To link to this article : DOI : 10.1016/j.cherd.2016.01.026
URL : http://dx.doi.org/10.1016/j.cherd.2016.01.026

To cite this version : You, Xinqiang and Rodriguez-Donis, Ivonne and Gerbaud, Vincent *Low pressure design for reducing energy cost of extractive distillation for separating Diisopropyl ether and Isopropyl alcohol.* (2016) Chemical Engineering Research and Design, vol. 109. pp. 540-552. ISSN 0263-8762

http://dx.doi.org/10.1016/j.cherd.2016.01.026

Low pressure design for reducing energy cost of extractive distillation for separating diisopropyl ether and isopropyl alcohol

Xinqiang You [a,b,c], *Ivonne Rodriguez-Donis* [b,c], *Vincent Gerbaud* [b,c,*]

[a] *Department of Chemistry and Laboratory for Advanced Material and Gemstone Testing Center of ECUST, East China University of Science and Technology, Shanghai 200237, China*
[b] *Université de Toulouse, INP, UPS, LGC (Laboratoire de Génie Chimique), 4 allée Emile Monso, F-31432 Toulouse Cedex 04, France*
[c] *CNRS, LGC (Laboratoire de Génie Chimique), F-31432 Toulouse Cedex 04, France*

ABSTRACT

We show how reducing pressure can improve the design of a 1.0-1a mixture homogeneous extractive distillation process and we use extractive efficiency indicators to compare the optimality of different designs. The case study concerns the separation of the diisopropyl ether (DIPE)–isopropyl alcohol (IPA) minimum boiling azeotrope with heavy entrainer 2-methoxyethanol. We first explain that the unexpected energy cost OF decrease following an increase of the distillate outputs is due to the interrelation of the two distillate flow rates and purities and the entrainer recycling through mass balance when considering both the extractive distillation column and the entrainer regeneration column. Then, we find that for the studied case a lower pressure reduces the usage of entrainer and increases the relative volatility of DIPE–IPA for the same entrainer content in the extractive column. A 0.4 atm operating pressure is selected to enable the use of cheap cooling water in the condenser. We run an optimization of the entrainer flow rate, both columns reflux ratios, distillates and feed locations by minimizing the total energy consumption per product unit. Double digit savings in energy consumption are achieved while TAC is reduced significantly. An extractive efficiency indicator that describes the ability of the extractive section to discriminate the desired product between the top and the bottom of the extractive section of the extractive section is calculated for comparing and explaining the benefit of lowering pressure on the basis of thermodynamic insight.

Keywords:
Extractive distillation
Energy saving
Low pressure distillation
Extractive efficiency indicator
Optimization

1. Introduction

Diisopropyl ether (DIPE) has become an important gasoline additive over the past decade and it is also widely used in many other fields, such as tobacco production and synthetic chemistry (Lladosa et al., 2008). Isopropyl alcohol (IPA) is extensively used in pharmaceutical industry as a chemical intermediate and solvent (Wang et al., 2008). IPA can be produced by using solid acid or liquid acid as catalytic agent, with DIPE as a coproduct (Logsdon and Loke, 2000). The separation of DIPE/IPA is the key downstream process that determines the entire process economic benefits. However, IPA and DIPE cannot be separated by conventional distillation process because they form a binary minimum boiling homogeneous azeotrope.

---

[*] Corresponding author at. Université de Toulouse, INP, UPS, LGC (Laboratoire de Génie Chimique), 4 allée Emile Monso, F-31432 Toulouse Cedex 04, France. Tel.: +33534323651.
E-mail address: Vincent.Gerbaud@ensiacet.fr (V. Gerbaud).

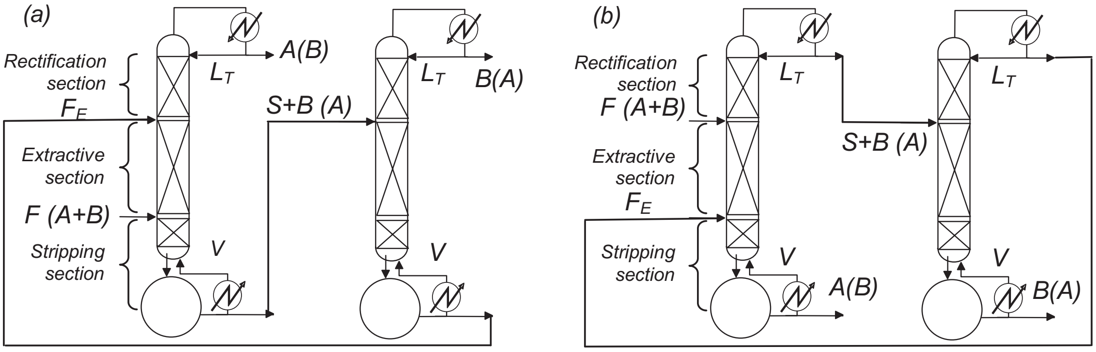

Fig. 1 – Flowsheet of typical extractive distillation with (a) heavy entrainer and (b) light entrainer.

Extractive distillation is the common method for the separation of azeotropic mixture in large scale productions (Doherty and Malone, 2001; Petlyuck, 2004; Luyben and Chien, 2010). The relative volatility of the original components is altered by adding an entrainer as it interacts differently with the light and heavy components. For the separation of a minimum- (resp. maximum-) boiling azeotropic mixture A–B by using a direct (resp. indirect) split configuration as shown in Fig. 1, the common but not exclusive thought is that one should add a heavy (resp. light) entrainer E that forms no new azeotrope. The corresponding ternary mixture A–B–E belongs to Serafimov's class 1.0-1a (Kiva et al., 2003), which accounts for 21.6% of all azeotropic ternary mixtures (Hilmen et al., 2002).

Thermodynamic insight of extractive distillation was studied by Laroche et al. (1991) through using the univolatility line and volatility order. They showed that once the volatility order diagram of the ternary mixture azeotrope is obtained, the feasible separation sequence flowsheet is determined. A general feasibility criterion was then derived for batch extractive distillation (Rodríguez-Donis et al., 2009a,b, 2012; Rodríguez-Donis et al., 2012a,b). Later, it was extended to continuous mode by Shen et al. who discussed the consequence on the process feasible ranges of reflux ratio and entrainer-to-feed flow rate ratio, and the interconnection of the composition profile in the three column section, rectifying, extractive and stripping (Shen et al., 2013; Shen and Gerbaud, 2013). Based on the thermodynamic insight analysis of residue curve map, univolatility line and univolatility order regions or alternatively of unidistribution curves and unidistribution order (Petlyuk et al., 2015), the feasibility of extractive distillation processes can be predicted by using the general feasibility criterion without any systematic calculations of composition profiles. In this paper, the thermodynamic insight of the process feasibility for the extractive distillation includes knowing which component will be withdrawn in the first distillate cut, what the adequate column configuration is, and whether there is some limiting operating parameter value or not (Rodríguez-Donis et al., 2009a). Subsequent calculation of composition profiles can then help refine the reflux ratio and entrainer feed flow rate range (Petlyuk et al., 2015).

According to Lladosa et al. (2007) the azeotrope of DIPE and IPA is very sensitive to pressure following the equilibrium diagrams of them based on experimental data. Therefore, the azeotrope can be separated by pressure swing distillation (Luyben, 2012; Luo et al., 2014). The author also reported that 2-methoxyethanol is an excellent solvent to break the azeotrope based on the vapor–liquid equilibrium experimental data. In 2014, Luo et al. (2014) compared the pressure-swing distillation and extractive distillation with 2-methoxyethanol for the separation of DIPE and IPA and performed a full heat integration of these processes. The results show that the fully heat-integrated pressure swing distillation system offers a 5.75% reduction in the total annual cost and 7.97% savings in energy consumption as compared to the extractive distillation process.

We showed in our previous work (You et al., 2015a,b) that a suitable decrease of the pressure in extractive distillation column for acetone–methanol minimum boiling azeotrope with water allowed for double digit savings in TAC and energy costs. However, in many cases, the cost of pulling vacuum to increase the relative volatility of a system overcomes what is saved by lowering the thermal duty thanks to lower boiling temperatures at lower pressures.

In most extractive distillation process design studies, a high product purity and recovery are sought (Luyben and Chien, 2010; Luo et al., 2014; You et al., 2015a,b) and a suitable distillate output flow rate is usually found by running a sensitivity analysis based on simulations in closed loop flow sheet where the entrainer leaving the regeneration column goes to the extractive column entrainer feed (You et al., 2015a,b). But several literature works have shown results where one cannot get the target high purity and recovery for A whatever the heat duty (Luo et al., 2014) or a high purity for both A and B products (Gil et al., 2009). Evidently with the entrainer recycling, distillate purities and flow rates are coupled through mass balances.

In this work, we derive in Section 2 for the first time so far, the relation of the two distillates in the extractive distillation process to rationally select adequate purities and distillate flow rates and to anticipate the maximum impurity content in the entrainer recycle stream. It allows us to later explain the non-intuitive behavior that the energy cost decreases following the increase of the distillate output flows. Then we investigate in Section 3 whether reducing the pressure is worth for the extractive distillation of the DIPE–IPA minimum boiling azeotrope with 2-methoxyethanol heavy entrainer system with the sake of reducing the energy cost and TAC for the separation process itself and whether it would be competitive with the best literature design proposed by Luo et al. (2014). Our methodology is shown in Fig. 2. It applies to all extractive distillation process for the often encountered separation of minimum boiling azeotropes AB with a heavy entrainer E where the univolatility curve $\alpha_{AB} = 1$ goes to the AE edge (1.0-1a-m1 extractive separation class separation). It relies upon using the thermodynamic insight analysis of residue curve, isovolatility line and ternary map to select pressure, and then running two step optimization procedure (You et al., 2015a,b)

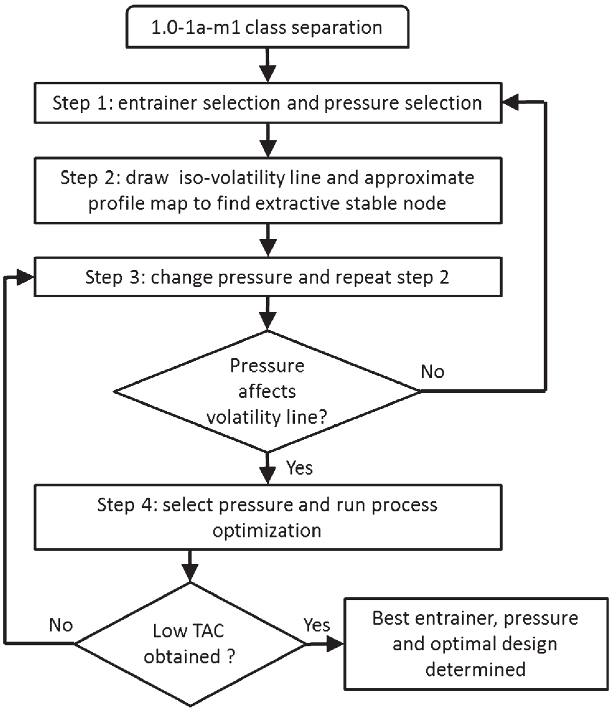

Fig. 2 – Block flow diagram of the proposed methodology for 1.0-1a-m1 extractive separation class.

to obtain the optimal design and evaluating its cost benefit. In Section 4, we compare the design results with the best literature designs and analyze them with the help of extractive efficiency indicators of extractive section E_{ext} and per stage in extractive section e_{ext} that we proposed recently (You et al., 2015a,b). Finally we investigate in Section 5 the sensitivity of the design over the extractive column pressure and over the total number of trays.

2. Steady state design

2.1. *Interrelation of distillates in the extractive distillation process*

Product purities and recovery are key specifications for at the design step for any separation process. For the extractive distillation of an azeotropic mixture AB, high purity A and high purity B columns distillates (resp. bottom liquids) are obtained for a direct (resp. indirect) split process configuration. We derive now the interrelation between them. For a binary azeotropic mixture AB separated in a direct split process configuration with flow rate F and content $x_{F,A}$, $x_{F,B}$, the product purities and process recovery are $x_{D1,A}$, $x_{D2,B}$ and ψ_A, ψ_B, and obey the relations

Table 1 – Relationship between distillates, purity and recovery for binary mixture for 100 kmol/h binary mixture.

Feed composition	Purity specification	
$x_{F,A}$	0.75 $x_{D1,A}$	0.98
$x_{F,B}$	0.25 $x_{D2,B}$	0.98
Range of distillate (Eqs. (1) and (2))		
D_1 (kmol/h) (Eq. (1))	75.00 ($\psi_A = 98\%$)	76.53 ($\psi_A = 100\%$)
D_2 (kmol/h) (Eq. (2))	25.00 ($\psi_B = 98\%$)	25.51($\psi_B = 100\%$)
Range of distillate (Eqs. (3) and (4))		
D_1 (kmol/h) (Eq. (4))	>76.53 ($\psi_B = 93.877\%$)	>75.00 ($\psi_B = 94\%$)
D_2 (kmol/h) (Eq. (3))	>25.51 ($\psi_A = 99.3197\%$)	>25.00 ($\psi_A = 99.333\%$)

$$\psi_A = \frac{D_1 x_{D1,A}}{F x_{F,A}} \rightarrow D_1 = \frac{F x_{F,A} \psi_A}{x_{D1,A}} \tag{1}$$

$$\psi_B = \frac{D_2 x_{D2,B}}{F x_{F,B}} \rightarrow D_2 = \frac{F x_{F,B} \psi_B}{x_{D2,B}} \tag{2}$$

But, we can also write the mass balance for A (Eq. (3)) and B (Eq. (4)) and use Eqs. (1) and (2) to obtain the relation influence of one component recovery on the other distillate flow rate:

$$\begin{aligned} D_2 &= \frac{F x_{F,A} - D_1 x_{D1,A}}{1 - x_{D2,B} - x_{D2,E}} = \frac{F x_{F,A} - \left(\frac{F x_{F,A} \psi_A}{x_{D1,A}}\right) x_{D1,A}}{1 - x_{D2,B} - x_{D2,E}} \\ &= \frac{F x_{F,A}\,(1 - \psi_A)}{1 - x_{D2,B} - x_{D2,E}} > \frac{F x_{F,A}\,(1 - \psi_A)}{1 - x_{D2,B}} \end{aligned} \tag{3}$$

$$\begin{aligned} D_1 &= \frac{F x_{F,B} - D_2 x_{D2,B}}{1 - x_{D1,A} - x_{D1,E}} = \frac{F x_{F,B} - \left(\frac{F x_{F,B} \psi_B}{x_{D2,B}}\right) x_{D2,B}}{1 - x_{D1,A} - x_{D1,E}} \\ &= \frac{F x_{F,B}\,(1 - \psi_B)}{1 - x_{D1,A} - x_{D1,E}} > \frac{F x_{F,B}\,(1 - \psi_B)}{1 - x_{D1,A}} \end{aligned} \tag{4}$$

where $x_{D1,E}$ and $x_{D2,E}$ *are* the entrainer content in the two distillates.

From these equations we observe that the distillate flow rate D_2 (resp. D_1) is controlled by the recovery and product purity of B (resp. A) and by the recovery of A (resp. B). So an unreasonable choice of distillate flow rate may lead to poor product quality and/or to enhance the difficulty of the separation, requiring more energy and cost to achieve the same product recovery. Based on the equation above, we test the DIPE–IPA system at low purity and recovery. The results are shown in Table 1.

From Table 1, we know that (1) following Eqs. (1) and (2), the value range of A-rich distillate D_1 and B-rich distillate D_2 is easy to calculate from ψ_A and ψ_B respectively, but it is not strict enough. For example, component A's recovery ψ_A (see Eq. (3)) has to be within a very narrow value range around 99.32%. Otherwise D_2 cannot reach the reasonable range value. Likewise for ψ_B (see Eq. (4)). Therefore, for a binary mixture of AB with 100 kmol/h and $x_{F,A} = 0.75$, if the two products specifications are set at 98%, we should choose ψ_A between [99.3197%, 99.333%], which will ensure that ψ_B is within [98%, 100%].

These relations also indicate that the choice of distillate impacts the necessary entrainer feed flow rate and its impurity content. For example, if we assume $D_1 = 75$, then equation 1 gives $\psi_A = 0.98$ for a purity of $x_{D1,A} = 0.98$. Thus there will be 75 × (1 − 0.98) = 1.5 kmol/h of A entering the second regeneration column. As $D_2 = 25$ kmol/h, the purity of B will be not higher than $x_{D2,B} = (1 - 1.5/25) = 0.94$ if neglect the loss of A in the recycled entrainer stream W_2. On the other hand, if we want to achieve $x_{D2,B} = 0.98$, the maximum value of A that should reach in D_2 is 0.5 kmol/h (25 × (1 − 0.98)). Subtracted from the 1.5 kmol/h entering the regeneration column, 1 kmol/h A has to be recycled with the entrainer recycle stream W_2. That impurity in the entrainer recycle implies that the entrainer flow rate has to be over 1000(1/(1 − 0.999)) kmol/h in order to guarantee our specification of 0.999 mol% pure entrainer recycled to the extractive column. This corresponds to a very large entrainer-to-feed flow rate ratio ($F_E/F = 10$), leading to large energy cost. A more reasonable example is to increase D_1 to 76.1 kmol/h. Then with $x_{D1,A} = 0.98$ Eq. (1) gives $\psi_A = 0.99437$ and $76.1 \times (1 - 0.\ 0.99437) = 0.428$ kmol/h of A will enter the second column. Being below the maximum 0.5 kmol/h of A to enter the regeneration column, the purities of B and recycling entrainer can be met and the entrainer-to-feed flow rate ratio does not have to be very high, which could results in energy cost savings.

2.2. *Objective function and optimization approach*

Our objective function is defined as follows (You et al., 2014)

$$\min \mathrm{OF} = \frac{Q_{r1} + m \cdot Q_{c1} + Q_{r2} + m \cdot Q_{c2}}{k \cdot D_1 + D_2}$$

$$\begin{aligned} &\text{subject to}: x_{\mathrm{DIPE,D1}} \geq 0.995 \\ &x_{\mathrm{DIPE,W1}} \leq 0.001 \\ &x_{\mathrm{IPA,D2}} \geq 0.995 \\ &x_{\text{2-methoxyethanol,W2}} \geq 0.999 \end{aligned} \tag{5}$$

where Q_{r1}: extractive column reboiler duty, Q_{c1}: extractive column condenser duty, Q_{r2}: entrainer regeneration column reboiler duty, Q_{c2}: entrainer regeneration column condenser duty, D_1: distillate flow rate of the extractive column, D_2: distillate flow rate of the entrainer regeneration column. Factors k and m respectively describe the price differences between products DIPE and IPA and between the condenser cooling and reboiler heat duties: $k = 3.9$ (product price index), $m = 0.036$ (energy price index). The meaning of OF is the energy consumption used per product unit flow rate (kJ/kmol). The OF we used in this work accounts for not only both columns' energy demand, but also reflects the weight coefficient of the two product prices k and reboiler–condenser cost price m. Another advantage of OF is that it can reflects the effects of the variables in entrainer regeneration column on the total process, as evidenced latter.

This objective function is used with the two step optimization methodology presented in previous work (You et al., 2015a,b). First, in open loop flow sheet with no recycle of the entrainer and fresh entrainer feed to ease convergence, Aspen plus' sequential quadratic programming (SQP) method is used for the optimization of the process over an energy consumption objective function, under purity and recovery constraints and a given column structure, by manipulating the continuous variables: column refluxes R_1, R_2 and the entrainer flow rate F_E for the choice of two distillates through comparing OF with Luo's design as initial values for other variables. Secondly, a sensitivity analysis tool is performed to find optimal values of the feed tray locations N_{FE}, N_{FAB}, N_{FReg}, while SQP is run for each set of discrete variable values. The final optimization is found through minimizing OF value and it is validated by rerunning the simulation in close loop flow sheet where the entrainer is recycled from the regeneration column to the extractive column and an entrainer make-up feed is added. The close-loop simulation requires adjusting the reflux ratio if necessary in order to overcome the effect of impurity in recycling entrainer on the distillate purity. Finally, the TAC is calculated to compare the separation sequences, similarly to what was done in You et al. (2015) by considering a 3 years payback period is and by using Douglas' cost formulas with Marshall and Swift (M&S) inflation 2011 index equals to 1518.1 (You et al., 2015a,b). The energy cost of the reboiler is 3.8 $ per GJ, after consulting a chemical company in Chongqing China.

An alternative optimization approach less sensitive to convergence issues has been used by us in another paper (You et al., 2015a,b). Coupling an external stochastic genetic algorithm with the process simulator, it proved suitable to optimize directly the closed loop configuration with all discrete and continuous variables and doing so with a multi-objective criterion, provided that the initial population of process design sets of parameters had enough individuals without convergence problems.

3. Process analysis

3.1. *Pressure sensitivity of the azeotropic mixture*

With the purpose of changing the operating pressure to improve the extractive distillation sequence, we report in Table 2 the DIPE–IPA azeotropic composition change with pressure. We used the same VLE model as the one used to compute the residue curve map in Fig. 3.

Table 2 shows that the DIPE/IPA azeotrope is sensitive enough to pressure change. The mixture exhibits a Bancroft point (Elliott and Rainwater, 2000) near 5.8 atm with a boiling temperature close to 134.8 °C, where their volatility order is reversed. Considering the large pressure sensitivity of the azeotrope, the PSD process is likely feasible for the mixture. Since this was investigated by Luo et al. (2014) we do not consider this process here. However, Table 2 also shows that the content of DIPE in the azeotropic mixture increases when the pressure decreases. As seen in Fig. 3 for $P_1 = 1$ atm and $P_1 = 0.4$ atm this also prompts the univolatility curve to intersect the A–E edge nearer the DIPE vertex. As cited in the literature survey and discussed in the next section, it means that less entrainer is needed to break the azeotrope, which could reduce the capital cost. Besides a lower operating pressure implies lower boiling temperatures and possible energy cost savings. In particular, if we assume that the extractive column distillate is almost pure DIPE and consider a conservative value of 40 °C as the minimum allowed temperature in the condenser to use cheap cooling water, 0.4 atm is the lowest pressure from Table 2 since the DIPE boiling point is then computed at 42.5 °C.

3.2. *Thermodynamic insight analysis of extractive process feasibility*

The separation of the minimum boiling azeotropes DIPE A (68.5 °C)–IPA B (82.1 °C) ($x_{azeo,A} = 0.78$ @66.9 °C) with heavy entrainer 2-methoxyethanol E (124.5 °C) belongs to the 1.0-1a-m1 extractive separation class (Gerbaud and Rodriguez-Donis, 2014). The univolatility curve $\alpha_{AB} = 1$ intersects the binary side A–E as shown in Fig. 3 displaying also the residue curve map and other isovolatility lines at 1 atm and 0.4 atm. The vapor–liquid equilibrium of the system is described with the nonrandom two-liquid (NRTL) (Renon and Prausnitz, 1968) thermodynamic model, while the vapor phase is assumed to be ideal. The binary parameters of the model are the same as Luo et al. (2014) who got the values by regressing from the experimental data (Lladosa et al., 2007).

From Fig. 3, component A (DIPE) is a residue curve map saddle $[S_{rcm}]$ and cannot be distilled by azeotropic distillation. But in extractive distillation, A (DIPE) can be obtained as distillate

Table 2 – DIPE–IPA azeotropic temperature and composition at different pressures with NRTL model.

P (atm)	T_{bDIPE} (°C)	T_{bIPA} (°C)	T_{bazeo} (°C)	Azeotrope DIPE mol fraction
10.0	161.8	155.72	154.6	0.2957
5.0	128.1	129.5	123.7	0.5551
4.0	118.4	121.9	114.6	0.6004
2.5	99.7	107.1	96.9	0.6732
1.0	68.5	82.1	66.9	0.7745
0.8	61.7	76.6	60.4	0.7950
0.6	53.4	69.8	52.4	0.8200
0.5	48.4	65.7	47.5	0.8351
0.4	42.5	60.9	41.8	0.8531

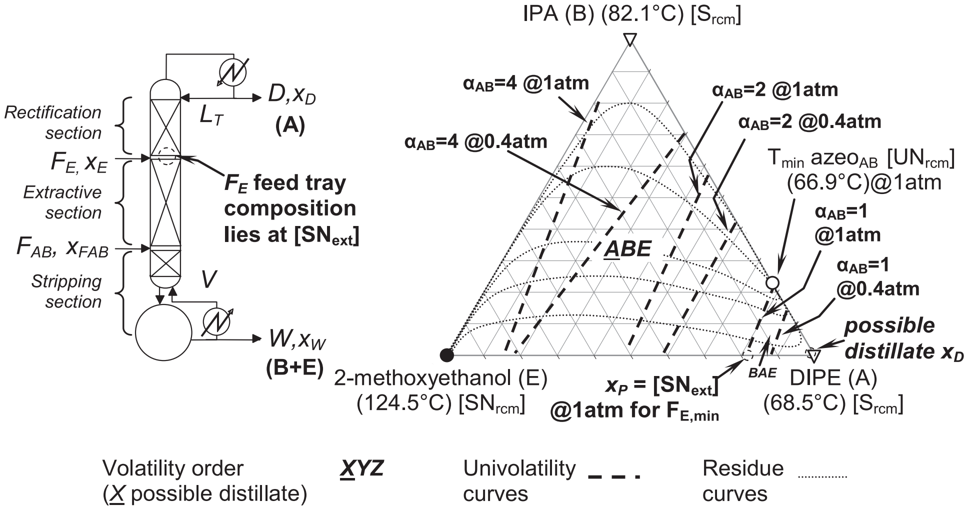

Fig. 3 – Extractive distillation column configuration and DIPE–IPA–2-methoxyethanol. Class 1.0-1a residue curve map at 1atm with isovolatility curves at 0.4 and 1 atm.

product thanks to the occurrence of an extractive section in the column by feeding the entrainer F_E at a different location than the main feed F_{AB}.

From thermodynamic insight, the region A̲BE in Fig. 3 satisfies the general feasibility criterion (Rodríguez-Donis et al., 2009a), so we can expect that (1) DIPE will be the distillate in the extractive column as A is the most volatile component in the region and there is a residue curve linked AE following the increase of temperature. Therefore, the column configuration is a direct split (Fig. 1a). (2) There is minimum entrainer-to-feed flow rate ratio $(F_E/F)_{min}$ that guarantees the process feasibility. When F_E/F is lower than $(F_E/F)_{min}$, the process for achieving a high purity distillate is impossible because the stable node of extractive section SN_{ext} is located on the $\alpha_{AB} = 1$ curve. Above that amount, the relative volatility α_{AB} is always greater than one. Indeed, the intersection point x_P of the univolatility curve and the triangle edge AE gives us the information to calculate the $(F_E/V)_{min}$ by the method shown in Lelkes et al. (1998) and then translate $(F_E/V)_{min}$ into $(F_E/F)_{min}$ by using the transferring equation (You et al., 2015a,b).

Fig. 3 also displays the isovolatility lines $\alpha_{AB} = 1$, $\alpha_{AB} = 2$ and $\alpha_{AB} = 4$ at 0.4 atm. They demonstrate clearly that the separation is easier in low pressure since much less entrainer is needed to achieve the same volatility of AB. Therefore, lowering pressure is likely a potential way to reduce energy cost and TAC for the studied system, but a detailed design is necessary to assess the benefit of lowering pressure.

Finally, we have drawn in Fig. 4 the liquid–vapor equilibrium curve for the binary mixtures 2-methoxyethanol–DIPE. It exhibits a pinch point near pure DIPE which remains at low pressure. This hints that a significant number of trays are necessary in the rectifying section to reach high purity DIPE. This point is further proved by our design in the next section.

4. Results and discussions

Aiming at saving energy cost for the extractive distillation sequence of DIPE–IPA with 2-methoxyethanol, the operating pressure of extractive column is adjusted to $P_1 = 0.4$ atm, which gives a top temperature near 42.5 °C enabling to use cheap cooling water at condenser. Intending to revisit Luo's

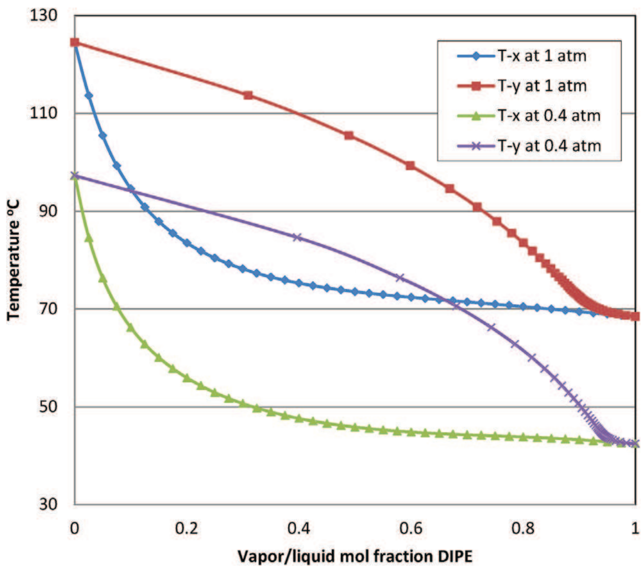

Fig. 4 – T–xy map of 2-methoxyethanol–DIPE.

Table 3 – Relationship between distillates, purity and recovery for DIPE–IPA.

Feed composition		Purity specification	
x_1	0.75	$x_{D1,A}$	0.995
x_2	0.25	$x_{D2,B}$	0.995
Range of distillate (Eqs. (1) and (2))			
D_1 (kmol/h) (Eq. (1))	75.00 ($\psi_A = 99.5\%$)		75.37 ($\psi_A = 100\%$)
D_2 (kmol/h) (Eq. (2))	25.00 ($\psi_B = 99.5\%$)		25.12 ($\psi_B = 100\%$)
Range of distillate (Eqs. (3) and (4))			
D_1 (kmol/h) (Eq. (4))	>75.37 ($\psi_B = 98.493\%$)		>75.00 ($\psi_B = 98.50\%$)
D_2 (kmol/h) (Eq. (3))	>25.12 ($\psi_A = 99.8325\%$)		>25.00 ($\psi_A = 99.833\%$)

design, we keep his proposed total number of trays in the extractive column ($N_{ext} = 66$) and in the entrainer regeneration column ($N_{Reg} = 40$). We also use the same feed as Luo et al. ($F_{AB} = 100$ kmol/h, 0.75(DIPE):0.25(IPA)) and preheat the entrainer to 328.15 K as they did. But we select higher product purity specifications equal to 0.995 molar fractions for both DIPE and IPA whereas they obtained 0.993 for DIPE and 0.996 for IPA. Other design parameters are found by using two steps optimization procedure. Luo's design at 1 atm is used as the initial point of the optimization that we run at 0.4 atm.

In the calculation of TAC, the heat exchanger annual cost for cooling recycling entrainer is taken into account in order to emphasize the effect of the recycling entrainer flow rate on the process. The pressure drop of per tray is assumed 0.0068 atm, the same as Luo et al. (2014) and the tray efficiency is 85% (Figueiredo et al., 2015) for calculating capital cost of the column.

It should be noticed that a vacuum pump is needed to produce low pressure in extractive column while the process is started, after that the operating pressure of the column is controlled by the condenser heat duty. The electricity cost and capital cost of the vacuum pump is much lower than that of the normal liquid-conveying pump because it only works a little time during each start-up and its vapor-conveying flow (the volume of the extractive column) is much smaller than that of the normal liquid-conveying pump (total liquid flow of recycling entrainer, feed and product for one year). Since the cost of liquid-conveying pump could be neglected in the conceptual design stage, the cost of vacuum pump should not be taken into account. The other costs such as pipes and valves are also neglected.

4.1. *Choice of distillate flow rate*

Having set new product purity specifications at 0.995, we use Eqs. (1)–(4) to select suitable distillate flow rate, as shown in Table 3.

Through the use of Eqs. (3) and (2), Table 3 shows that the recovery of A (DIPE) should be at least greater than 99.83% and that the recovery of B (IPA) should be above 99.5%. Our final design results shown later overcome these values. This table also explain why Luo' design that fixed $D_1 = 75.44$ kmol/h prevented him to reach a purity of 0.9950 for DIPE since it is above the 75.37 kmol/h limit value for that purity. He obtained 0.9930 which corresponds to a $\psi_A = 99.88\%$ from Eq. (1).

A side effect of the strongly nonlinear dependency of D_1 and D_2 on the product purity is that the simulation cannot be converged steadily when we directly treat the distillates as an optimized variable in the SQP method. So D_1 is varied with a discrete step of 0.05 kmol/h from 75 kmol/h ($\psi_A = 99.5\%$) to 75.35 kmol/h ($\psi_A = 99.96\%$) and D_2 is varied with a discrete step of 0.03 kmol/h from 25 kmol/h ($\psi_B = 99.5\%$) to 25.12 kmol/h ($\psi_B = 99.98\%$), and the SQP optimization is run to obtain F_E, R_1 and R_2. The results shown in Fig. 5 display the value of the objective function OF vs. D_1 and D_2.

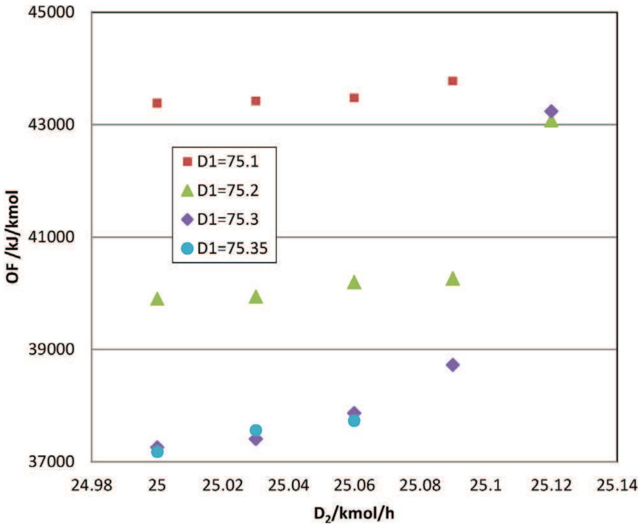

Fig. 5 – Effects of D_1 and D_2 on OF with D_1, D_2, F_E, R_1 and R_2 as variables.

From Fig. 5, we observe that OF describing the total energy demand per product flow rate decreases quickly with the increase of D_1. The same statement was made in our previous study for the extractive distillation of the acetone–methanol azeotropic mixture with water as a heavy entrainer. Also this phenomenon is counterintuitive: normally, the more product at specified purity is obtained, the more energy (reboiler duty) should be used. But as explained in Section 2.4 and evidenced in Fig. 5, less product (e.g. a distillate D_1 of 75 kmol/h) induced a large entrainer feed–main feed ratio in column 1 to meet the purity specifications. Besides, seeking a larger D_1 DIPE-rich distillate increases the separation difficulty in the extractive column but eases the separation in the entrainer regeneration column as less DIPE impurity enters it, here inducing global energy savings. Obviously, our objective function OF accounting for both columns can describe quantitatively the trade-off between the two columns. Meanwhile, Fig. 5 shows that an increase in D_2 increases the OF value. Notice that for D_1 lower than 75.1 kmol/h, the OF value is not displayed as it is well above 45,000 kJ/kmol because of too much DIPE entering regeneration column, leading to high energy cost. This point agrees with the relation of two distillate mentioned before. Thus D_1 lower than 75.1 kmol/h cannot be considered further as a suitable value.

As we will optimize other variables such as N_{FE}, N_{FF}, N_{FReg}, N_{ext} and N_{Reg} in the subsequent steps, we select $D_1 = 75.35$ kmol/h and $D_2 = 25$ kmol/h; those values correspond to a product recovery of 99.96% for DIPE-rich distillate and 99.5% for IPA-rich distillate, respectively. The corresponding

Table 4 – Optimized values of F_E, R_1, and R_2 for the extractive distillation of DIPE–IPA with 2-methoxyethanol, case A at 1 atm and case B at 0.4 atm.

	Case A	Case B
P_1 (atm)	1	0.4
P_2 (atm)	1	1
N_1	66	66
N_2	40	40
D_1 (kmol/h)	75.35	75.35
D_2 (kmol/h)	25	25
N_{FE}	30	30
N_{FAB}	56	56
N_{FReg}	10	10
F_E (kmol/h)	96.9	84.6
R_1	1.85	1.70
R_2	1.80	1.33
OF (kJ/kmol)	37174.9	30639.9

Table 5 – Open loop optimal results of F_E, R_1, R_2, N_{FE}, N_{FAB}, N_{FReg} under fixed D_1 and D_2 for the extractive distillation of DIPE–IPA with 2-methoxyethanol, P_1 = 0.4 atm and P_2 = 1 atm.

N_{FE}	N_{FAB}	N_{FReg}	F_E	R_1	R_2	OF (kJ/kmol)
26	58	13	75.1	1.76	1.20	30292.8
27	59	14	75.0	1.75	1.17	30081.9
28	58	13	75.1	1.76	1.17	30144.8
28	59	15	74.1	1.77	1.16	30110.5
28	60	15	75.0	1.74	1.17	30042.9
28	60	16	74.0	1.77	1.16	30122.2
28	61	15	74.0	1.78	1.15	30213.2
29	55	9	80.0	1.73	1.37	30827.4
30	56	10	84.6	1.70	1.33	30639.9
30	57	11	84.4	1.66	1.34	30410.7
31	55	10	86.5	1.67	1.39	30740.8
31	56	11	86.6	1.65	1.38	30619.0

OF value is 37174.9 kJ/kmol, with F_E = 96.9 kmol/h, R_1 = 1.85 and R_2 = 1.80 at P_1 = 0.4 atm.

4.2. Continuous variables F_E, R_1 and R_2

The optimized F_E, R_1, R_2 values are shown in Table 4 while the other variables are kept constant. Notice that the initial values of the three feed locations in case A and case B are taken from Luo's design.

We observe (1) under lower pressure (case B), the values of F_E, R_1, R_2 in case B are lower and OF decreases by 17.6%. It materializes the benefit of the pressure reduction that was anticipated through the analysis of residue curve map and univolatility line for a 1.0-1a class mixture. (2) The reduction in R_2 is more pronounced that in R_1. If less entrainer is fed to the extractive column, a greater R_1 is needed to get the same separation effect. Meanwhile the concentration of entrainer fed to the regeneration column decreases due to mass balance, and less energy (R_2 decrease) is used to recycle the entrainer. Overall, these observations agree with the study for the separation of acetone-methanol-water system (You et al., 2015a,b). These results also show the benefit of optimizing both columns together to improve further the OF.

4.3. Selecting suitable feed locations

The sensitivity analysis over the three feed positions with ranges [20; 40] for N_{FE}, [>N_{FE}; 66] for N_{FAB}, [5; 40] for N_{FReg} was made by using experimental planning procedure so as to avoid local minimum. For each set of values, F_E, R_1, R_2 are optimized while D_1 and D_2 are fixed. Table 5 shows the results considering now P_1 = 0.4 atm and P_2 = 1 atm as in case B above.

As a whole, the shifting of the three feed locations improves further the OF value by 1.9% but also impacts the process efficiency that will be discussed in Section 4.5. A few statements can be made from Table 5: (1) OF is moderately sensitive to small changes of the three feed locations when F_E, R_1, *and* R_2 are optimized. (2) In conventional distillation an increase of the number of trays in the rectifying section allows to use a lower reflux ratio R_1, but here for an extractive column, the opposite is found as feed location of entrainer moves up the column from 30 to 28 for the lowest OF design. The reason was stated in Lelkes et al. (1998): too much trays in the rectifying section is not recommended in extractive distillation for the 1.0-1a class because the pure product DIPE is a saddle in the RCM and lengthening the rectifying composition profile will approach instead the unstable node that should lie near the unwanted azeotrope. (3) The minimum value of OF is found with six extra number of trays in the extractive section than Luo's design. As discussed earlier, a key factor to achieve the extractive separation is to reach the extractive section stable node SN_{ext} near the DIPE–2-methoxyethanol edge. This can be achieved by more trays in the extractive section. Another consequence is that the efficiency of the extractive section that will be discussed in Section 4.5 is improved. (4) The lowest energy cost for per unit product OF is 30042.9 kJ/kmol with N_{FE} = 28, N_{FAB} = 60 and N_{FReg} = 15. It represents a further 1.9% reduction in energy cost compared the design with N_{FE} = 30, N_{FAB} = 56 and N_{FReg} = 10.

4.4. Closed loop design and optimal design parameters

The optimal design is re-simulated in closed loop flowsheet in order to make sure the product purity is achieved and that the effect of impurity in recycling entrainer on the process is accounted for. For more detailed information, see our earlier study (You et al., 2015a,b). Case 2 under P_1 = 0.4 atm corresponds to the open loop design of case B. It is compared to case 1 that corresponds to our best closed loop design under P_1 = 1 atm. Indeed case A (P_1 = 1 atm) in Table 4 that corresponded to a design with Luo's feed locations did not allowed under closed loop simulation to reach the targeted purity for the distillates and cannot be used for comparison.

The design and operating variables and the cost data are shown in Table 6, referring to the flow sheet notations in Fig. 3. Table 7 displays the product purity and recovery values. Figs. 6 and 7 show the temperature and composition profiles of the extractive and entrainer regeneration columns for the best case, namely case 2, where ME notation holds for 2-methoxyethanol.

Table 6 confirms that a process design operating at 1 atm like case 1 can be improved further, while keeping the same number of trays in the extractive and regeneration columns. In summary, (1) the entrainer flow rate decreased drastically by 25% from 100 kmol/h in case 1 to 75 kmol/h in case 2, showing that improvement was possible due principally to a combination of a shift of feed locations and pressure reduction, as deduced from the pressure dependency of the azeotrope composition and isovolatility curves. (2) The energy consumption underlying the OF value in case 2 is reduced by 11.2% and 13.4% compared to case 1 and case Luo, respectively. It is mostly attributed to a reduction in the entrainer flow rate allowed

Table 6 – Optimal design parameters and cost data from closed loop simulation for the extractive distillation of DIPE–IPA with 2-methoxyethanol.

Column	Case Luo[a]		Case 1		Case 2	
	C_1	C_2	C_1	C_2	C_1	C_2
N_{ext}	66		66		66	
P_1 (atm)	1		1		0.4	
F_{AB} (kmol/h)	100		100		100	
F_E (kmol/h)	100		100		75	
D_1 (kmol/h)	75.44		75.35		75.35	
N_{FE}	30		29		28	
N_{FAB}	56		59		60	
R_1	1.54		1.86		1.83	
Q_C (MW)	1.553		1.746		1.838	
Q_R (MW)	2.279		2.205		1.948	
N_{Rreg}		40		40		40
P_2 (atm)		1		1		1
D_2 (kmol)/h		25.03		25		25
N_{FReg}		10		12		15
R_2		1.93		1.88		1.18
Q_C (MW)		0.823		0.811		0.614
Q_R (MW)		0.748		0.737		0.658
Column	C_1	C_2	C_1	C_2	C_1	C_2
Diameter (m)	1.44	0.78	1.37	0.69	1.66	0.65
Height (m)	46.33	28.05	46.33	28.05	46.33	28.05
I_{CS} (10^6\$)	0.720	0.251	0.683	0.220	0.838	0.207
A_C (m^2)	66	23	74	22	164	18
A_R (m^2)	116	38	112	38	99	34
I_{HE} (10^6\$)	0.347	0.172	0.354	0.170	0.443	0.151
$Cost_{cap}$ (10^6\$)	1.184	0.449	1.145	0.412	1.426	0.378
$Cost_{ope}$ (10^6\$)	0.938	0.313	0.911	0.308	0.809	0.274
$Cost_{CA}$ (10^6\$)	1.333	0.462	1.293	0.445	1.284	0.399
Q_{HA} (MW)	0.407		0.407		0.305	
$Cost_{HA}$ (10^6\$)	0.016		0.016		0.013	
TAC (10^6\$)	1.810		1.754		1.696	
OF (kJ/kmol)	35098.7		34245.2		30398.9	

[a] Luo's process distillate molar purity for DIPE-rich product is below our specifications.

Table 7 – Product purities and recoveries for case Luo, cases 1 and 2 designs.

Mole fraction	D_1	D_2	W_2	W_1	Recovery	
Case Luo @1 atm	DIPE	0.99350	0.00202	4.67E−27	0.00041	99.93%
	IPA	0.00044	0.99637	0.00028	0.20044	99.64%
	ME	0.00606	0.00161	0.99972	0.79915	
Case 1 @1 atm	DIPE	0.99504	0.00096	5.67E−26	0.00019	99.97%
	IPA	0.00076	0.99772	0.00034	0.20033	99.78%
	ME	0.00420	0.00132	0.99966	0.79948	
Case 2 @0.4 atm	DIPE	0.99501	0.00105	1.39E−23	0.00026	99.96%
	IPA	0.00090	0.99730	0.00042	0.25044	99.73%
	ME	0.00409	0.00165	0.99958	0.74930	

by the reduced pressure. (3) Meanwhile, TAC savings reach 3.4% mainly due to the decrease of the entrainer flow rate and reflux ratio in the second regeneration column. (4) There are also drawbacks of lowering pressure except the negligible cost of the vacuum pump mentioned above. If we compare the extractive column in case 1 and case 2, the decrease of the pressure leads to a 21.2% increase of the column diameter, and a 2.2 times increase of the condenser heat exchanger area due to the decrease of condenser temperature. However, the decrease of the pressure results in the decrease of reboiler duty by 11.6%. As a result, the benefit of decreasing pressure overcomes the punishment because the annual cost of extractive column is slightly reduced from 1.293 to 1.284 (10^6\$ per year).

Recall in Table 7, Luo's design does not meet our molar purity specification on the DIPE distillate. To meet that specification, case 1 result shows that R_1 must be increased and the heat duty as well. Despite all this, Table 6 shows that case 1 gives a 3.1% and 2.4% reduction in TAC and energy cost OF over Luo's design at the same pressure due to the decrease of reboiler duty thanks to more suitable distillate and feed locations. This proves the effectiveness of the two step optimization procedure we used.

Table 6 also shows that shifting the feed tray locations and running a new optimization improves the OF and thus reduces the process energy consumption. This point is evidenced by comparing the total reboiler heat duty of case 1 (2.942 MW) and case 2 (2.606 MW): a 11.4% total heat duty is saved. Regarding product purity and recovery, Table 7 shows that purity targets are met and that recoveries are high and in agreement with the relationship between the two distillate flow rates as discussed in Section 2.1.

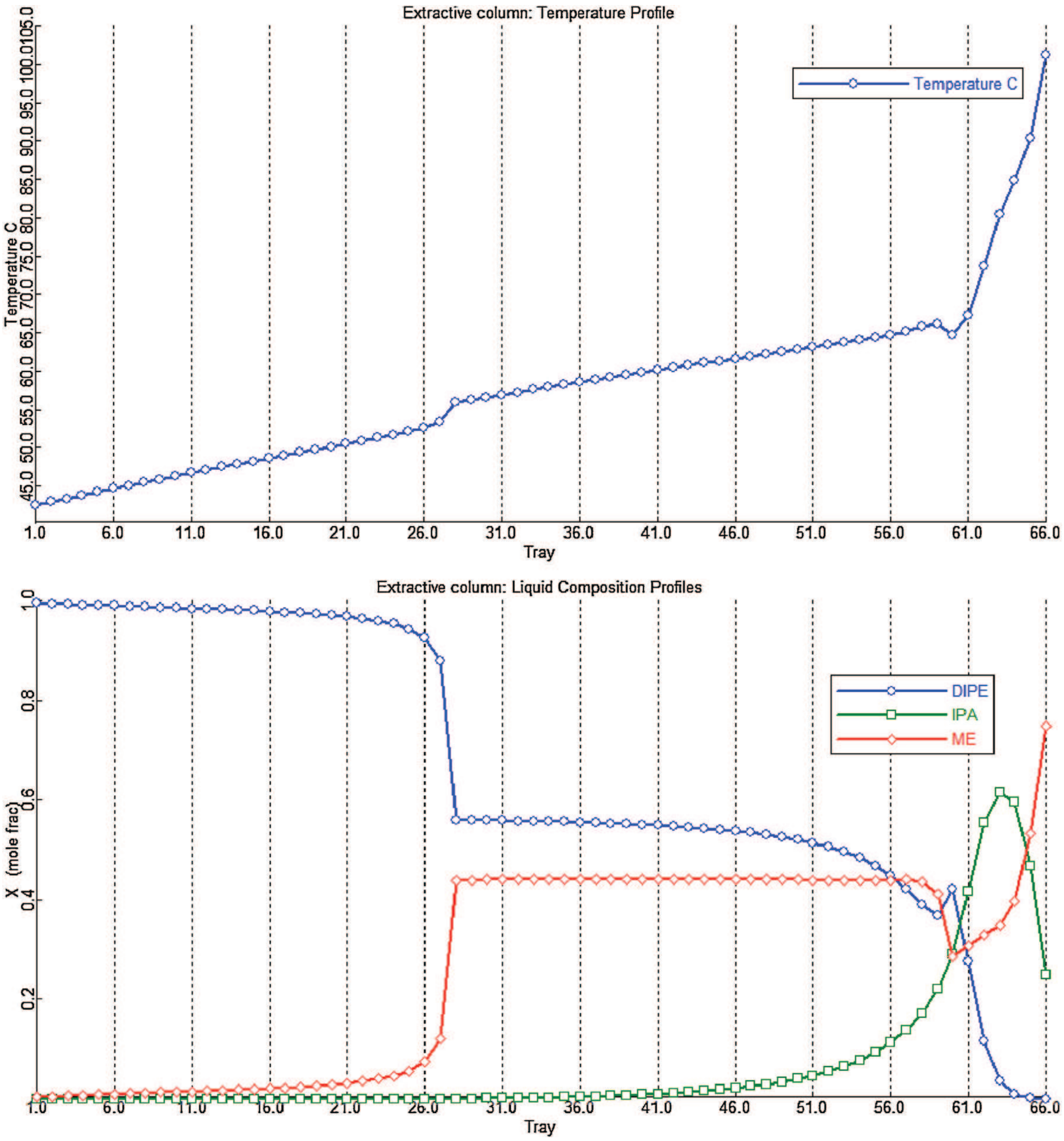

Fig. 6 – Temperature and composition profiles of case 2 extractive column for the extractive distillation of DIPE–IPA with 2-methoxyethanol.

4.5. *Analysis from extractive efficiency indicators and ternary composition profile map*

Shifting feed tray locations induces changes in the number of trays in each section. We already discussed the impact of the number of trays in the rectifying section. But for the extractive distillation process, the general feasibility criteria (Rodríguez-Donis et al., 2009a; You et al., 2015a,b) and the feasibility analysis we have conducted in Section 2.1 show that the number of trays in the extractive section, N_{ext}, should be high enough to allow the column composition at the entrainer feed tray to lie close to the stable node of the extractive profile map. In our previous work on another 1.0-1a extractive separation class mixture, we proposed extractive efficiency indicators describing the ability of the extractive section to discriminate the desired product between the top and the bottom of the extractive section.

$$E_{\text{ext}} = x_{\text{P,H}} - x_{\text{P,L}} \tag{6}$$

$$e_{\text{ext}} = \frac{E_{\text{ext}}}{N_{\text{ext}}} \tag{7}$$

where E_{ext}: the total extractive efficiency indicator of extractive section, $x_{\text{P,H}}$: product mole fraction at one end of extractive section, $x_{\text{P,L}}$: product mole fraction at another end of extractive section, e_{ext}: extractive efficiency indicator per tray, N_{ext}: tray number of extractive section. Here, we use the entrainer feed and the main feed trays locations as ends of the extractive section.

The extractive efficiency indicators E_{ext} and e_{ext} are shown in Table 8 for the cases 1 and 2 and Luo's design, along with the DIPE composition at the feed trays. Fig. 8 displays the extractive column composition profiles in a ternary map.

From Table 8 and Fig. 8, we remark that (1) Luo's design extractive efficiency indicators are negative, stating that the extractive section is not able to improve the DIPE purity. (2) A lower entrainer flow rate as in case 2 operating at low pressure allows the top end of the extractive section SN_{ext} to lie closer to the product vertex. (3) The extractive efficiency

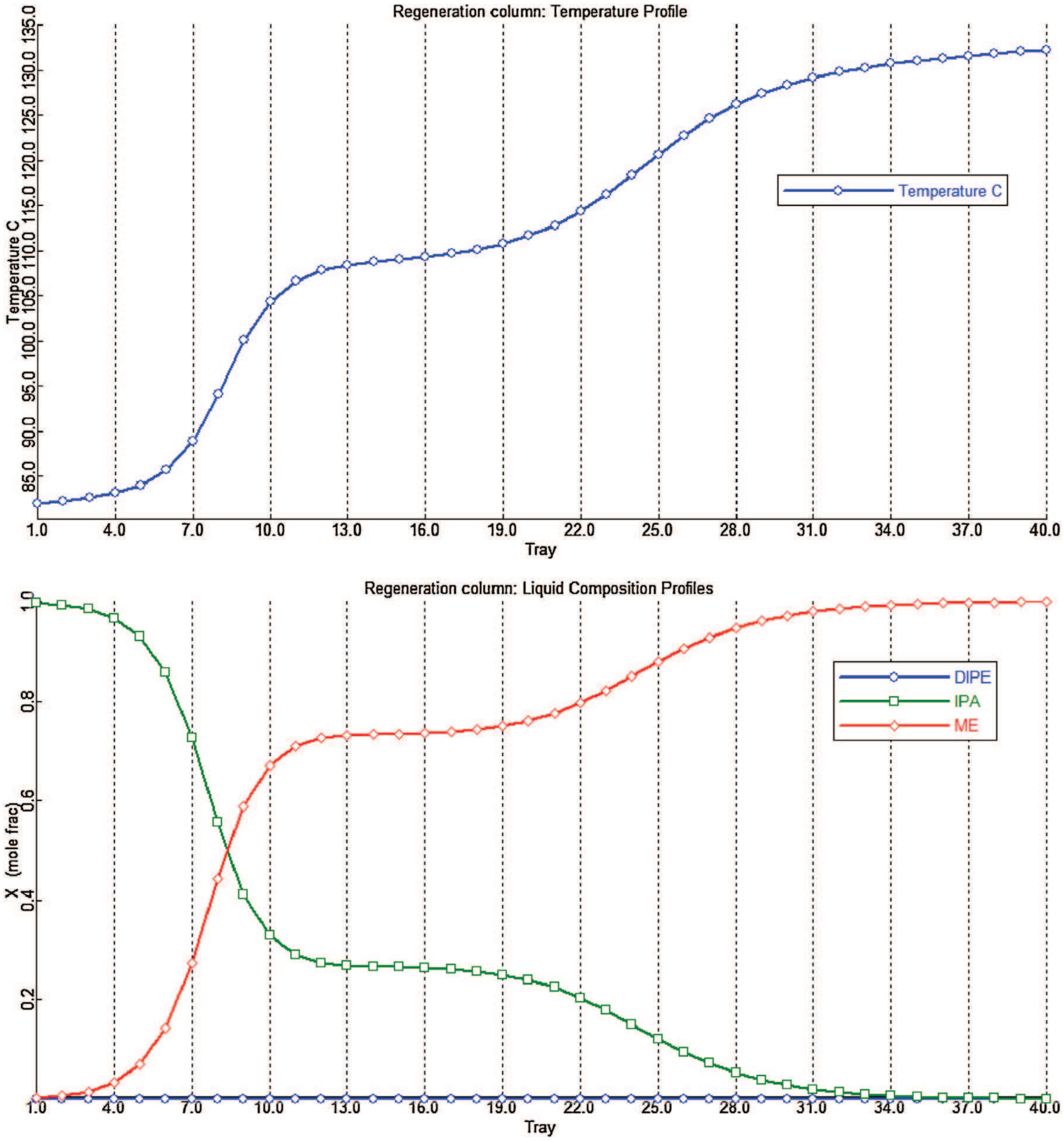

Fig. 7 – Temperature and composition profiles of case 2 entrainer regeneration column for the extractive distillation of DIPE–IPA with 2-methoxyethanol.

indicators are slightly higher for case 2 than for case 1. Indeed the lower operating pressure leads to more favorable isovolatility curves and SN_{ext} location as shown in Figs. 3 and 8, which directly affect the extractive efficiency indicators E_{ext} and e_{ext}.

Compared with Luo's design, both case 1 and case 2 show positive and evidently higher extractive efficiency indicators. Case 2 with a lower TAC has a higher efficiency than case 1. But we cannot conclude that the design with a more suitable extractive efficiency indicator is more economical and we have shown that there exists an optimal extractive efficiency indicator value corresponding to the lowest TAC design in another work (You et al., 2015a,b).

5. Design sensitivity to the extractive column pressure and the total number of trays

In this part, we do a sensitivity analysis of the process design by over the extractive column pressure and over the total number of trays.

Table 8 – Efficiencies of per tray and total extractive section for the extractive distillation of DIPE–IPA with 2-methoxyethanol.

	DIPE composition		N_{ext}	$E_{ext}/10^{-3}$	$e_{ext}/10^{-3}$
	Entrainer feed tray (SN_{ext})	Feed tray			
Case Luo	0.463	0.492	27	<0	<0
Case 1	0.501	0.393	31	108	3.48
Case 2	0.560	0.422	33	138	4.18

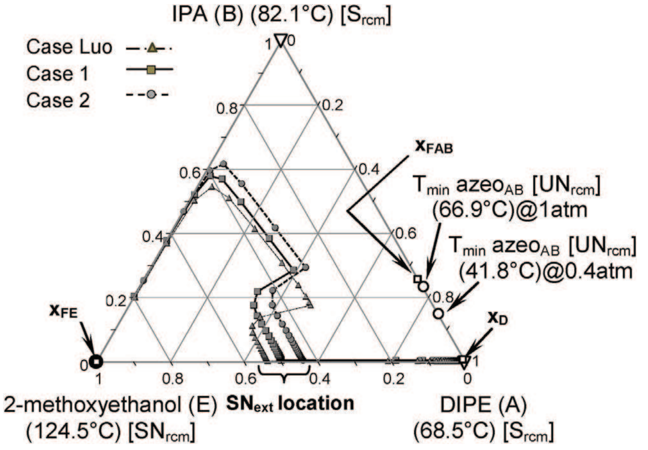

Fig. 8 – Liquid composition profiles for case Luo, cases 1 and 2 extractive distillation column designs for the extractive distillation of DIPE–IPA with 2-methoxyethanol.

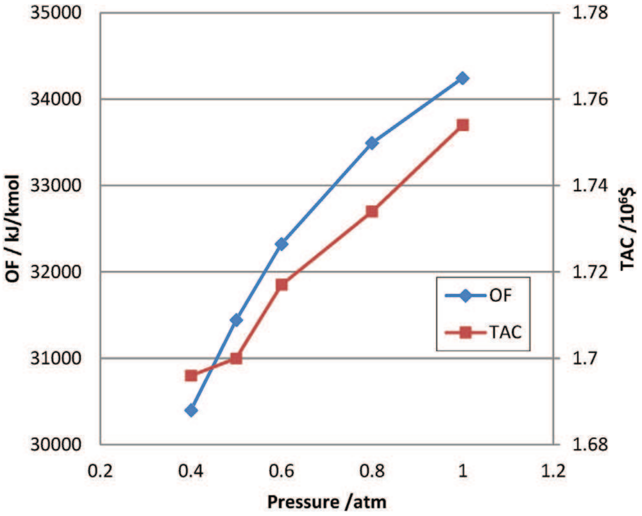

Fig. 9 – Effect of pressure on energy cost OF and TAC.

Pressure is only varied for the first extractive distillation column with values between 1 atm and a lower limit equal to 0.4 atm that we selected for using cooling water for the condenser keeping the same total tray number. The total number of trays is increased one by one from 66 to 70 after selecting the most suitable pressure, namely 0.4 atm.

The two step nonlinear programming optimization methodology with SQP method is run for each case. Carrying a full optimization of the pressure and tray number at the same time than the other variables would require solving a mixed-integer nonlinear programming (MINLP) problem with adequate optimization schemes that we have not considered here. Comparison is done on the OF value only, namely the energy demand per product flow rate and TAC. For reasons given earlier, we do not account for additional costs at low pressure like technological price factor increase and vacuum pump and sub-cooled fluid costs.

5.1. *Selection of the pressure for the extractive column*

Results of the sensitivity to pressure of the extractive column on the process OF and TAC values are displayed in Fig. 9. Lines are shown for eye guidance.

From Fig. 9, the lower bound of the pressure range studied, 0.4 atm gives the design with the lowest OF and TAC values while keeping the same total tray number. First, this agrees well with thermodynamics insight analysis displayed in Fig. 3: the relative volatility increases quickly at lower pressure and the boiling temperature is lower, which lead together to use less energy to achieve the same separation in terms of purity and recovery. Second, the process TAC decrease at lower pressure is mainly due to the decrease of the process energy cost. Third, TAC decreases little from 0.5 atm to 0.4 atm is because the benefit of lowering pressure is crippled by the increase of capital cost for condenser due to the decrease of temperature driving force.

5.2. *Selection of the total trays number for the extractive column*

Fig. 10 displays the OF and TAC values for the total tray number of the extractive column, and Table 9 shows the design at the TAC minimum value. The lower bound, 66 trays, is the one used in the previous sections, and was taken from Luo's design (Luo et al., 2014).

For a constant pressure, we find that the process design would benefit from an increase of the extractive column number of tray up to 68 as both OF and TAC decrease. The TAC decrease is due to capital cost decrease from the reduction of column diameter and reboiler-condenser heat transfer area thanks to a lower vapor flow rate, and also due to the operating cost decrease as the lower reflux allows a smaller heat duty to be used. For these values it compensates fully the capital cost increase due to the higher column height. Then for tray numbers equal to 69 and 70, the reflux remains similar to the 68 tray case value. The operating costs are similar but the extra capital cost of the column height dominates again and the TAC increases. In the meanwhile, correlated to the energy demand, the OF value remains similar to that for $N_{ext} = 68$. Hence, one should prefer to design with 68 trays in the extractive distillation column when pressure is kept at 0.4 atm.

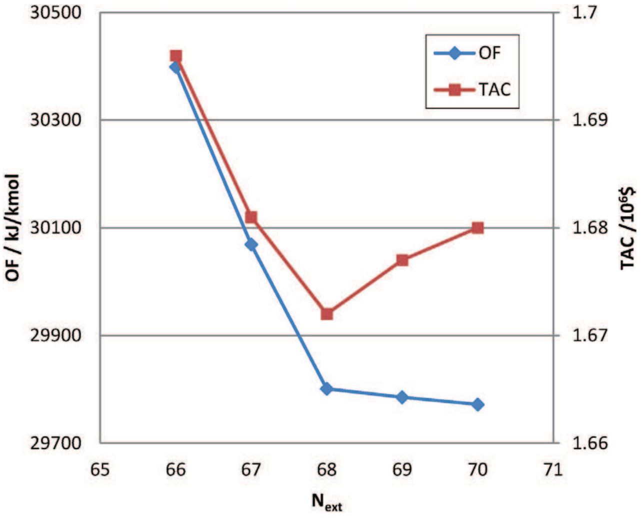

Fig. 10 – Effect of total tray number of extractive column on energy cost OF and TAC.

Table 9 – Effect of N_{ext} on the design parameters and cost data from closed loop simulation for the extractive distillation of DIPE–IPA with 2-methoxyethanol.

N_{ext}	67		68		69	
Column	C_1	C_2	C_1	C_2	C_1	C_2
P_1 (atm)	0.4		0.4		0.4	
F_{AB} (kmol/h)	100		100		100	
F_E (kmol/h)	76		77		75	
D_1 (kmol/h)	75.35		75.35		75.35	
N_{FE}	29		31		31	
N_{FAB}	61		62		63	
R_1	1.75		1.70		1.71	
Q_C (MW)	1.786		1.754		1.760	
Q_R (MW)	1.901		1.873		1.874	
N_{Rreg}		40		40		40
P_2 (atm)		1		1		1
D_2 (kmol/h)		25		25		25
N_{FReg}		14		13		13
R_2		1.25		1.27		1.27
Q_C (MW)		0.634		0.639		0.639
Q_R (MW)		0.677		0.682		0.679
Column	C_1	C_2	C_1	C_2	C_1	C_2
Diameter (m)	1.63	0.66	1.62	0.66	1.62	0.66
Height (m)	46.94	28.05	47.55	28.05	48.77	28.05
I_{CS} (10^6\$)	0.831	0.210	0.834	0.210	0.851	0.210
A_C (m^2)	159	18	156	18	157	18
A_R (m^2)	97	35	95	35	95	35
I_{HE} (10^6\$)	0.435	0.154	0.430	0.155	0.431	0.155
$Cost_{cap}$ (10^6\$)	1.408	0.385	1.407	0.385	1.429	0.385
$Cost_{ope}$ (10^6\$)	0.790	0.282	0.778	0.284	0.778	0.282
$Cost_{CA}$ (10^6\$)	1.259	0.410	1.247	0.412	1.255	0.411
Q_{HA} (MW)	0.309		0.313		0.304	
$Cost_{HA}$ (10^6\$)	0.013		0.014		0.013	
TAC (10^6\$)	1.681		1.672		1.677	
OF (kJ/kmol)	30069.1		29801.1		29785.1	

6. Conclusions

Aiming at evaluating the benefit of lowering pressure for saving energy cost and total annual cost, we have optimized the design of a homogeneous extractive distillation process for the separation of the DIPE–IPA minimum boiling azeotrope with heavy entrainer 2-methoxyethanol. The process flow sheet includes both the extractive distillation column and the entrainer regeneration column. The curious behavior that the energy cost OF decreases following the increase of distillate are clarified by the interrelation of the two distillate flow rates and purities and the entrainer recycling through mass balance.

Our methodology stated in Section 1 is illustrated with the studied case. By using insight from the analysis of the ternary residue curve map and isovolatility curves, we have noticed the beneficial effect of lowering the pressure in the extractive distillation column. A lower pressure reduces the usage of entrainer as it increases the relative volatility of DIPE–IPA for the same entrainer content in the distillation region where the extractive column operates. A 0.4 atm pressure was selected to enable the use of cheap cooling water in the condenser.

Then we have run an optimization aiming at minimizing the total energy consumption per product unit, thus defining the objective function OF. OF includes both products and both columns energy demands at boiler and condenser and accounts for the price difference in heating and cooling energy and for the price difference in product sales. Rigorous simulations in closed loop flow sheet were done in all cases. The total number of column trays is identical to literature works of Luo et al. for the sake of comparison. Other variables have been optimized; two distillates, entrainer flow rate, reflux ratios, entrainer feed location and main feed location. The total annualized cost (TAC) was calculated for all processes.

A competitive design is found: energy cost and TAC are reduced by 13.4% and 6.3%, respectively compared to Luo's design. The causes are examined in the light of the design parameter interrelations and through explanations of the extractive efficiency indicators and profile map based on the analysis of thermodynamic insight. Three important issues have emerged. First the reduction of the pressure is beneficial to the separating case. Second, the decrease of the energy cost function OF when the distillate flow rate increases at constant purity has been explained by the interrelation of two distillates through mass balance. Third, extractive efficiency indicators of the extractive section that describes the ability of the extractive section to discriminate the desired product between the top and the bottom of the extractive section are relevant criterions to assess the performance of an extractive distillation process design.

Finally, the sensitivity analysis over the pressure and the total number of trays in the extractive column was done. The results showed that energy cost per unit product is reduced by 15.1% meanwhile TAC is saved by 7.6%.

A further investigation is conducted to assess the relation of the extractive efficiency indicators on the process TAC and total energy consumption by using multiobjective genetic algorithm. The number of total trays in the two columns and the value of the operating pressure will be regarded as optimization variables.

Acknowledgment

Xinqiang You thanks the Chinese Scientific Council for its support.

Appendix A. Sizing and economic cost calculation

The diameter of a distillation column is calculated using the *tray sizing* tool in Aspen Plus software.

The height of a distillation column is calculated from the equation:

$$H = \frac{N}{e_T} \times 0.6096$$

N tray stage except condenser and reboiler, e_T tray efficiency is taken as 85% in this work.

The heat transfer areas of the condenser and reboiler are calculated using following equations:

$$A = \frac{Q}{u \times \Delta T}$$

u: overall heat transfer coefficient (kW K^{-1} m^{-2}), $u = 0.852$ for condenser, 0.568 for reboiler.

The capital costs of a distillation column are estimated by the following equations:

$$\text{Shell cost} = 22522.8 D^{1.066} H^{0.802}$$

$$\text{Tray cost} = 1423.7 D^{1.55} H$$

$$\text{Heat exchanger cost} = 9367.8 A^{0.65}$$

References

Doherty, M.F., Malone, M.F., 2001. Conceptual Design of Distillation Systems. McGraw-Hill, New York.

Elliott, J.R., Rainwater, J.C., 2000. The Bancroft point and vapor–liquid equilibria in the system benzene + isopropanol. Fluid Phase Equilibria 175, 229–236.

Figueiredo, M.F., Brito, K.D., Ramos, W.B., Vasconcelos, L.G.S., Brito, R.P., 2015. Effect of solvent content on the separation and the energy consumption of extractive distillation columns. Chem. Eng. Commun. 202, 1191–1199.

Gerbaud, V., Rodriguez-Donis, I., 2014. Extractive distillation. In: Gorak, A., Olujic, Z. (Eds.), Distillation Book, II. Elsevier, Amsterdam, p. 201, ISBN 978-0-12-386878-7 (Chapter 6).

Gil, I.D., Botía, D.C., Ortiz, P., Sánchez, O.F., 2009. Extractive distillation of acetone/methanol mixture using water as entrainer. Ind. Eng. Chem. Res. 48, 4858–4865.

Hilmen, E.K., Kiva, V.N., Skogestad, S., 2002. Topology of ternary VLE diagrams: elementary cells. AIChE J. 48, 752–759.

Kiva, V.N., Hilmen, E.K., Skogestad, S., 2003. Azeotropic phase equilibrium diagrams: a survey. Chem. Eng. Sci. 58, 1903–1953.

Laroche, L., Andersen, H.W., Morari, M., Bekiaris, N., 1991. Homogeneous azeotropic distillation: comparing entrainers. Can. J. Chem. Eng. 69, 1302–1319.

Lelkes, Z., Lang, P., Benadda, B., Moszkowicz, P., 1998. Feasibility of extractive distillation in a batch rectifier. AIChE J. 44, 810–822.

Lladosa, E., Montón, J.B., Burguet, M.C., Munoz, R., 2007. Effect of pressure and the capability of 2-methoxyethanol as a solvent in the behaviour of a diisopropyl ether–isopropyl alcohol azeotropic mixture. Fluid Phase Equilibria 262, 271–279.

Lladosa, E., Montón, J.B., Burguet, M.C., De la Torre, J., 2008. Isobaric (vapour + liquid + liquid) equilibrium data for (di-*n*-propyl ether + *n*-propyl alcohol + water) and (diisopropyl ether + isopropyl alcohol + water) systems at 100 kPa. J. Chem. Thermodyn. 40, 867–873.

Logsdon, J.E., Loke, R.A., 2000. Isopropyl Alcohol. Kirk-Othmer Encyclopedia of Chemical Technology. Wiley, New York.

Luo, H., Liang, K., Li, W., Li, Y., Xia, M., Xu, C., 2014. Comparison of pressure-swing distillation and extractive distillation methods for isopropyl alcohol/diisopropyl ether separation. Ind. Eng. Chem. Res. 53, 15167–15182.

Luyben, W.L., 2012. Pressure-swing distillation for minimum- and maximum-boiling homogeneous azeotropes. Ind. Eng. Chem. Res. 51, 10881–10886.

Luyben, W.L., Chien, I.L., 2010. Design and Control of Distillation Systems for Separating Azeotropes. Wiley, New York.

Petlyuck, F.B., 2004. Distillation Theory and its Application to Optimal Design of Separation Units. Cambridge University Press, Cambridge, UK.

Petlyuk, F., Danilov, R., Burger, J., 2015. A novel method for the search and identification of feasible splits of extractive distillations in ternary mixtures. Chem. Eng. Res. Des. 99, 132–148.

Renon, H., Prausnitz, J.M., 1968. Local compositions in thermodynamic excess functions for liquid mixtures. AIChE J. 14, 135–144.

Rodríguez-Donis, I., Gerbaud, V., Joulia, X., 2009a. Thermodynamic insights on the feasibility of homogeneous batch extractive distillation. 1. Azeotropic mixtures with heavy entrainer. Ind. Eng. Chem. Res. 48, 3544–3559.

Rodríguez-Donis, I., Gerbaud, V., Joulia, X., 2009b. Thermodynamic insights on the feasibility of homogeneous batch extractive distillation. 2. Low-relative-volatility binary mixtures with a heavy entrainer. Ind. Eng. Chem. Res. 48, 3560–3572.

Rodríguez-Donis, I., Gerbaud, V., Joulia, X., 2012a. Thermodynamic insights on the feasibility of homogeneous batch extractive distillation. 3. Azeotropic mixtures with light boiling entrainer. Ind. Eng. Chem. Res. 51, 4643–4660.

Rodríguez-Donis, I., Gerbaud, V., Joulia, X., 2012b. Thermodynamic insights on the feasibility of homogeneous batch extractive distillation, 4.azeotropic mixtures with intermediate boiling entrainer. Ind. Eng. Chem. Res 51, 6489–6501.

Shen, W., Gerbaud, V., 2013. Extension of thermodynamic insights on batch extractive distillation to continuous operation. 2. Azeotropic mixtures with a light entrainer. Ind. Eng. Chem. Res. 52, 4623–4637.

Shen, W., Benyounes, H., Gerbaud, V., 2013. Extension of thermodynamic insights on batch extractive distillation to continuous operation. 1. Azeotropic mixtures with a heavy entrainer. Ind. Eng. Chem. Res. 52, 4606–4622.

Wang, S.J., Wong, D.S.H., Yu, S.W., 2008. Effect of entrainer loss on plant-wide design and control of an isopropanol dehydration process. Ind. Eng. Chem. Res. 47, 6672–6684.

You, X., Rodriguez-Donis, I., Gerbaud, V., 2014. Extractive distillation process optimisation of the 1.0-1a class system, acetone-methanol with water. In: Klemes, J.J., Varbanov, S.V., Liew, P.Y. (Eds.), 24th European Symposium on Computer Aided Process Engineering. Elsevier, Amsterdam, ISBN 978-0-444-63456-6.

You, X., Rodriguez Donis, I., Gerbaud, V., 2015a. Improved design and efficiency of the extractive distillation process for acetone-methanol with water. Ind. Eng. Chem. Res. 54, 491–501.

You, X., Rodriguez Donis, I., Gerbaud, V., 2015b. Investigation of separation efficiency indicator for the optimization of the acetone-methanol extractive distillation with water. Ind. Eng. Chem. Res., http://dx.doi.org/10.1021/acs.iecr.5b02015.