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Extending Batch Extractive Distillation Thermodynamic Feasibility Insights to Continuous for Class 1.0-2 Case A

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Abstract. The feasibility of batch and continuous extractive distillation analysis for the separation azeotropic mixtures is addressed. Based on batch feasibility knowledge, batch and continuous separation feasibility is studied under reflux ratio and entrainer flow-rate for a working example ternary system acetone-chloroform-benzene, which belonging to the 1.0-2 class case (a). Possible feasible regions are determined by finding the feasible points based on continuous methodology, they show minimum and maximum feed ratio as a function of the reflux, and a lower bound for the reflux ratio. Later on, simulations verified the feasibility of calculating results based on theoretical methodology.

Keywords: extractive distillation, univolatility line, reflux ratio, feed flow-rate

1. Introduction

The separation of azeotropic and low relative volatility mixtures by extractive distillation is often faced in pharmaceutical and chemical industries. Extractive distillation differs from azeotropic distillation by the fact that the third-body solvent E is fed continuously in another column position other than the mixture feed. Distillation can be operated either in batch mode, suitable for small scale plants and high value added products, to recover several products in single column and specification of the separation task are often changing; or in continuous mode, suitable for large scale plant and as part of a sequence of columns. In addition, the continuous column has a stripping section more than the batch column. For both modes feasibility was investigated separately based on the reflux ratio R and the solvent to feed flow-rate ratio F_E/F for continuous method and a function of R and F_E/V , where V is the vapor flow-rate going up from the boiler, for batch process. In the literature, the continuous mode was investigated for a special case of ternary mixture ABE, class 1.0-1a, where a heavy entrainer is added to separate an azeotropic mixture with minimum azeotrope [1]. The batch operation feasibility was studied under infinite reflux for all 26 Serafimov's classes and found feasible for classes 1.0-1a, 1.0-1b, 1.0-2, 2.0-1, 2.0-2a, 2.0-2b and 2.0-2c [2-4]. We intend to show how information on the feasibility of batch mode could be extended to the feasibility of continuous mode with understanding of limiting values for reflux or feed ratio.

For illustration, a special case of separation of an acetone-chloroform mixture using benzene as a heavy entrainer is selected. which belongs to class 1.0-2 case (a), matching the separation of maximum boiling temperature azeotropes using a heavy entrainer. Acetone and chloroform formed a maximum azeotrope at 65.1°C, and addition of the entrainer benzene in an extractive distillation column enabled to broke the original binary azeotrope [5]. Thermodynamic properties calculations are carried out by Simulis®thermodynamics and rigorous simulation with ProSim Plus® [6].

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2. Batch mode thermodynamics feasibility criteria

Batch extractive distillation of acetone-chloroform by adding benzene illustrates the case (a) when the univolatility line α_{AB} reaches the binary B-E side. Case (b) is not shown here and concern mixtures where the univolatility line α_{AB} reaches the binary A-E side. As shown in Fig.2, both original components A and B are unstable nodes, the entrainer (E) is the stable node, while the maximum boiling azeotrope $T_{\max} \text{azeo}_{AB}$ is a saddle point. The rcm stable separatrix, so-called distillation boundary, links the azeotrope to E. The univolatility curve $\alpha_{AB} = 1$ starts at $T_{\max} \text{azeo}_{AB}$ until it intersects the B-E side at the so-called x_p point. According to the general feasibility criteria for extractive distillation under infinite reflux [4]: both acetone (A) and chloroform (B) are the most volatile in their respectively region (see volatility order $B > A > E$ and $A > B > E$ in Fig.2a) where there exists a residue curve with decreasing temperature from E to their location. The other univolatility line α_{BE} affects the relative volatility of only component B and entrainer E but does not affect the relative volatility of components A and B and has no incidence for the product cut prediction. Therefore, either A or B are possible distillates of the extractive distillation process. As explained in [4], there is a maximum value $(F_E/V)_{\max, B, R \rightarrow \infty}$ to recover component B whereas no entrainer flow rate restriction applies to recover component A at infinite reflux [7-8] (See $[SN_{\text{extr}, A}]$ and $[SN_{\text{extr}, B}]$ range in Figure 2a).

Figure 2b displays the extractive composition profile for $(F_E/V) < (F_E/V)_{\max, B, R \rightarrow \infty}$, under infinite reflux ratio. Extractive singular points and separatrices behave as previously described. The extractive unstable separatrix links S_{extr} with the node UN_{extr} (vertex E) and a point x_{AB} located on the binary side acetone-chloroform, having an acetone composition of 0.33., pure B can be obtained from the initial charge composition x_{S1} by adding even a small quantity of E. Indeed, x_{S1} lies in the regions I and II where extractive composition profiles reach $[SN_{\text{extr}, B}]$ which is able to cross a rectifying profile reaching the unstable rectifying node vertex B. above $(F_E/V)_{\max, B, R \rightarrow \infty}$, $[SN_{\text{extr}, B}]$ would disappear under composition x_p . In contrast starting from x_{S2} in regions III and IV, all extractive profiles reach $[SN_{\text{extr}, A}]$ whatever the entrainer flowrate and enable to recover distillate x_{DA} .

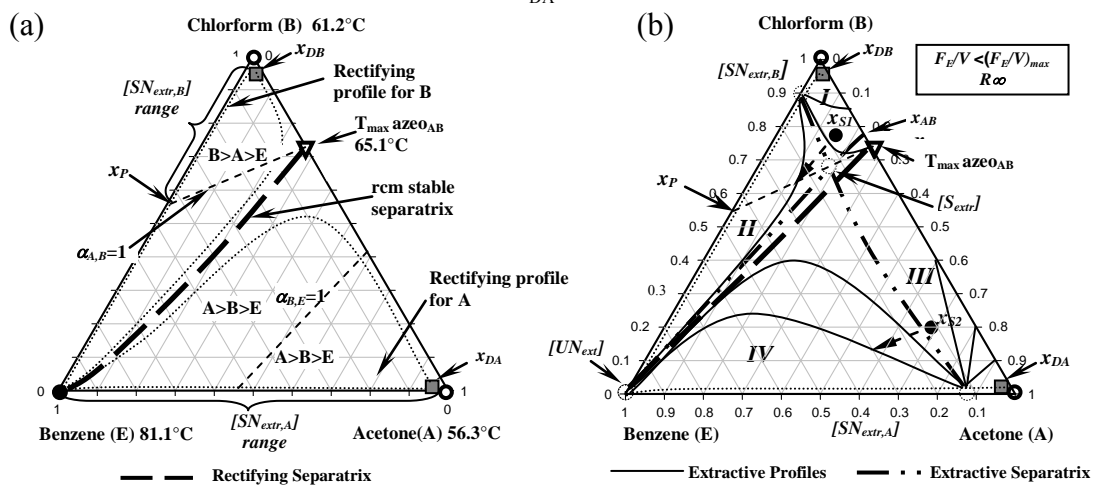


Figure 2. Feasibility analysis of the separation of acetone-chloroform using benzene at infinite reflux ratio: (a) residue curve map (rcm) and (b) extractive composition profile map at $F_E/V < (F_E/V)_{\max}$.

3. Continuous mode feasibility assessment

The feasibility always rely upon intersection for composition profiles in the various column sections (rectifying, extractive, stripping), joining the top and bottom composition, whatever the operation parameter values (reflux, flow-rates...) [9]. Here we use geometrical analysis but mathematical ones could be used as well. The column section profiles are described by the finite differential model of Lelkes et al.:

$$\frac{dx_i}{dh} = \pm \frac{V}{L} \cdot [y(x) - y_i^*] \quad (1)$$

Where V and L are the vapor and liquid flow-rates, the vapor composition y^* in equilibrium with x is computed by the liquid-vapor equilibrium relation and the actual vapor composition y is computed from the mass balance in each column section, depending on the chosen column configuration [10]. Table 1 displays equations derived from the differential equation and mass balance model. There is a direct relation from mass balances between F_E/V in batch and F_E/F in continuous.

Table 1. Column profile equations for three sections

Column section	Rectifying section	Stripping section
Profile equations	$\frac{dx_i}{dh} = \frac{R+1}{R} \cdot \left[\left(\frac{R}{R+1} \right) \cdot x_i + \frac{1}{R+1} \cdot x_D - y_i^* \right]$	$\frac{dx_i}{dh} = \frac{S}{S+1} \cdot \left[\left(1 + \frac{1}{S} \right) \cdot x_i - \frac{1}{S} \cdot x_N - y_i^* \right]$
Column section	Extractive section	
Profile equations	$\frac{dx_i}{dh} = \frac{R+1}{R + \left(\frac{S}{F} \right) \cdot \left(\frac{F}{D} \right)} \cdot \left[\left(\frac{R}{R+1} + \frac{1}{R+1} \cdot \left(\frac{S}{F} \right) \cdot \left(\frac{F}{D} \right) \right) \cdot x_i + \frac{1}{R+1} \cdot x_D - \frac{1}{R+1} \cdot \left(\frac{S}{F} \right) \cdot \left(\frac{F}{D} \right) \cdot x_E - y_i^* \right]$ (Continuous)	
Profile equations	$\frac{dx_i}{dh} = \frac{R+1}{R + (R+1) \cdot \left(\frac{F_E}{V} \right)} \cdot \left[\left(\frac{R}{R+1} + \left(\frac{F_E}{V} \right) \right) \cdot x_i + \frac{1}{R+1} \cdot x_D - \left(\frac{F_E}{V} \right) \cdot x_E - y_i^* \right]$ (Batch)	

4. Simulation results and discussion

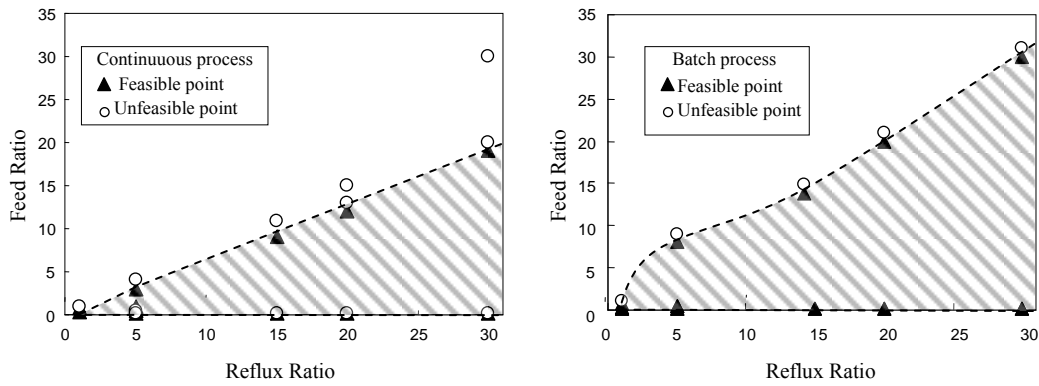


Figure 3. Feed ratio F_E/F as a function of the reflux ratio to recover acetone (A) at $x_F = \{0.9, 0.1, 0\}$: (a) batch extractive distillation (b) continuous extractive distillation

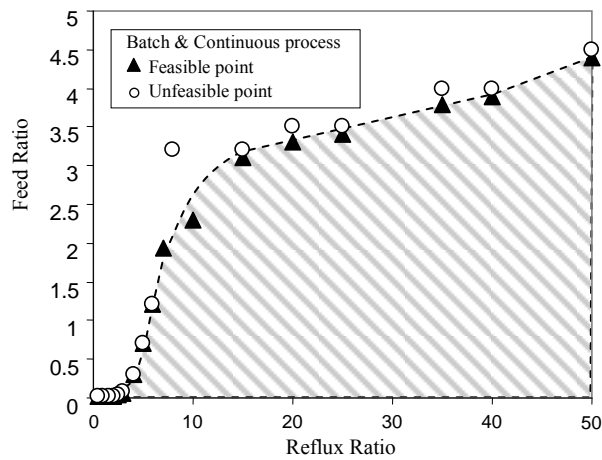


Figure 4. Feed ratio F_E/F versus reflux ratio to recover chloroform (B) for batch and continuous extractive distillation at $x_F = \{0.1, 0.9, 0\}$, $x_E = \{0, 0.3, 0.7\}$

As a consequence of the above theoretical methodology, limiting key operating parameters (entrainer/feed flowrate ratio and reflux ratio) required to obtain a target top and bottom product compositions are obtained by a series of calculation for extractive distillation process of system acetone-chloroform-benzene which are summarized in Fig. 3 (for an acetone distillate) and Fig. 4 (for a chloroform distillate) respectively. Feasible regions (shaded) are sketched by drawing these series of points (Filled Triangle Up represents a feasible point; Open Circle represents an unfeasible point). It can be seen that the feasible region is contained by the minimum and maximum feed ratio as a function of the reflux, and a lower bound for the reflux ratio, which gained based on criteria provided by the theories explained before.

Fig. 3 concerns an acetone (A) distillate. As expected from the infinite reflux analysis there exists a maximum value for F_E above which the process is unfeasible. That maximum gradually reduces as reflux gets smaller, until a minimum reflux. A detailed calculation of the profile map shows that the feasible rectifying section profiles region gets smaller until it can no longer intersect the extractive profile region. The same holds for the continuous mode as a maximum F_E/V in batch translates into a maximum F_E/F in continuous.

However, the batch (Fig. 3a) and continuous mode (Fig. 3b) have a large difference on the maximum value of the feed ratio, because in continuous process the stripping section is now involved and its conditions can limit feasibility, the operations requirement become more rigorous because all of parameters choice need occur over more narrow range.

When distillate is chloroform (B) (Fig. 4), infinite reflux analysis shows no limit for the feed ratio. However when the reflux decreases, an unstable extractive separatrix reduces the feasible region (see [3]), thus setting a maximum value for the feed ratio. Batch and continuous modes display the same features. Similarly to Fig. 3, there is a minimum reflux value below which the separation becomes impossible no matter how big the amount entrainer feed given.

5. Rigorous simulation

Continuous distillation rigorous simulations were carried out with ProSim Plus®, with thermodynamic model UNIFAC modified Dortmund 1993 for all conditions reported in Figure 3 and 4. They agreed with the feasibility analysis based on equations in Table 1.

The separation is performed under continuous entrainer feed, the temperature of mixture is 298K, the column is operated under atmospheric pressure and pure solvent is used. The column consists of three main parts: stages above the entrainer feed stage named rectifying section, stages between entrainer feed and azeotropic mixture feed named extractive section, stages below is stripping section. The column contains 50 theoretical stages (total condenser and reboiler), the entrainer feed in the fifth stage, the mixture feed stage is 25.

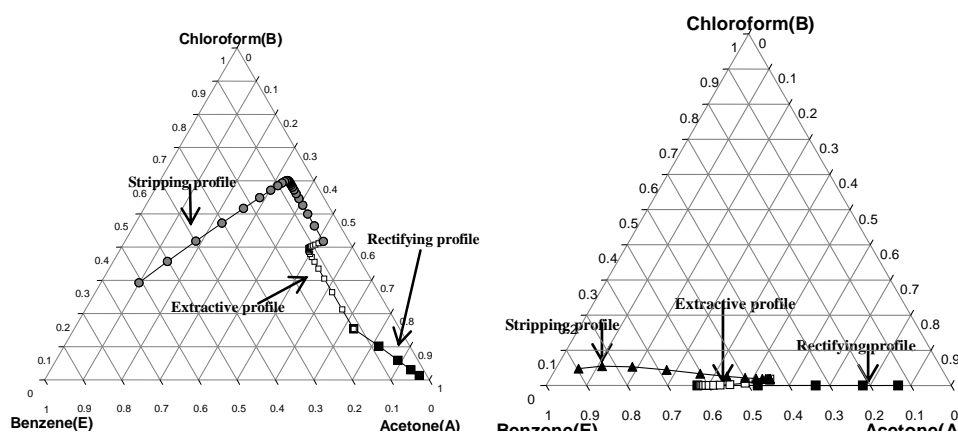


Figure 5. Rigorous simulation results to recover A Reflux ratio($R=5$): (a) feed ratio ($F_E/F=0.2$) and (b) feed ratio ($F_E/F=5$)

Figure 5 show the composition profiles computed from rigorous simulation. A feed rich in acetone (A) $x_F = \{0.1, 0.9, 0.0\}$ is used. The prescribed liquid distillation flow rate is 0.9 kmol/hr to recover acetone as distillate, with a high purity. Reflux ratio($R=5$) and feed ratio ($F_E/F=0.2$). Fig. 5a Results indicate that this process is feasible, because starting from the charge of given composition (x_F) under the given operation conditions the specified distilled composition x_D can be obtained satisfying the necessary and sufficient condition of the feasibility to have at least one possible column profile

connecting still path with the point x_D . Regarding purity, the composition of distillate is {0.0869, 0.9671, 0.1220} compared to residue composition {0.0329, 0.8780, 0.9131}.

However, as it can be expected by the results of feasibility studies above, under the same condition of reflux ratio ($R=5$) but a much larger feed ratio ($F_E/F=5$) (see Fig.5b), the distillate composition x_D , set in the feasibility analysis at 0.99; can not be reached: x_D purity in acetone is 0.87 only. This is in compliance with the result in Figure 3a where these operating parameter values lies in the unfeasible distillation region.

6. Conclusions

Feasibility method based on batch process was extended to the investigation of potential feasible region under the operating parameters reflux ratio (R) and feed ratio (F_E/F , F_E/V) for both continuous or batch process, In the case of the mixture chloroform-acetone using benzene as entrainer, which belong to the ternary diagram class 1.0-2 case a (any binary maximum boiling azeotrope with a heavy entrainer forming no new azeotrope), the univolatility curve $\alpha_{AB}=1$ intersects the B-E edge. The batch feasibility criterion under infinite reflux then states that A or B can be distilled out, depending on the starting composition. However, the process has its best potential for the component that is located in the concave side of the residue curve map (rcm) where the rcm is C-shaped.

At infinite reflux ratio, an unfeasible region occurs (either for component A or component B), because of the extractive unstable separatrix always occurring for this 1.0-2 class. Furthermore, because the $\alpha_{AB}=1$ curve intersects the B-E edge, a maximum entrainer flow rate exists for component B.

For continuous extractive distillation, these results translate well. Regarding the distillation of A, there is still a maximum entrainer flowrate at any reflux, above a minimum reflux value occurring because of the happening of a rectifying profile stable separatrix that limits the feasibility [3]. However, the batch and continuous mode have a difference on the maximum value of the feed ratio, because the continuous feasibility is limited by the stripping profiles region.

Regarding the distillation of A, batch analysis predicts no entrainer limitation under infinite reflux, but there exists one under finite reflux because of the reduction of the rectifying profile region as reflux decreases.

As these observations are corroborated by rigorous simulations, we demonstrate that feasibility analysis based in simple thermodynamic insight (the ternary class, the univolatility line intersect with the diagram) can be exploited to evaluate the feasibility under finite reflux and both for batch and continuous operation.

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