

Entrainer selection using the Infinitely Sharp Split method for separating binary minimum boiling azeotrope by extractive distillation

Ivonne Rodriguez Donis^a, Jens Abildskov^b, Nataliya Shcherbakova^c, Vincent Gerbaud^c

^a Laboratoire de Chimie Agro-industrielle, LCA, Université de Toulouse, INRA, Toulouse, France.

^b PROSYS, Department of Chemical and Biochemical Engineering, Technical University of Denmark, Building 229, 2800 Kgs Lyngby, Denmark.

^c Laboratoire de Génie Chimique, Université de Toulouse, CNRS, INP, UPS, Toulouse, France.

ivonne.rodriguezdonis@ensiacet.fr; ja@kt.dtu.dk; nshcherb@ensiacet.fr; vincent.gerbaud@ensiacet.fr

Abstract. Entrainer selection for extractive distillation process to separate binary azeotropes is still challenging because current criteria are mainly based on thermodynamic guidelines and limited to infinite dilution entrainer domain. Commonly, the resulting entrainer ranking is not always validated by further optimization studies. In this work, the "Infinitely Sharp Split" (ISS) method is applied for entrainer screening along with other thermodynamic criteria (univolatility curve and driving force). The ISS method allows the fast computation of the minimum value of the entrainer flowrate and the reflux ratio by using a simplified mass balance around the extractive section and only needing the equilibrium model of the ternary mixture. The methodology is applied to the acetone – methanol separation with water and DMSO as benchmark entrainers. We also investigate ethylene glycol as a potential candidate. The entrainer ranking from ISS method agrees with previous optimisation results showing that water leads to a costly process because of a higher entrainer flow rate and reflux ratio.

Keywords extractive distillation, entrainer screening, infinitely sharp split method

Introduction

Extractive distillation is a leading process for separating binary azeotropic mixtures and close boiling components A – B [1]. However, the conceptual design of this process is still challenging due to the large number of process variables, where the economic and environmental effectiveness strongly depend on the selected entrainer E. The entrainer enables the separation by interacting differently with the azeotrope compounds and altering the thermodynamic equilibrium in the extractive section of the column. The entrainer selection has been historically done by comparing single thermodynamic criterion such as entrainer selectivity $S_{A,B}^{\infty E}$ and capacity $C_B^{\infty E}$. Both criteria require the calculation of the activity coefficient of A ($\gamma_A^{\infty E}$) and B ($\gamma_B^{\infty E}$) in a ternary mixture under infinite dilution entrainer condition. Kossack et al. [2] proposed a new criterion given by the product $S_{A,B}^{\infty E} \cdot C_B^{\infty E}$ instead of using the two quantities individually:

$$S_{A,B}^{\infty E} \cdot C_B^{\infty E} = \frac{\gamma_A^{\infty E}}{\gamma_B^{\infty E}} \cdot \frac{1}{\gamma_B^{\infty E}} \quad (\text{Eq.1})$$

Hypothetically, entrainers with high selectivity and capacity may enable the separation of A and B with a low entrainer flowrate (FE) and reflux ratio (R), and therefore, with low energy consumption and total annual cost. Kossack et al. [2] also proposed a systematic Computer Aided Molecular Design (CAMD) framework coupled with the Rectification Body Method [3] to select optimal entrainers enabling the separation of acetone (A) – methanol (B) with a minimum energy demand. The entrainer candidates were initially screened based on either $S_{A,B}^{\infty E}$ or $S_{A,B}^{\infty E} \cdot C_B^{\infty E}$ criterion. Results from optimization studies found that DMSO was the best candidate with 30% reduction of the TAC comparing to water as the worst candidate. However, the relative difference of $S_{A,B}^{\infty E}$ and the combined criterion $S_{A,B}^{\infty E} \cdot C_B^{\infty E}$ of water compared to DMSO were 17% and 80% higher, respectively. A more critical situation was found for ethylene glycol (EG) which was suggested as a good candidate based on the intersection of the univolatility curve ($\alpha_{AB}=1$) on the edge AE and the maximum value of the driving force of A (DF_A^{AE} and DF_B^{BE}) in a binary mixture with E [4]. Optimization studies showed that DMSO provides the separation with both reflux ratio and total heat consumption similar to ethylene glycol. DMSO beats EG by only a 3% lower TAC despite a relative difference of $S_{A,B}^{\infty E} \cdot C_B^{\infty E}$ of 57% between both entrainers. These results showed the poor agreement between entrainer ranking using these thermodynamic criteria and the TAC. We understand this as a logical result because the maximum value of the relative volatility α_{AB} does not always occur close to the entrainer vertex where infinite dilution holds in the ternary diagram ABE. Figure 1 displays the topology of the isovolatility curve maps for the three entrainers water, DMSO and EG. Good values of the aforementioned thermodynamic criteria under entrainer infinite dilution is only realistic valid for water.

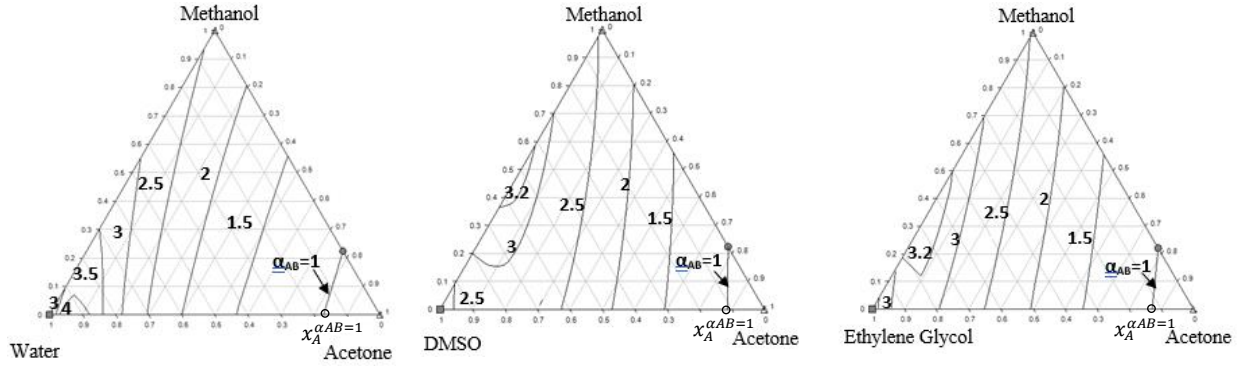


Fig. 1 Isovotility curves map for the ternary mixture acetone(A) – methanol(B) – entrainer

Ideally, a robust entrainer selection methodology for extractive distillation should include some criteria considering the full spectrum of thermodynamic equilibrium information and assess the minimum value of the main operating parameters, typically the entrainer flow rate (FE) and the reflux ratio $\mathcal{R}$ because of their direct effect on the TAC and the heat consumption. The computation of FE and R can be done in a systematic manner by the use of either an algebraic criterion [5] or by mathematical approaches like bifurcation theory [6] or by the coupling of bifurcation – RBM [2]. In particular, these methods enable the calculation of the singular points (nodes and saddles) limiting the feasible extractive region. Even though all these rigorous methods allow a reliable entrainer screening, they are time-consuming and complex, and their comprehension is a daunting task for non-experts. Petlyuk et al. [7] extended their Infinitely Sharp Split (ISS) method for simple feed distillation column to extractive distillation process in order to identify feasible splits. Although it bears some limits, the ISS method enables the calculation of the minimum value of FE and R in a simpler way than other methods. It is based on a simplified mass balance around the extractive section and only requires a ternary vapour – liquid equilibrium model. Besides, ISS method delimits the bundle of the liquid profiles into the column sections with a comparable precision to other methods [7]. In this paper, the ISS method is extended to the entrainer screening task for separating binary minimum boiling azeotropic mixtures with high boilers entrainers (Serafimov class 1.01-a) by extractive distillation. A more robust methodology for entrainer screening is suggested herein by combining the thermodynamic criteria such as the univolatility curve intersection ($x_A^{\alpha_{AB}=1}$, Fig.1) and the driving forces DF_A^{AE} and DF_B^{BE} suggested elsewhere [4] with the minimum values of FE and R computed using ISS method, all criteria based on the ternary phase equilibrium data. The methodology is applied to compare benchmark entrainers, water and DMSO, as well as the ethylene glycol already studied in the literature [4]. The resulting entrainer ranking is compared with TAC and heat consumption from optimization studies of each process alternative published elsewhere [4].

Infinitely sharp split (ISS) method

The Infinitely Sharp Split (ISS) method assumes that each column section has an infinite height. Hence, one azeotropic compound (A or B) is absent at the entrainer feeding tray and in the bottom product. Figure 2a shows how the compounds split inside the extractive distillation column for a high boiler entrainer interacting with B whereas A is withdrawn in the distillate product. The separation of a ternary mixture takes place in the extractive distillation column if the extractive liquid profile (ELP) crosses both the rectifying and the stripping liquid profile. Indeed, the feasible extractive region (FER) contains all ELP starting at the same lowest temperature point (unstable node N_e^-), approaching the same intermediate temperature point (saddle S^E) and arriving at the same highest temperature point (stable node N_e^+) placed on the edge AE. The FER is limited by a precise ELP passing through the three singular points N_e^- , S^E and N_e^+ that is usually called boundary of the feasible extractive region (BFER). Figure 2b displays several BFER for a molar flowrate ratio entrainer/distillate (E/D) = 0.7 and different reflux ratios (L/V) [8]. The single variation of (L/V) at a fixed E/D will change the location of the saddle point S^E . Indeed, the trajectory of the saddle points S^E corresponds to the first pinch branch that connects the B vertex with the root x_A^{r1} . Shaded region in Figure 2b represents the total feasible extractive region (TFER) that contains all ELP calculated for the same E/D=1.9 and L/V=0.8 and different compositions from the bottom to the top of the column. Computation of the ELP can be done by using a differential mass balance [1]. TFER of the ternary system is usually composed by two FER, I and II, where all ELP share the same N_e^+ and saddle S^E but start at different unstable nodes N_{e1}^- (FER I) and N_{e2}^- (FER II). It should be noted that N_{e2}^- lies

outside the edge AB (Fig. 2b). Indeed, feasible values of E/D and L/V are linked to the existence of both N_e^+ on the edge AE and S^E inside the composition simplex [5]. Petlyuk et al. [7] showed that minimum value of (L/V) in the extractive section occurs when S^E and x_A^{r1} are coincident on the edge AE. When $(L/V) < (L/V)_{\min}$, S^E vanishes and there is no connection between the extractive liquid profile and the rectifying liquid profile on the edge AE. Similarly, the root x_A^{r2} of the second pinch branch coming from the azeotrope AB^{azeo} is associated to the maximum value of $(L/V)_{\max}$ for the same E/D . Both roots move towards each other when FE decreases and the $(E/D)_{\min}$ condition happens when $x_A^{r1} = x_A^{r2}$. Further reduction of E/D moves N_e^+ towards the second pinch branch avoiding again the intersection between the extractive and the rectifying liquid profiles on the edge AE. In practice, the operating L/V is computed using $(L/V)_{\min}$ for an operating $(E/D)_{OP}$ around 1.5-2 times of $(E/D)_{\min}$.

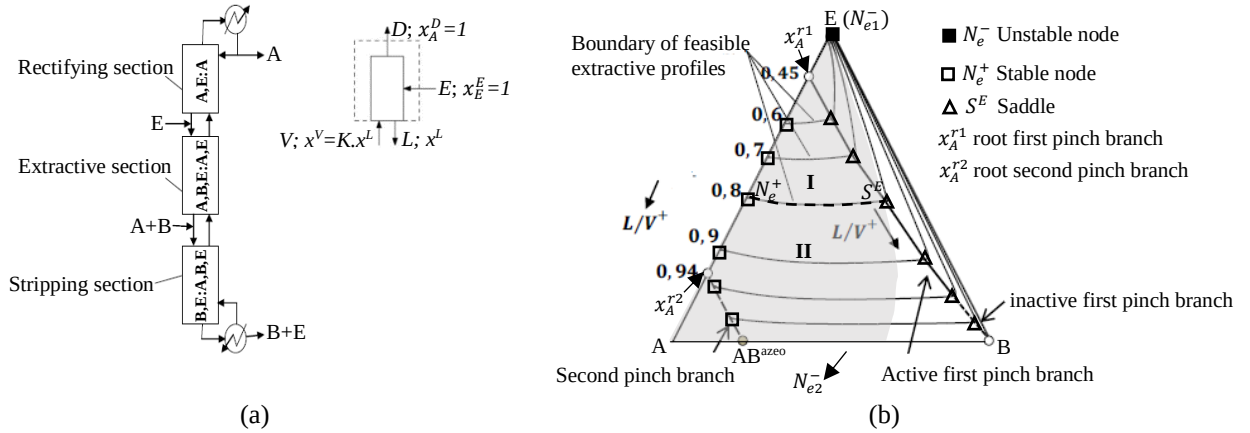


Fig. 2 (a) Distribution of components according to the Infinitely Sharp Splits method. (b) Pinch branches for the acetone(A) – methanol(B) – water(E) at $E/D=1.9$ and different reflux ratios L/V in the extractive section.

The ISS methodology is based on a simplified mass balance around the extractive section under the assumption of constant molar flow rates and the infinite height of each column section. The material balance is set up around the extractive section in Fig. 2a considering that the stable node N_e^+ is in the extractive tray and B is the absent compound. Under pinch conditions in the extractive tray, the molar fraction of A satisfies $x_A^{m+1} = x_A^m = x_A^r$. Pure distillate ($x_A^D = 1$; $x_B^D = x_E^D = 0$) and pure entrainer ($x_E^E = 1$, $x_A^E = x_B^E = 0$) are assumed too. The full details of the system of equations are summarized in the following:

- Mass balance of B (absent compound on the edge AE)

$$V \cdot K_B^r \cdot x_B^r = L \cdot x_B^r + D \cdot x_B^D - E \cdot x_B^E = L \cdot x_B^r$$

$$\frac{L}{V} = K_B^r$$

(Eq. 2)

- Mass balance of A for computing the delta point x_A^Δ as a difference between the entrainer feeding and the distillate product

$$\Delta = D - E$$

$$(D - E) \cdot x_A^\Delta = D \cdot x_A^D - E \cdot x_A^E = D$$

$$E/D = \frac{x_A^\Delta - 1}{x_A^\Delta}$$

(Eq. 3)

- Mass balance for component A at the root point x_A^r on the edge AE to set a relationship between x_A^r and x_A^Δ

$$V \cdot K_A^r \cdot x_A^r = L \cdot x_A^r + D \cdot x_A^D - E \cdot x_A^E = L \cdot x_A^r + (D - E) \cdot x_A^\Delta$$

$$x_A^\Delta = x_A^r \cdot \frac{(K_A^r - K_B^r)}{(1 - K_B^r)}$$

(Eq. 4)

- Relationship between $(L/V)_{TOP}$ at the rectifying section with $(L/V) = K_B^r$ computed for the extractive section

$$L/V_{TOP} = \frac{K_B^r \cdot \frac{E}{D}}{1 - \frac{E}{D}}$$

(Eq. 5)

Important observations can be made from the Eqs. 2-4: (1) the equality between the ratio L/V in the extractive section and the distribution coefficient of the absent compound B at a given E/D according to the Eq. 2. At the root point of the first pinch branch x_A^{r1} that is located at the edge AE, $K_B^r = K_B^{\infty AE}$ and $(L/V)_{\min} = K_B^{\infty AE}(x_A^{r1})$ because S^E is located at x_A^{r1} providing a FER with zero surface. When $E/D > (E/D)_{\min}$, Petlyuk et al. (2015) also demonstrated that $(L/V)_{\max}$

$= K_B^{\infty AE}(x_A^{r2})$. Hence, the Eq. 4 have two roots satisfying the condition $x_A^{r1} < x_A^{r2} < x_A^{\alpha AB=1}$; (2) according to the Eq. 3, $(E/D)_{\min}$ happens when x_A^{Δ} reaches its minimum value; (3) Scanning the molar fraction of A (x_A^{AE}) on the edge AE with $x_A^r = x_A^{AE}$, the trajectory for E/D and x_A^{Δ} versus x_A^r can be computed from the combined Eqs. 3-4 enabling the identification of $(E/D)_{\min}$. The corresponding value of $K_B^{\infty AE}(x_A^r)$ is the $(L/V)_{\min}$ of the extractive section at $(E/D)_{\min}$. Petlyuk et al. [7] highlighted that intersection between the first and the second pinch branch can happen on the edge AE at $x_A^r = x_A^{r1} = x_A^{r2}$ or inside the ternary diagram at $(E/D)_{\min}$. Indeed, different patterns of both pinch branches at $(E/D)_{\min}$ and $(L/V)_{\min}$ can appear even for the most used Serafimov ternary class 1.01-a. For U-shape pinch branches, their intersection occurs at the edge AE when $x_A^{r1} = x_A^{r2}$ at $(E/D)_{\min}$. For other shape types, both pinch branches intersect within the ternary diagram giving a $(L/V)_{\min}$ higher than those related to U-shape patterns. In this work, we assume that all entrainers provide U-shaped patterns in order to simplify the methodology for the entrainer screening.

Methodology for entrainer based on screening on ISS models

A suitable model for vapor – liquid equilibrium of the ternary mixture ABE is required for the application of the ISS method. The variation of the main operating parameters delta point x_A^{Δ} , (E/D) and $R_{\min}$ with the root composition x_A^r on the edge AE can be calculated using the Eqs. 2-5 according to the following algorithm:

1. Scan the edge AE for fixing x_A^r with a fixed step length and setting the composition of the absent compound $x_B^{AE} = 1.10^{-6}$.
2. Compute K_A and $K_B^{\infty AE}$ for each x_A^r by using the thermodynamic model of the ternary mixture
3. Calculate the trajectory of x_A^{Δ} for each x_A^r using Eq. 4.
4. Calculate $(E/D)_{\min}$ for each x_A^r by the Eq. 3.
5. Find the $x_{A,\min}^r$ corresponding to the minimum of the curve x_A^{Δ} and $(E/D)_{\min}$.
6. Set $(L/V)_{\min} = K_B^{\infty AE}(x_{A,\min}^r)$ of the extractive section.
7. Calculate the minimum reflux $R_{\min}$ for the rectifying section using Eq.5.
8. Set the potential candidate list with the entrainers providing low values of $(E/D)_{\min}$ and $R_{\min}$.

Case study

In this section, we compare the entrainers for the separation of acetone – methanol by extractive distillation. Benchmark entrainers water and DMSO are compared with ethylene glycol as a new potential candidate according to the optimization results published elsewhere [4]. Computation of the distribution coefficients K_A and K_B on the edge AE were carried out by using the Simulis Thermodynamics® property server package and services available in Excel [9]. The extended Antoine equation was selected for computing the vapor pressure with the coefficients available from the DIPPR database. UNIQUAC model for the ternary mixture ABE was applied with the binary interaction parameters (BIP) available in ASPEN Plus V7.3 for water and DMSO. UNIFAC modified model was used for predicting the BIP of the binary mixture of acetone - EG and methanol - EG in Simulis Thermodynamics® property server. Table 1 displays the BIP of the UNIQUAC model for all binary mixtures considered in the case study.

Table 1. Binary interaction parameters of the UNIQUAC model

BIP (cal/mol)	acetone(i) methanol(j)	acetone(i) water(j)	methanol(i) water(j)	acetone(i) DMSO(j)	methanol(i) DMSO(j)	acetone(i) EG(j)	methanol(i) EG(j)
A_{ij}	431.231	6205.2	-860.216	125.058	-257.068	139.261	-236.875
A_{ji}	-104.51	-3203.76	640.139	40.510	-46.670	175.48	478.52
$A(T)_{ij}$	0	-17.1	2.119	0	0	0.8778	2.659
$A(T)_{ji}$	0	9.606	-1.279	0	0	-0.14E-06	-6.73E-06

Figure 3 shows the trajectories of the distribution coefficients K_A^{AE} and $K_B^{\infty AE}$ along with the delta point x_A^{Δ} and the ratio E/D on the edge AE. The curve x_A^{Δ} always exhibits a minimum value for any types of extractive regions described by Petlyuk et al. [7]. The minimum value of x_A^{Δ} is directly connected to the minimum E/D and it is located in the positive y-axis when $(E/D)_{\min} < 1$ (displayed only for ethylene glycol in Fig. 3). This feature is not always valid for the curve $K_B^{\infty AE} = (L/V)_{\min}$ even for the well-known Serafimov class 1.01-a [7]. However, even if the curve of $K_B^{\infty AE}$ does not have a minimum at $(E/D)_{\min}$, the condition $K_B^{\infty AE} = (L/V)_{\min}$ is unchanged. In general, a low molar fraction $x_A^{\alpha AB=1}$ at the intersection of the curve $\alpha_{AB}=1$ on the edge AE provides $(E/D)_{\min} < 1$. But, depending on the thermodynamic model, similar values of $x_A^{\alpha AB=1}$ can be associated with different $(E/D)_{\min}$ even for the same ternary mixture. It is the case of EG where the use of the UNIFAC original model and the UNIQUAC model (this work) provided $(E/D)_{\min}$ of 1.006 and 0.78, respectively for similar $x_A^{\alpha AB=1} (\approx 0.87)$. It can be explained by the topological

difference of the portrait of the isovolatility curves resulting from each model (not shown here). We tested several thermodynamic models for water and DMSO and found that a low value of $x_A^{\alpha_{AB}=1}$ is generally linked to $(E/D)_{\min} < 1$. Table 2 displays the parameters computed by the ISS method which can be used for entrainer comparison as well as the criteria concerning the driving forces DF_A^{AE} and DF_B^{BE} proposed in previous paper [4].

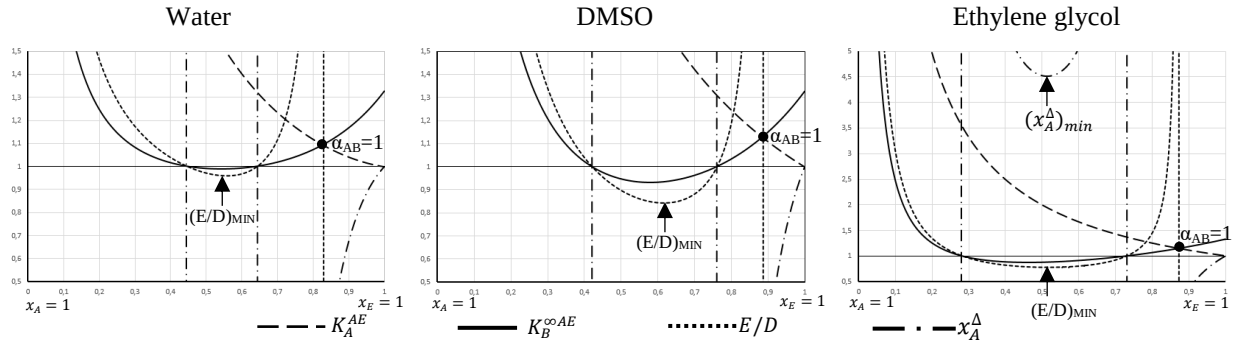


Fig. 3 Trajectories of distribution coefficients, E/D ratio and delta point composition vs composition root x_A^{r1} .

Table 2. Parameters computed by the ISS method allowing entrainer comparison

Entrainers	$T_b(K)$	ΔH_{vap} (kJ/mol)	$x_A^{\alpha_{AB}=1}$	DF_A^{AE} $ y_A - x_A _{AE}$	DF_B^{BE} $ y_B - x_B _{BE}$	$K_B^{\infty AE}$	$(x_A^{\Delta})_{\min}$	$(E/D)_{\min}$	$R_{\min}$	$(E/D)_{OP}$	R_{OP}
Water	273	40.8	0.172	0.6308	0.3843	0.9884	24.54	0.9592	2.3256	3.11	2.46
DMSO	462	43.8	0.115	0.8016	0.6883	0.9339	6.326	0.8419	1.3507	1.5	1.41
EG	470	64.5	0.129	0.9104	0.8284	0.8895	4.5998	0.7826	0.9678	1.63	1.45

According to the results in Table 2, all criteria classify water as the worst entrainer. Water has the highest values of $x_A^{\alpha_{AB}=1}$, $(E/D)_{\min}$ and $R_{\min}$ as well as the lowest driving forces (DF_A^{AE} , DF_B^{BE}). EG matches all criteria for the best entrainer except for $x_A^{\alpha_{AB}=1}$. This entrainer exhibits the lowest $(E/D)_{\min}$ and $R_{\min}$ along with the highest driving forces. Optimization results also show that limiting values of E/D and R have a good agreement with the computed optimal values. Hence, they can be used as initial values in optimal design study. Figure 4 displays the first and the second pinch branch calculated at different values of $(E/D)_{\min}$ for all entrainers by combining equations 3 and 4. Once E/D is fixed, the x_A^r satisfying the Eq.4 is computed where $(L/V) = K_B^r$. Indeed, x_A^r corresponds to the molar fraction of A at the location of S^E on the first pinch branch when $R_{\min} < (L/V) < R_{\max}$. One can observe that all pinch branches in Fig. 4 follows the U-shape type and they intersect each other at N_e^+ when $(E/D) = (E/D)_{\min}$. When $(E/D) < (E/D)_{\min}$ both pinch branches go inside the ternary diagram and becomes one pinch branch linking the B vertex with the azeotrope AB. Hence, the extractive distillation process becomes infeasible because the saddle point S^E vanishes and no pinch branch connects the vertex B with the extractive element on the edge AE.

Optimization studies were carried out in a previous work by Cignitti et al. [4] including the optimization of two objective functions: TAC and the ratio of the total energy consumption to total distillate flowrate. Water was confirmed as the worst entrainer allowing the separation of three compounds with 31.4% greater of energy consumption and 35.5% of TAC than DMSO (best entrainer). Indeed, the extractive column for water requires the double of equilibrium trays compared to the DMSO process as well as higher values of $(E/D)_{OP}$ and R_{OP} . Conversely, DMSO beats ethylene glycol (EG) by a small difference of energy consumption (-2.8%) and TAC (-4%). Acetone is withdrawn in the distillate with less total number of trays for DMSO (41 vs 58 for EG), slightly lower entrainer flowrate $(E/D)_{OP}$ and similar reflux ratio R_{OP} (see Table 2). Even if DMSO resulted as the best option from the optimisation study, the final choice must be guided by the health, safety and environment of the entrainer.

Finally, the good agreement between the entrainer ranking proposed by ISS method and the optimization study demonstrates that the ISS method can be associated to existing criteria for entrainer's comparison relying on the whole ternary phase equilibrium. The values of $(E/D)_{\min}$ and $R_{\min}$ calculated from ISS method are directly related to the entrainer efficiency for separating the azeotrope AB in the extractive distillation column only. Therefore, the driving force DF_B^{BE} has to be used as an additional criterion to assess the ease of separation of the compounds BE in the second distillation column. The criterion related to the intersection of the univolatility line at the edge AE given by the value

$x_A^{\alpha AB=1}$ can be neglected due to the mismatch with $(E/D)_{\text{MIN}}$ values calculated by ISS method. The initial list of potential candidates may be composed by entrainers having low values of $(E/D)_{\text{MIN}}$ and $(L/V)_{\text{MIN}}$ as well as high driving forces DF_A^{AE} and DF_B^{BE} .

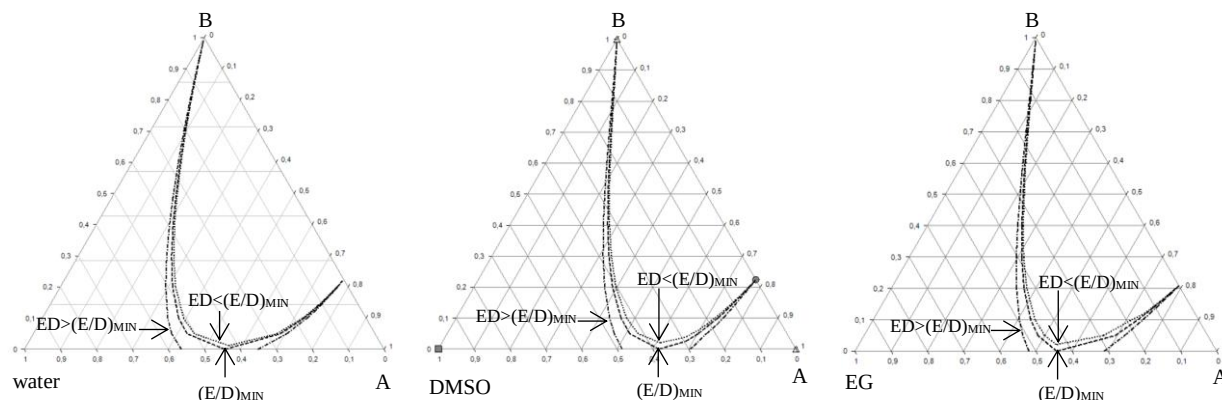


Fig. 4 Pinch branches at several (E/D) computed by the ISS method.

Conclusion

The short-cut method of infinite sharp splits (ISS) developed for conceptual design of extractive distillation columns was extended to entrainer selection along with the driving force criteria that all are based on the calculation of the ternary phase equilibrium. A simplified mass balance around the extractive section with infinite height allows computing the minimum value of the entrainer flowrate and the reflux ratio by only applying the thermodynamic model of the ternary mixture on the binary edge AE where compound B is at infinite dilution. The proposed methodology was applied for separating the minimum boiling azeotrope acetone – methanol with the benchmark high boilers water and DMSO in addition to ethylene glycol as a new potential candidate. The entrainer ranking based on the values of $(E/D)_{\text{MIN}}$ and R_{min} computed from ISS method along with the driving force criteria showed a good agreement with the entrainers permitting the separation with low energy consumption and TAC. The concepts described here can contribute to develop an improved framework for computer-aided molecular design of potential entrainer candidates based on integrated process/product design approach. Similar to the ISS method, the framework can be generalized to other types of ternary mixtures fitting with feasible Serafimow class diagrams for extractive distillation process.

References

1. V. Gerbaud, I. Rodriguez-Donis, L. Hegely, P.Lang, F. Denes, X. You, *Review of extractive distillation. Process design, operation, optimization and control*, Chemical Engineering Research and Design, 2019, 141, 229–271.
2. S. Kossack, K. Kraemer, R. Gani, W. Marquardt, *A Systematic Synthesis Framework for Extractive Distillation Processes*, Chemical Engineering Research and Design, 2008, 86, 781-792.
3. S. Brüggemann, W. Marquardt, *Shortcut methods for nonideal multicomponent distillation: 3. Extractive distillation columns*, AIChE J, 2004, 50, 1129–1149.
4. S. Cignitti, I. Rodriguez-Donis, J. Abildskov, X. You, N. Shcherbakova, V. Gerbaud. *CAMD for entrainer screening of extractive distillation process based on new thermodynamic criteria*, Chemical Engineering Research and Design, 2019, 147, 721-733.
5. S.G. Levy, D.B. Van Dongen, M.F. Doherty, *Design and synthesis of homogeneous azeotropic distillations. 2. Minimum reflux calculations for nonideal and azeotropic columns*, Industrial and Engineering Chemistry Fundamentals, 1985, 24, 463-474.
6. J.P. Knapp and M.F. Doherty, *Minimum entrainer flows for extractive distillation: A bifurcation theoretic approach*, AIChE J., 1994, 40, 243-268.
7. F. Petlyuk, R. Danilov, J. Burger, *A novel method for the search and identification of feasible splits pf extractive distillations in ternary mixtures*, Chemical Engineering Research and Design, 2015, 99, 132-148.
8. F.Z. Seihoub, PhD thesis *Design et développement des procédés de séparation des mélanges idéaux et non idéaux dans des colonnes de distillation et distillation extractive à cloison*. Université des Sciences et de la Technologie d'Oran Mohamed Boudiaf. Algérie. 2018
9. ProSim S.A., <http://www.prosim.net>.