TAC by 6.43% compared with TED. Finally, three control structures of DEDP process are explored according to the peak transient deviations and offset when faced with  $\pm 10\%$  fresh feed flowrate and composition disturbances, in which CS3 with  $Q_R/F$  control structure is able to provide a better dynamic control for the proposed DEDP process.

Of note is that the proposed systematic approach can be further employed in separating other complex multi-azeotropes mixtures. Moreover, the selection idea implied in the improved control structure may provide a guideline for the process control of multi-variable control loops (extractive or reactive dividing wall columns).

## Acknowledgments

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## Supporting Information

The supporting information associated with this article can be found online.

## Nomenclature

IPA= isopropyl alcohol

IPAC= isopropyl acetate

ED= extractive distillation

DEDP= double-column extractive distillation with a pre-concentrator

TED= triple-column extractive distillation

TAC= the total annual cost

RCMs= residue curve maps

DMSO= dimethyl sulfoxide

EG= ethylene glycol

DEG= diethylene glycol

TEG= triethylene glycol

NF= feed locations

NS= recycled solvent feed location

NT= the number of stage

S= recycled solvent feed flow rate

D= distillate flow rate

RR= reflux ratio

$S_{ij}^{\infty}$  = the infinite dilution activity coefficient

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