A Heuristic for Extractive Agent Flow Rate in Extractive Distillation

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Distillation is the most widely used separation process for liquids separation in the industry. Even when the volatilities of the mixture are not favorable, then enhanced distillation is used. Extractive distillation is the enhanced distillation most widely used that consists in introducing a large flow rate of a third compound called extractive agent with a high boiling point that it is collected at the column bottoms and recovered in another column and reused again. Some heuristics are available for distillation column design, e.g. the optimum reflux is around 1.2 to 1.35 times the minimum reflux (or 1.1-1.2 times for refrigerated systems). Unfortunately, there is not a similar heuristic to determine the optimum extractive agent flow rate. Based on a literature review of rigorous simulations of extractive distillation processes, a heuristic is proposed that indicates that the optimum extractive distillation flow rate is which provides a Distillation Sequence Efficiency at 78 % of its maximum value. The maximum value is calculated assuming infinite flow rate of extractive agent. The Distillation Sequence Efficiency is a shortcut method available for distillation columns sequencing.

1. Introduction

Distillation is the unit operation most used for liquids separation and the base case reference for all other separation alternatives. Distillation separation driving force is the volatility difference of the mixture compounds. In some cases, the compounds volatility is very close each other and therefore unfavorable for distillation, nevertheless enhanced distillation is also considered for these cases. The enhanced distillation most widely used in the industry is the extractive distillation where a heavy compound with a very high boiling point increases the distillation efficiency acting as extractive agent. In some cases, is not only the preferred option for its simplicity but also the most advantageous, e.g. Liu et al. (2017).

Figure 1 shows a general process scheme for extractive distillation. A mixture of compounds A and B are feed to the first column (extractive column) with mole fractions x_A and x_B respectively. The extractive agent (E) has a greater affinity for B compound that is collected at the first column bottoms and A compound is collected in the distillate. The first column bottoms is a mixture of the separated compound B and the extractive agent with a molar fraction of extractive agent x_E that depends on the extractive agent flow rate feed to the first column. A second column recovers the extractive agent at the bottoms, that is recycled to the first column and the compound B is recovered in the distillate of this second column. The first column distillate temperature corresponds to the boiling point of the compound A, the second column distillate temperature corresponds to the boiling point of the compound B, the first column bottoms temperature depends on the binary mixture composition of B and E and the second column bottoms temperature corresponds to the extractive agent boiling point. Notice that only the second column temperature depends on the extractive agent flow rate and as this flow rate increase, this temperature becomes closer to the extractive agent boiling point temperature.
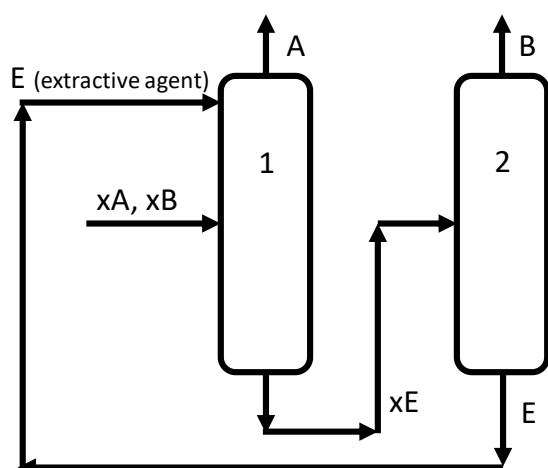
Figure 1: Extractive distillation general process scheme

The extractive agent should be with a high boiling point, thermally stable, economic and non-toxic. The solvent screening is out of the scope of the present study and there are works dealing this issue in literature, e.g. Zhu et al. (2017). Although the extractive agent flow rate used is quite high, it is not detrimental for the process efficiency as it is collected at the distillation column bottoms. Nowadays, there is no rule of thumb or shortcut method to propose a suitable extractive agent flow rate and its value is determined according a tedious trial and error procedure during rigorous simulation of the process. The goal of the present study is to review and analyze different rigorously simulated extractive distillation processes available in the literature to establish a heuristic useful to provide the required flow rate of extractive agent.

2. Methodology

A literature review provides around 600 articles related to extractive distillation and from these 37 are selected according to the popularity classification by Scopus®. The selected articles provide 58 cases where the extractive agent flow rate was provided and rigorous simulations performed. The Distillation Sequence Efficiency (DSE) (Plesu et al., 2015) for this particular case is calculated according to the Eq(1). x_A and x_B are the molar fractions of the compounds A and B respectively in the crude feed. η_1 and η_2 are the Carnot efficiencies of the first and second columns respectively (Eq(2)). T_A, T_B and T_E are the boiling point temperatures of the compounds A, B and E respectively and T is the boiling point of the first column bottoms that depends on the composition of the binary mixture B and E. The DSE efficiency becomes higher as the boiling point temperature of the extractive agent increases, for this reason some authors find advantageous the use of ionic liquids that provide high reboiler temperatures (T_E), e.g. normal boiling point of [EMim]Br IL of 541 K (Graczová et al., 2017).

$$DSE = x_A \cdot \eta_1 + x_B \cdot \eta_2 \tag{1}$$

$$\eta_1 = \frac{T - T_A}{T} \ , \ \eta_2 = \frac{T_E - T_B}{T_E}, \ T = \mathrm{f}(x_E) \tag{2}$$

For DSE∞: $T = T_E$ (3)

DSE assumes that the distillation columns are Carnot heat engines producing separation instead of work. The DSE is determined for all the selected cases under two different assumptions. Firstly, the DSE of the process is calculated assuming that the extractive agent flow rate is infinite, in this way the extraction column bottoms temperature coincides with the extractive agent temperature. The DSE calculated under this assumption is called DSE∞. DSE increases with the boiling point temperature of the extractive agent. Secondly, the DSE of the process is calculated assuming that the extractive flow rate provided by the articles is optimum. In this case, the bottoms boiling point is not the one of the extractive agent, but a lower boiling point corresponding to the mixture of products collected at the bottoms together with the extractive agent. Therefore, the decrease of temperature means that the optimum DSE is lower than DSE∞ previously calculated. Obviously, an infinite extractive agent flow rate is not practical but provides the maximum value reachable. This work provides a procedure to calculate the optimum extractive agent flow rate.

3. Results

A first analysis of the collected data shows that: most of the cases do not use a prefractionator (90 %); ethylene glycol and water are the extractive agents most used (28 and 20 % respectively); many case studies involve the presence of alcohols (72 %). The case studied covers a DSE∞ range from very low values around 3 % to high values of 37 %. When the DSE calculated using the extractive agent from the articles is represented versus the DSE∞, a linear correlation between both variables is observed from low values to 33 % (Figure 2). The optimal DSE is at 78 % of the DSE∞ (Eq(4)) with a correlation coefficient of 0.94. At DSE∞ values higher than 33 %, the optimum DSE remains around 21 %. Notice that for extractive agents with high boiling points, the column bottoms temperature becomes limited by the heating services available. Eq(5) is obtained combining Eq(1) to Eq(4) and isolating the first column bottoms temperature. This temperature is calculated from the crude feed composition and the boiling point of the components present in the mixture. The vapor liquid equilibrium between E and B provides the mole fraction at the first column bottoms. Once calculated the optimal mole fraction of E at the first column bottoms (x_E), the mass balance of E and B to the first column provides the optimal entrainer flow rate w_E related to the crude feed flow rate (w_F), the molar fraction of B in the crude feed (x_B) and the molar fraction of E in the first column bottoms (Eq(6)).

$$DSE = 0.78 \cdot DSE_\infty \tag{4}$$

$$T = f(x_E) = \frac{x_A \cdot T_A \cdot T_E}{0.22 \cdot T_E - 0.22 \cdot T_B \cdot (x_A - 1) + 0.78 \cdot T_A \cdot x_A} \tag{5}$$

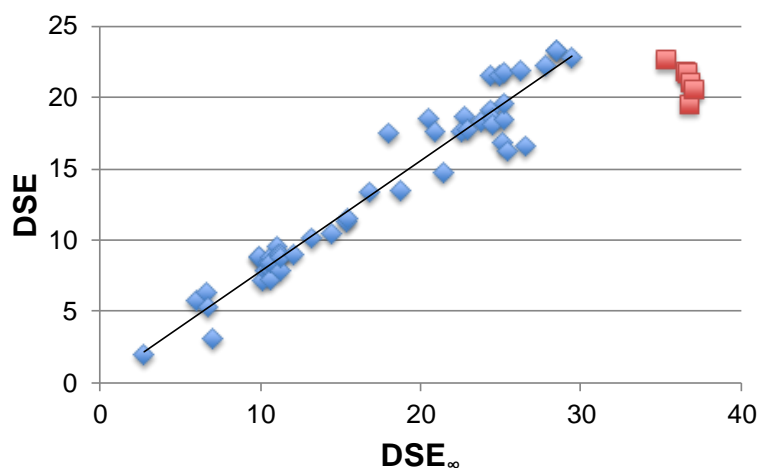$$w_E = w_F \cdot \frac{x_B \cdot x_E}{1 - x_E} \tag{6}$$

Figure 2: Correlation between the DSE and DSE∞

4. Case study

To illustrate the proposed methodology to determine the optimal extractive agent flow rate, an equimolar mixture of acetone (A) and methanol (B) is selected, using water as extractive agent (E) to break the azeotrope between acetone and methanol. The crude feed composition and boiling point of pure compounds are presented in Table 1. The compound B that is collected at the first column bottoms together with the extractive agent is not determined by their boiling point temperatures but using the residue curve maps. When the residue curves approach to the pure extractive agent stable node, they deviate towards the binary edge for which the extractive agent has a greater chemical affinity: this is the compound that will be collected at the bottoms together with the extractive agent (Figure 3). In the case study selected, methanol is collected together with water because methanol is more polar than acetone and hence has a greater chemical affinity with water. The first step is to determine the optimal first column bottoms temperature according to Eq(5) obtaining a temperature of 346.2 K (Eq(7)). Figure 4 shows that this temperature corresponds to a molar fraction of E of 0.78, that substituted in Eq(6), provides an optimum flow rate of extractive agent that is 1.8 times the crude feed flow rate. It is usual for the extractive distillation that the extractive agent flow rate is higher than the crude feed flow rate.
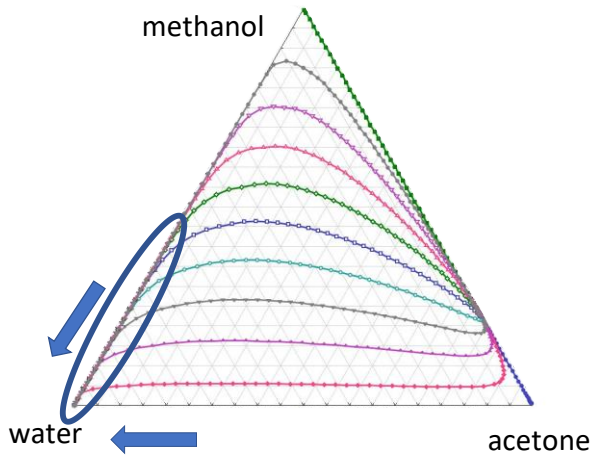
Figure 3: Residue curve map for acetone-methanol-water mixture (plot using Aspen Plus®)

Table 1: Crude feed composition and boiling point temperatures of pure compounds

Crude feed	Value
x_A	0.5
x_B	0.5
T_A [K]	329.3
T_B [K]	337.7
T_E [K]	373.2

Therefore, from Eq(5): $T = \frac{x_A \cdot T_A \cdot T_E}{0.22 \cdot T_E - 0.22 \cdot T_B \cdot (x_A - 1) + 0.78 \cdot T_A \cdot x_A} = \frac{0.5 \cdot 329.3 \cdot 373.2}{0.22 \cdot 373.2 - 0.22 \cdot 337.7 \cdot (0.5) + 0.78 \cdot 329.3 \cdot 0.5} = 354K$
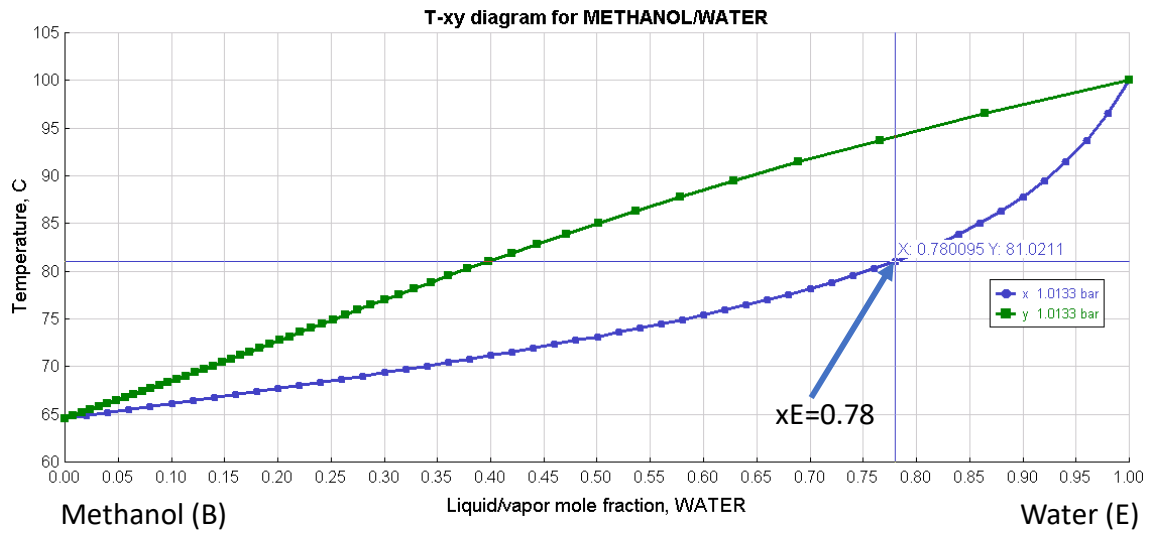

Figure 4: Vapor-liquid equilibrium for methanol-water mixture (plot using Aspen Plus®)

Therefore, from Eq(6): $w_E = w_F \cdot \frac{x_B \cdot x_E}{1 - x_E} = w_F \cdot \frac{0.5 \cdot 0.78}{1 - 0.78} = w_F \cdot 1.8$

5. Considerations about the use of a prefractionator

In some processes, a prefractionation distillation column is used to separate a component that is in large excess respect to the azeotropic composition to break using the extractive distillation (Figure 5). In this section, some guidelines when this prefractionator (column number 0) is advantageous are provided.

The DSE for this process is presented in Eq(7) or Eq(8) depending if the crude feed is richer in compound B or A with respect to the azeotropic composition respectively. The prefractionator bottoms stream is collected with a high efficiency but the efficiency of the other two product streams collected by the distillates becomes lower. Comparing the DSEs with and without prefractionator (Eq(1) and Eq(7)), it is obtained that the prefractionator is favourable when the fraction of compound B collected at the prefractionator bottoms is higher than the value defined by right side of the inequality (Eq(9)). Notice that for the system without prefractionator, the azeotropic composition was irrelevant but when the prefractionator is considered its value defines according to the B mass balance the maximum flow rate that can be collected at the prefractionator bottoms (Eq(10)). Furthermore, the highest Carnot efficiency for the prefractionation column is obtained assuming the azeotrope boiling point temperature (T_{Az}) in the distillate and the boiling point of the compound in excess in the crude feed with respect to the azeotropic composition at the bottoms.
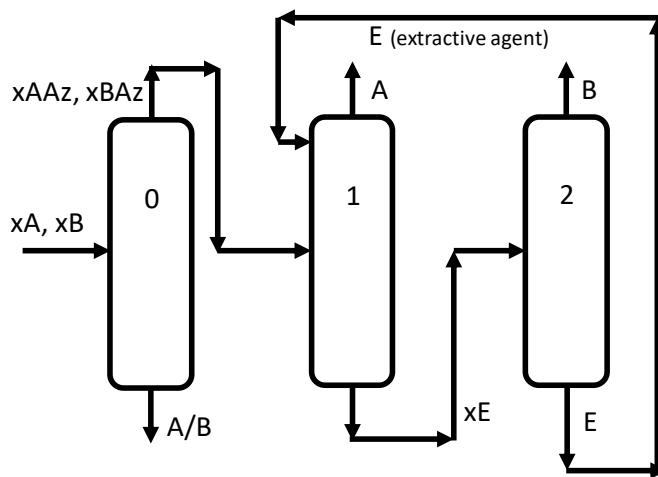

Figure 5: Extractive distillation process scheme with prefractionator

$$DSE = \frac{wB_0}{wF} + x_A \cdot \eta_0 \cdot \eta_1 + (x_B - \frac{wB_0}{wF}) \cdot \eta_0 \cdot \eta_2 \text{ , where } \eta_0 = \frac{T_{Az}-T_B}{T_B} \tag{7}$$

$$DSE = \frac{wB_0}{wF} + (x_A - \frac{B_0}{wF}) \cdot \eta_0 \cdot \eta_1 + x_B \cdot \eta_0 \cdot \eta_2 \text{ , where } \eta_0 = \frac{T_{Az}-T_A}{T_A} \tag{8}$$

$$\frac{wB_0}{wF} \geq \frac{(1-\eta_0)}{(1-\eta_0 \cdot \eta_2)} \cdot [x_A \cdot (\eta_1 - \eta_2) + \eta_2] \tag{9}$$

$$\frac{wB_0}{wF} = \frac{(x_B-x_{BAz})}{(1-x_{BAz})} \tag{10}$$

The case study proposed previously is also used as illustrative example for the prefractionator use. Table 2 provides the azeotropic data for the mixture methanol – acetone. The Carnot efficiencies for each column are calculated assuming the more favourable situation, i.e. azeotrope temperature at column 0 distillate and extractive agent temperature at column 1 bottoms. Carnot efficiencies are 2.7 % (column 0), 11.8 % (column 1) and 9.5% (column 2) that substituted in Eq(9) with the A crude mole fraction of 0.5 (x_A) indicates that wB_0/wF ratio must be higher than 0.10. Eq(10) indicates that the maximum wB_0/wF ratio according to the mass balance is 0.35. Hence, as there is an excess of B with respect to the azeotrope, the possibility of using a prefractionator should be taken into account. Notice that according to Eq(10), as the crude feed composition becomes closer to the azeotropic composition, the use of the prefractionator is less favourable. Although for many cases the prefractionator could be advantageous, in the cases analyzed from the literature the prefractionator is only used when it is clearly advantageous. In the case study selected, the DSE without prefractionator is around 10 % and with prefractionator is similar to the fraction of crude feed collected by the first column bottoms, i.e. 35 %. Figure 6 shows that for compositions close to the azeotropic composition, the prefractionator is not advantageous,

however, as the fraction of compound B increases in the crude feed, the prefractionator becomes more advantageous.

Table 2: Azeotropic composition and boiling point temperature

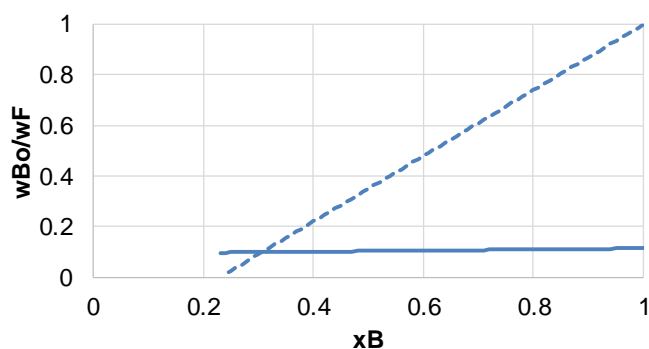| Mixture characteristics	Value
$x_{A,Az}$	0.77
$x_{B,Az}$	0.23
T_{Az} [K]	328.6

Figure 6: Ratio of feed collected at the prefractionator bottoms according to DSE (continuous line) and mass balances (dashed line)

6. Conclusions

The required flow rate of extractive agent for extractive distillation is easily determined based on the distillation sequence efficiency (DSE) of the process. According to rigorous simulations results available in literature, a heuristic is established, providing that the optimum DSE (involving optimum extracting agent flowrate) corresponds to 78 % of the DSE_∞ (calculated assuming an infinite flow rate of extractive agent used). Therefore, for any case study, the optimum extracting agent flowrate value is the one that provides a certain composition of the extractive column bottoms with a boiling point fulfilling the above-mentioned heuristic. A prefractionator to separate part of the compound feed in excess with respect to the azeotrope is only used when the increase of DSE is very important. The above heuristic has been obtained based on the results of 58 cases of the available literature on extractive distillation, and therefore more examples are available to corroborate it in future work.

Acknowledgments

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