ENTRAINER SELECTION FOR SEPARATION OF AZEOTROPIC MIXTURES BY DISTILLATION METHODS

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Received: 8 August 2018; Accepted for publication: 10 October 2018

ABSTRACT

Azeotropic or close–boiling mixtures often extrude conventional distillation as a method of separation. Instead, extractive or azeotropic distillations are commonly used to separate azeotropic or close–boiling mixtures. For the design of those separation units, selecting suitable entrainers (solvents) is a key step. The traditional method for solving this problem is to use experimentation which is time consuming and expensive. Currently available selection criteria are inadequate. They contradict one another and often leading to incorrect conclusions. Indeed, for a minimum boiling azeotrope, the existing entrainer selection rules state that one should use a high boiling component that introduces no additional azeotrope, an intermediate boiling component that introduces no additional azeotrope, a component which introduces no distillation boundary between the azeotropic constituents, and either a low boiling component that introduces no additional azeotrope or a component that introduces new minimum boiling azeotrope.

In this work, Aspen Plus simulator was used to propose an entrainer selection procedure based on the criteria: 1) A good entrainer is a component that eliminates the azeotrope easily (i.e. even when it’s concentration is small). 2) A component that yields relative volatilities $\alpha_{AB}$ between the two azeotrope constituents more different from unity in the whole concentration range (0÷1).

Keywords: azeotropic distillation, entrainer selection, relative volatility, entrainer capacity, activity coefficient.

1. INTRODUCTION

The success of a distillation process which separates a binary azeotrope into two pure products, relies on the choice of an entrainer whose selection criteria are related to thermodynamics (selectivity and boiling point) and to process operation (entrainer–feed flow rate ratio, low corrosion, price, toxicity, and high thermal stability) [1, 2].

The entrainer E is introduced to depart the relative volatility $\alpha_{AB}$ as far away from unity as possible. Some entrainers enhance the volatility, while others reduce it [3, 4]. Generally $\alpha_{AB}$ is
calculated from the ratio of the distillation coefficients $K_i = y_i/x_i$, which can be written as follows if the pure liquid fugacity in a reference state is supposed to be equal to the vapor pressure $P_0$ [5]:

$$
\alpha_{ab} = K_a = \frac{y_a}{x_a} = \frac{P_a^0 \gamma_A}{P_b^0 \gamma_B}
$$

(1)

Since the ratio $P_a^0/P_b^0$ is almost constant for small temperature changes, the relative volatility is mainly affected by introducing an entrainer that changes the ratio of the activity coefficients $\gamma_A/\gamma_B$. In the pressure of the entrainer, this ratio is called the selectivity $S_{AB}$:

$$
S_{AB} = \frac{\gamma_A E}{\gamma_B E}
$$

(2)

The traditional method for determining this ratio is to use experimentation which is time-consuming and expensive. In this work the activity coefficients of the components of the azeotropic mixtures are determined by computing with a thermodynamic model (here the NRTL model was chosen).

At infinite dilution in the entrainer the selectivity $S_{AB}^{\infty}$ is determined as follows:

$$
S_{AB}^{\infty} = \frac{\gamma_A^\infty E}{\gamma_B^\infty E}
$$

(3)

$S_{AB}^{\infty}$ departures from unity can only provide a preliminary guidance because the selectivity may change as the solute concentration increases. The entrainer capacity for component B can be evaluated from equation (4):

$$
C_{BE}^{\infty} = 1/\gamma_{BE}^{\infty}
$$

(4)

The smaller the value of the activity coefficient $\gamma_{BE}^{\infty}$ is, the stronger are the interactions between component B and the entrainer, which results in a larger capacity.

### 2. Determination of the Activity Coefficients and the Relative Volatility $\alpha_{AB}$ by Simulation Method

In this work the activity coefficients of the components of the azeotropic mixtures are determined by computing with the thermodynamic model NRTL [5]:

$$
\ln \gamma_1 = x^2 \left[ \tau_{21} \left( \frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_1 + x_2 G_{12})^2} \right]
$$

(5)

$$
\ln \gamma_2 = x^2 \left[ \tau_{12} \left( \frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right]
$$

(6)

here

$$
\tau_{12} = (g_{12} - g_{22}) / RT ; \tau_{21} = (g_{12} - g_{11}) / RT ; G_{12} = \exp(-\alpha_{12} \tau_{12}) ; G_{21} = \exp(-\alpha_{12} \tau_{21}) ;
$$

$g_0$-the Gibbs energies.

This model has three independent parameters $\alpha_{12}$, $\tau_{12}$, and $\tau_{21}$. The NRTL model usually represents binary equilibrium data quite well with its three parameters. It is superior to the
Wilson and UNIQUAC in that, it is applicable to a multicomponent system with three phases Liquid–Liquid–Vapor.

The equilibrium flash distillation model is very simple and was used to investigate the changes of the activity coefficients which are a function of the solute concentration and the entrainer - feed flow rate ratio S/F. The flash distillation process is shown in Fig.1.

![Equilibrium Flash Separation](image)

Figure 1. Equilibrium Flash Separation.

To propose an entrainer selection procedure the following case studies were considered. A proposal of entrainer selection procedure will be based on the results of the computation of the activity coefficients of the azeotropic mixture components for those case studies:

2.1. Case study 1: Separation of the minimum boiling system Ethanol–Water with Benzene as the entrainer

The triangular diagram of this system is shown in Figure 2. In this diagram there are two binary homogeneous azeotropes, one binary heterogeneous azeotrope and one ternary heterogeneous azeotrope. There are three interior distillation boundaries in this diagram running from the ternary azeotrope to the three binary azeotropes. The boundaries separate the composition space in three distillation regions, so we can not separate this mixture by traditional distillation method [5]. The activity coefficients of ethanol $\gamma_A$ and water $\gamma_B$ at the different concentration of ethanol and at the different entrainer–feed flow rate ratios S/F are determined by computing with the NRTL model and are presented in Tab.1–3 [6].

![Triangular diagram](image)

Figure 2. Triangular diagram for the separation of Ethanol–Water mixture with Benzene as entrainer, at P = 1 atm.

The calculated values of the relative volatility $\alpha_{AB}$ are also presented in Tab.1-3 and in Fig. 4. Note that the ratio $P_A^0/P_B^0$ is almost constant. The results also show that if the ratio S/F increases the azeotrope moves towards decreasing the ethanol concentration and at the
entainer–feed ratio S/F = 0.6 all values of the relative volatility $\alpha_{AB}$ are smaller than unity. This means that the minimum boiling azeotrope Ethanol–Water was eliminated (Figs 3, 4), and the azeotropic distillation becomes a standard one. The value S/F at which the azeotrope was eliminated, is called the minimum entainer–feed ratio (S/F)_{min}. The elimination of azeotrope opens up many new attractive possibilities in the process synthesis and design for separation of azeotropic systems.

Table 1. Effect of ethanol concentration $x_A$ and entainer–feed ratio on activity coefficients and relative volatility $\alpha_{AB}$ at S/F = 0.1 ($x_E = 0.091$ - concentration of entrainer Benzene).

| $x_A$ | 0.01 | 0.05 | 0.10 | 0.20 | 0.30 | 0.40 | 0.50 | 0.60 | 0.70 | 0.80 | 0.90 | 0.95 | 0.99 |
|-------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| $x_E$ | 0.143| 0.143| 0.143| 0.143| 0.143| 0.143| 0.143| 0.143| 0.143| 0.143| 0.143| 0.143| 0.143|
| $\gamma_A$ | 1.543| 1.527| 1.481| 1.353| 1.228| 1.131| 1.064| 1.021| 0.999| 0.991| 0.995| 1.001| 1.007|
| $\gamma_B$ | 1.135| 1.170| 1.216| 1.327| 1.465| 1.632| 1.827| 2.049| 2.297| 2.571| 2.869| 3.026| 3.156|
| $\gamma_A/\gamma_B$ | 1.359| 1.305| 1.218| 1.020| 0.838| 0.693| 0.582| 0.498| 0.435| 0.385| 0.347| 0.331| 0.319|
| $P^0_A$ (bar) | 0.040| 0.057| 0.085| 0.169| 0.283| 0.404| 0.512| 0.599| 0.666| 0.721| 0.770| 0.794| 0.814|
| $P^0_B$ (bar) | 0.016| 0.022| 0.034| 0.069| 0.118| 0.170| 0.218| 0.256| 0.280| 0.311| 0.332| 0.343| 0.352|
| $P^0_A/P^0_B$ | 2.500| 2.591| 2.500| 2.449| 2.398| 2.376| 2.349| 2.340| 2.329| 2.318| 2.319| 2.315| 2.313|
| $\alpha_{AB} = \gamma_A^0P^0_A/\gamma_B^0P^0_B$ | 3.399| 3.381| 3.045| 2.497| 2.010| 1.647| 1.368| 1.166| 1.013| 0.894| 0.804| 0.766| 0.738|

Table 2. Effect of ethanol concentration $x_A$ and entainer–feed ratio on activity coefficients and relative volatility $\alpha_{AB}$ at S/F = 0.6 ($x_E = 0.375$ - concentration of entrainer Benzene).

| $x_A$ | 0.01 | 0.05 | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 | 0.95 | 0.99 |
|-------|------|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| $x_E$ | 0.375| 0.375| 0.375| 0.375| 0.375| 0.375| 0.375| 0.375| 0.375| 0.375| 0.375| 0.375| 0.375|
| $\gamma_A$ | 1.136| 1.115| 1.092| 1.058| 1.037| 1.029| 1.033| 1.047| 1.071| 1.104| 1.146| 1.169| 1.189|
| $\gamma_B$ | 2.684| 2.756| 2.856| 3.09| 3.372| 3.703| 4.085| 4.519| 5.008| 5.549| 6.14| 6.451| 6.706|
| $\gamma_A/\gamma_B$ | 0.423| 0.405| 0.382| 0.342| 0.308| 0.278| 0.253| 0.232| 0.214| 0.199| 0.187| 0.181| 0.177|
| $P^0_A$ (bar) | 0.33| 0.342| 0.356| 0.385| 0.413| 0.441| 0.468| 0.495| 0.525| 0.56| 0.602| 0.628| 0.652|
| $P^0_B$ (bar) | 0.138| 0.143| 0.15| 0.162| 0.174| 0.186| 0.198| 0.21| 0.224| 0.239| 0.258| 0.269| 0.28|
| $P^0_A/P^0_B$ | 2.391| 2.392| 2.373| 2.377| 2.374| 2.371| 2.364| 2.357| 2.344| 2.343| 2.333| 2.335| 2.329|
| $\alpha_{AB} = \gamma_A^0P^0_A/\gamma_B^0P^0_B$ | 1.012| 0.968| 0.907| 0.814| 0.730| 0.659| 0.598| 0.546| 0.501| 0.466| 0.436| 0.423| 0.413|
Table 3. Effect of ethanol concentration $x_A$ and entrainer–feed ratio on activity coefficients and relative volatility $\alpha_{AB}$ at S/F = 0.8 ($x_E = 0.444$ - concentration of entrainer Benzene).

| $x_A$ | 0.01 | 0.05 | 0.10 | 0.20 | 0.30 | 0.40 | 0.50 | 0.60 | 0.70 | 0.80 | 0.90 | 0.95 | 0.99 |
|-------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| $x_E$ | 0.444 | 0.444 | 0.444 | 0.444 | 0.444 | 0.444 | 0.444 | 0.444 | 0.444 | 0.444 | 0.444 | 0.444 | 0.444 |
| $\gamma_A$ | 1.229 | 1.204 | 1.177 | 1.139 | 1.110 | 1.116 | 1.133 | 1.161 | 1.197 | 1.243 | 1.269 | 1.291 |
| $\gamma_B$ | 3.441 | 3.531 | 3.655 | 3.944 | 4.289 | 4.692 | 5.154 | 5.679 | 6.266 | 6.914 | 7.615 | 7.981 | 8.279 |
| $\gamma_A/\gamma_B$ | 0.357 | 0.341 | 0.322 | 0.289 | 0.260 | 0.237 | 0.217 | 0.200 | 0.185 | 0.173 | 0.163 | 0.159 | 0.156 |
| $P^0_A$ (bar) | 0.378 | 0.385 | 0.395 | 0.414 | 0.432 | 0.451 | 0.471 | 0.493 | 0.519 | 0.551 | 0.593 | 0.619 | 0.644 |
| $P^0_B$ (bar) | 0.159 | 0.162 | 0.166 | 0.175 | 0.183 | 0.191 | 0.200 | 0.209 | 0.221 | 0.235 | 0.254 | 0.265 | 0.276 |
| $P^0_P/P^0_B$ | 2.376 | 2.375 | 2.373 | 2.369 | 2.365 | 2.361 | 2.358 | 2.354 | 2.350 | 2.345 | 2.338 | 2.334 | 2.331 |
| $\alpha_{AB} = \frac{\gamma_A/P_A^0}{\gamma_B/P_B^0}$ | 0.849 | 0.810 | 0.764 | 0.684 | 0.559 | 0.511 | 0.470 | 0.435 | 0.406 | 0.382 | 0.371 | 0.363 |

2.2. Case study 2: Separation of the minimum boiling system Ethanol–Water with Cyclohexane as the entrainer.
The triangular diagram of this system is presented in Fig. 5 [7]. Similarly, the activity coefficients of ethanol $\gamma_A$ and water $\gamma_B$ at the different entrainer - feed flow rate ratios $S/F$ are determined by computing with the NRTL model and the results are presented in Tab. 4 and in Fig. 7.

**Figure 5.** Triangular diagram for the separation of Ethanol–Water mixture with Cyclohexane as the entrainer, at $P = 1$ atm.

**Table 4.** Effect of ethanol concentration $x_A$ and entrainer–feed ratio on activity coefficients and relative volatility $\alpha_{AB}$ at $S/F = 1.8$ ($x_E = 0.643$ - concentration of entrainer Cyclohexane).

| $x_A$  | 0.01 | 0.05 | 0.10 | 0.20 | 0.30 | 0.40 | 0.50 | 0.60 | 0.70 | 0.80 | 0.90 | 0.95 | 0.99 |
|-------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| $x_E$ | 0.643| 0.643| 0.643| 0.643| 0.643| 0.643| 0.643| 0.643| 0.643| 0.643| 0.643| 0.643| 0.643|
| $\gamma_A$ | 2.983| 2.806| 2.622| 2.349| 2.168| 2.053| 1.987| 1.961| 1.998| 2.052| 2.085| 2.113| 2.145|
| $\gamma_B$ | 7.309| 7.546| 7.876| 8.657| 9.61 | 10.751| 12.096| 13.659| 15.438| 17.405| 19.479| 20.504| 21.289|
| $\gamma_A / \gamma_B$ | 0.408| 0.372| 0.333| 0.271| 0.226| 0.191| 0.164| 0.144| 0.127| 0.115| 0.105| 0.102| 0.099|
| $P^0_A$ (bar) | 0.401| 0.4  | 0.4  | 0.399| 0.4  | 0.404| 0.41  | 0.42  | 0.438| 0.465| 0.51  | 0.542 | 0.575|
| $P^0_B$ (bar) | 0.169| 0.169| 0.169| 0.168| 0.169| 0.17  | 0.173  | 0.178 | 0.185| 0.197| 0.217 | 0.231 | 0.245|
| $P^0_A / P^0_B$ | 2.373| 2.367| 2.367| 2.375| 2.367| 2.376| 2.370  | 2.360 | 2.368| 2.360| 2.350 | 2.346 | 2.347|
| $\alpha_{AB} = \frac{\gamma_A P_A^0}{\gamma_B P_B^0}$ | 0.968| 0.880| 0.788| 0.644| 0.534| 0.454| 0.389  | 0.339 | 0.302| 0.271| 0.248 | 0.239 | 0.233|

Note that at the entrainer–feed ratio $S/F = 1.8$ all values of the relative volatility $\alpha_{AB}$ are smaller than unity ($\alpha_{AB} < 1.0$) (Fig. 7), so $(S/F)_{\text{min}} = 1.8$ and at this $(S/F)_{\text{min}}$ the minimum azeotrope Ethanol–Water was eliminated (Fig. 6).
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2.3. Case study 3: Separation of the minimum boiling system Ethanol–Water with n-Pentane as the entrainer

The triangular diagram of this system is presented in Fig. 8 [8]. Similarly, the activity coefficients of ethanol $\gamma_A$ and water $\gamma_B$ at the different entrainer–feed flow rate ratios S/F are determined by computing with the NRTL model and the results are presented Tab. 5 and Fig. 8. Note that in the case of n–Pentane as the entrainer when the entrainer–feed ratio S/F = 0.2 all
values of relative volatility $\alpha_{AB} < 1.0$ so $(S/F)_{\text{min}} = 0.2$ and at this $(S/F)_{\text{min}}$ the minimum azeotrope Ethanol–Water was eliminated (see Figs. 9 and 10).

**Table 5.** Effect of ethanol concentration $x_A$ and entrainer–feed ratio on activity coefficients and relative volatility $\alpha_{AB}$ at $S/F = 0.2$ ($x_E = 0.167$ - concentration of entrainer n-Pentane).

| $x_A$   | 0.01 | 0.05 | 0.10 | 0.20 | 0.30 | 0.40 | 0.50 | 0.60 | 0.70 | 0.80 | 0.90 | 0.95 | 0.99 |
|---------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| $x_E$   | 0.167| 0.167| 0.167| 0.167| 0.167| 0.167| 0.167| 0.167| 0.167| 0.167| 0.167| 0.167| 0.167|
| $\gamma_A$ | 0.246| 0.347| 0.467| 0.652| 0.763| 0.824| 0.888| 0.913| 0.938| 0.967| 0.983| 0.997|
| $\gamma_B$ | 1.621| 1.657| 1.702| 1.806| 1.943| 2.117| 2.323| 2.561| 2.829| 3.127| 3.454| 3.627| 3.77 |
| $\gamma_A/\gamma_B$ | 0.152| 0.209| 0.274| 0.361| 0.393| 0.389| 0.371| 0.347| 0.323| 0.300| 0.280| 0.271| 0.264|
| $P_A^0$ (bar) | 0.015| 0.019| 0.026| 0.051| 0.097| 0.167| 0.254| 0.347| 0.436| 0.517| 0.591| 0.628| 0.657|
| $P_B^0$ (bar) | 0.006| 0.007| 0.010| 0.020| 0.039| 0.068| 0.105| 0.146| 0.184| 0.220| 0.253| 0.269| 0.282|
| $P_A^0/P_B^0$ | 2.500| 2.714| 2.600| 2.550| 2.487| 2.456| 2.419| 2.377| 2.370| 2.350| 2.336| 2.335| 2.330|
| $\alpha_{AB} = \frac{Z_A^0P_A^0}{Z_B^0P_B^0}$ | 0.379| 0.568| 0.713| 0.921| 0.977| 0.956| 0.897| 0.824| 0.765| 0.705| 0.654| 0.633| 0.616|

### 3. COMPARISON OF ENTRAINERS

Although the final selection of entrainers must be determined by means of an economic evaluation in which all variables and criteria are considered for the whole process including the recovery process, screening entrainer at the preliminary stage should consider two aspects: separation enhancement which can be expressed by relative volatility $\alpha_{AB}$ (or selectivity) and entrainer capacity (which can be expressed approximately by entrainer–feed flow rate ratio S/F). For the entrainers Benzene, Cyclohexane, and n-Pentane used in separation of the Ethanol–Water system, the comparison is shown in Tab. 6.

**Figure 9.** Effect of entrainer–feed ratio S/F on relative volatility $\alpha_{AB}$ in Ethanol - Water system with n-Pentane as entrainer.

**Figure 10.** Effect of entrainer–feed ratio S/F on the shift of the azeotropic point in Ethanol–Water system with n-Pentane as the entrainer.
Table 6. Comparison for the entrainers Benzene, Cyclohexane and n–Pentane.

- At the dilute ethanol concentration \( x_F = 0.05 \)

|                | Benzene | Cyclohexane | n-Pentane |
|----------------|---------|-------------|-----------|
| Relative volatility \( \alpha_{AB} \) | 0.968   | 0.880       | 0.568     |
| \((S/F)_{\text{min}}\)    | 0.6     | 1.8         | 0.2       |

- At the concentration range near the azeotrope point \( x_F = 0.85 – 0.95 \)

|                | Benzene | Cyclohexane | n–Pentane |
|----------------|---------|-------------|-----------|
| Relative volatility \( \alpha_{AB} \) | 0.451 ÷ 0.423 | 0.258 ÷ 0.239 | 0.680 – 0.633 |
| \((S/F)_{\text{min}}\)    | 0.6     | 1.8         | 0.2       |

The results show that for dilute ethanol solution \( x_F < 0.1 \) the entrainer n–Pentane is the best. But for concentration range near the azeotrope point, both Cyclohexane and n–Pentane can be chosen as entrainers for the separation of the minimum boiling azeotrope system Ethanol–Water, so the final selection of entrainer must be determined by means of an economic evaluation.

4. CONCLUSIONS

A critical review of four existing entrainer screening rules has revealed that they contradict each other and that none of them can be used reliably for selecting a feasible entrainer and why there is a necessity to propose the entrainer selection procedure. Throughout the results of this work, the procedure has been proposed and includes the following steps:

First of all, the activity coefficients of the key components in the presence of entrainer are determined by computing with one of the thermodynamic models (e.g. NRTL).

Second, the relative volatility between the azeotropic constituent components at the different entrainer - feed flow rate ratios \( S/F \) is determined. From the obtained results, we can determine the value of the ratio \( (S/F)_{\text{min}} \) at which the azeotropic point will be eliminated.

Third, the final entrainer selection for the azeotropic separation is made by the criteria “selectivity” \( \alpha_{AB} \) and “entrainer capacity” \( (S/F)_{\text{min}} \).

The elimination of azeotrope opens up many new attractive possibilities in the process synthesis and design for separation of azeotropic systems.

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