Separation sequencing in batch distillation under closed mode operation

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Abstract— **Separation of multicomponent mixtures using a batch distillation column plays a vital role in chemical industry. Closed mode (total reflux) operation is preferred to improve the separation efficiency. Separation of a multicomponent mixture in closed mode requires multiple binary separation tasks to obtain pure products. This work proposes a novel quantitative approach for sequencing these separation tasks for batch distillation in closed mode. The optimal sequence is identified based on a concept of marginal N_{min} (minimum number of stages), which captures the impact of non-key components on separation. A case study consisting of a ternary mixture is considered to illustrate this method. The proposed approach is verified using a simulation case study, where the overall batch time is used as the performance indicator to define the optimal sequence.**

I. INTRODUCTION

Distillation is one of the most widely used techniques for separating liquid mixtures, and batch distillation is particularly effective for small-scale separation, offering flexibility and a low-cost alternative. In batch distillation, a multicomponent mixture can be separated using a single column, with the desired products collected sequentially in the order of volatility. Traditionally, the separation of a multicomponent mixture involves charging the feed mixture into the reboiler and sequentially withdrawing the distillate fractions in decreasing order of volatility (direct sequence). Alternatively, in an inverse column, the feed is charged to the reflux drum, and the products are sequentially withdrawn from the bottom in an increasing order of relative volatility (indirect sequence). This sequential withdrawal of products, either as distillate fractions or bottom fractions, yields off-specification fractions in between two product cuts, known as slop. This slop formation during the separation of a multicomponent mixture results in increased energy consumption and material losses, thereby reducing the overall efficiency of the separation process [1]. To eliminate these slop cuts, a total reflux operation, also known as a closed operation, has been proposed in the literature [2], [3]. In total reflux operation, the separation of a N-component mixture into pure products in a batch configuration is accomplished through different sequences that involve distinct operational phases. At each operational phase, a binary separation is considered. Hence, one possible sequence begins with the most volatile component in the first phase removed as distillate. The bottom fraction left is then sent to the next phase for separation. In this phase, the intermediate component is removed as distillate, and the heaviest component is removed as the bottom product in the last phase. Alternatively, the separation can start with the heaviest component as the bottom product in the first phase. The distillate fraction left is then sent to the next phase for separation. In this phase, the intermediate component is removed as the bottom product, and the most volatile component is removed as the distillate in the last phase. These different approaches result in different separation sequences. These sequences produce the same amount of overall product but differ in the amount of individual products, capital, and operating costs. Hence, in the context of design of batch distillation operating in total reflux mode, there is a need to find an efficient and systematic way to determine the optimal separation sequence.

There are very few studies that focus on the separation sequencing of batch distillation. Existing studies, primarily based on sequencing in continuous distillation, have emphasized heuristic [4] or rigorous optimization [5] approaches. Modi and Westerberg [6] introduced a column sequencing approach based on marginal price. The method evaluates the marginal price by comparing the minimum cost of performing a split in the absence of non-key components with the corresponding cost when those components are present. Sharma and Jogwar [7] extended the marginal vapor rate method, originally developed for sequencing of continuous distillation, to multicomponent batch distillation in open mode, i.e., with finite reflux and product removal. The unsteady nature of batch distillation was addressed by approximating the batch distillation process as a sequence of continuous distillation tasks with varying feed compositions. Using Underwood's equations, the instantaneous vapor requirement was estimated and integrated over the batch time to obtain the total vapor required for a given separation task. The marginal total vapor for a sequence was then determined by summing the marginal vapor of all individual separation tasks. Finally, the sequence with the lowest marginal total vapor was recommended as the optimal sequence. The method is mainly used for batch distillation systems operated under finite reflux, as it relies on Underwood's equation to determine the minimum vapor rate. However, operating the batch column in total reflux implies an infinite reflux ratio, and Underwood's equation becomes irrelevant. Hence, the marginal total vapor method is not useful in determining the optimal sequence for batch processes operating under total reflux. Motivated by this, the present work proposes a separation-sequencing approach based on a novel concept of marginal minimum number of stages (marginal N_{min}) for total-reflux operation. The proposed quantitative approach is

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simple and can be evaluated quickly.

In this article, the separation of a ternary mixture using batch distillation under closed mode operation is discussed. In the next section, the methodology for the marginal N_{min} approach is presented. A case study consisting of pentane, hexane, and heptane is considered to illustrate the method. To verify the methodology, dynamic simulations are carried out where the overall batch time is used as a performance metric to identify the best sequence.

II. Marginal N_{min} Approach

In separation-sequencing approaches, the optimal sequence is determined by a design variable that quantifies the difficulty of separation. In the marginal price method [6], the difficulty of separation was evaluated using the vapor rate, which depends on the minimum reflux ratio determined using Underwood's equation. For batch distillation columns operating under open mode, the total amount of vapor is employed as a measure of separation difficulty [7]. This approach also relies on Underwood's equations to estimate the vapor amount corresponding to each separation task. For batch columns operated under total reflux, the reflux ratio becomes infinite; hence, Underwood's equation becomes irrelevant for such a system. Therefore, for these systems, there is a need to have an alternative design variable to represent the difficulty of separation. The proposed approach considers the minimum number of stages (N_{min}) as a measure to quantify the difficulty of separation. Similar to the marginal total vapor method, the proposed approach considers the marginal N_{min} for the separation sequencing to obtain the optimal sequence. The marginal N_{min} is defined as the difference between the minimum number of stages required to perform a task in the presence of non-key components and the minimum number of stages in their absence. The objective of this separation sequencing approach is to identify the optimal sequence in terms of N_{min}. The sequence that is least affected by the presence of non-keys is considered the most effective sequence.

In this work, this methodology is developed and illustrated for a ternary mixture. A conventional batch distillation (CBD) column operating under total reflux can separate two components (light-key and heavy-key) simultaneously. Hence, to separate the N-component mixture into pure products in a conventional batch distillation column requires a sequence of $(N-1)$ binary separation tasks. The number of such sequences (N_s) can be computed as [8].

$$N_s = \frac{[2(N-1)]!}{N!(N-1)!} \tag{1}$$

Using equation (1), a ternary mixture (ABC), with A being the most volatile component, and component C being the heaviest component, yields two possible separation sequences, which are listed in Table I. The respective configurations for the direct and indirect sequences are shown in Figures 1 and 2.

TABLE I: Sequences for ternary mixture

Sequence	Sequence name	Phase 1	Phase 2
1	Direct	A/BC	B/C
2	Indirect	AB/C	A/B

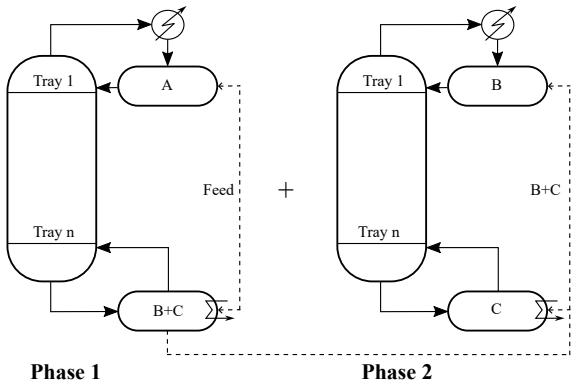

Fig. 1: Direct Sequence

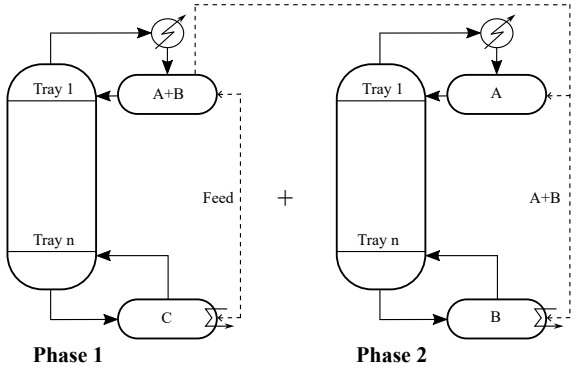

Fig. 2: Indirect Sequence

For each sequence, two operational phases are carried out under total reflux conditions, during which the products accumulate either in the reflux drum or in the reboiler. Fig. 1 represents the direct sequence where the most volatile component (A) is recovered as the overhead product and collected in the reflux drum in the first operational phase, and the residue, which consists of intermediate component (B) and the heaviest component (C), is retained as the bottom product in the reboiler. The residue in the reboiler is then fed to the second operational phase, where the intermediate component (B) is recovered as the overhead product in the reflux drum, while the heaviest component (C) is obtained as the bottom product in the reboiler. Similarly, the Fig. 2 shows the indirect sequence where the heaviest component (C) is recovered as the bottom product in the reboiler in the first operational phase, while the overhead distillate, containing the intermediate component (B) and the most volatile component (A), is accumulated in the reflux drum. The collected distillate is then fed to the second operational phase. In this second phase, the intermediate component (B)

is recovered as the bottom product in the reboiler, whereas the most volatile component (A) is collected as the overhead product in the reflux drum.

A. Marginal N_{min} Approach for Ternary mixture

The minimum number of stages (N_{min}) for total reflux operation can be computed using the Fenske equation, as:

$$N_{min} = \frac{\log\left[\left(\frac{x_{D,LK}}{x_{B,LK}}\right)\left(\frac{x_{B,HK}}{x_{D,HK}}\right)\right]}{\log\left(\frac{\alpha_{LK}}{\alpha_{HK}}\right)} \tag{2}$$

Here, x represents mol fraction, α represents volatility, and subscripts LK, HK, B, and D represent light key, heavy key, bottom, and top product, respectively. For a ternary mixture (ABC), the composition values in the Fenske equation correspond to the product and the residue compositions for the first operational phase. To get these composition values, material balance over the column is conducted. For a given amount of feed (F), the total amount of feed is initially distributed among the distillate vessel (D), the bottom vessel (B), and the trays (T). It is considered that during any operational phase, a specified fraction of the total feed gets accumulated on the trays and contributes towards tray holdup (T). In this method, this is specified as a percentage of the total feed. The overall material balance is given as,

$$F = D + B + T \tag{3}$$

Here, F, D, B, and T represent the total amount of feed, distillate vessel holdup, bottom vessel holdup, and tray holdup, respectively. The balance for component i is given by,

$$Fx_{Fi} = Dx_{Di} + Bx_{Bi} + T_i \qquad \forall i \in A,B \tag{4}$$

where x_{Fi}, x_{Di}, x_{Bi}, and T_i represent feed composition, distillate composition, bottom composition, and total amount of component i on trays, respectively. Along with this, the following summation constraints are also applicable

$$\sum_{i=A}^{C} x_{Bi} = 1 \tag{5}$$

$$\sum_{i=A}^{C} x_{Di} = 1 \tag{6}$$

$$\sum_{i=A}^{C} T_i = T \tag{7}$$

It can be noted that these material balance equations have five degrees of freedom. These are specified as follows. The desired purity is specified for each product. It is considered that the product stream contains only light key and heavy key components, and a non-key component is accumulated in the residue vessel and trays. The remaining three degrees of freedom are specified as the recoveries of the three components.

Let us illustrate this for the first operational phase, A/BC of the direct sequence. For this operational phase, the first product is the most volatile component (A), which is accumulated in the reflux drum. Hence, for the distillate compositions based on the desired purity constraint, the value of x_{DA} is specified as the desired product purity, and the value of x_{DC} is taken as zero. Since the composition values of x_{DA} and x_{DC} are known, the value of x_{DB} can be determined using the summation constraint given in equation (6). For this operational phase, by specifying the recovery of the most volatile component (A), the distillate amount can be computed as,

$$D = \frac{R_A F x_{FA}}{x_{DA}} \tag{8}$$

where, R_A represents recovery of component A.
From equation (3),

$$B = F - D - T \tag{9}$$

Hence, using this bottom vessel holdup, the bottom composition values for components B and C are determined by incorporating the recoveries of components B and C as:

$$x_{Bi} = \frac{R_i F x_{Fi}}{B} \qquad \forall i \in B,C \tag{10}$$

Lastly, using these composition values of x_{BB} and x_{BC}, the value of x_{BA} can be determined using the summation constraint given in equation (5). For simplicity, the recovery values of the light and heavy key components are considered to be equal. The recovery value of A or B is taken, such that $x_{BA} > 0$. To maintain this non-zero value, a minor portion of non-key component C is taken on trays, which makes the recovery of non-key component less than 100%.

Finally, using equation (2), the N_{min} in the presence of the non-key component C is determined for the operational phase A/BC. To obtain the N_{min} in the absence of the non-key component, the feed amount is updated by removing the non-key component. The desired purity for the products and the recovery values for the key components are kept the same as those used in the presence of the non-key component.

For the A/BC operational phase, the A/B separation is treated as the split carried out in the absence of component C. Hence, using the same purity and recovery values for A/B as those used for the A/BC phase, the distillate compositions and distillate holdup remain unchanged. However, the bottom composition and the bottom vessel holdup will vary. The bottom vessel holdup is found using equation (9), and using this value, the bottom composition for x_{BB} is calculated as,

$$x_{BB} = \frac{R_B F x_F}{B} \tag{11}$$

Using the summation constraint, x_{BA} is evaluated, and the N_{min} for the split A/B is obtained using these composition values. Hence, the marginal N_{min} for the operational phase A/BC is obtained as,

$$MN_{min}(A/BC) = N_{min}(A/BC) - N_{min}(A/B) \tag{12}$$

Similarly, the marginal N_{min} for operational phase AB/C of the indirect phase can be computed. For the operational phase 2 of both the direct and indirect sequences, no non-key component is present. Hence, the marginal N_{min} for these phases is zero. Therefore, the overall marginal N_{min} for the direct and indirect sequence for a ternary mixture is the marginal N_{min} for the first operational phase of the sequences. It can be argued that the recovery values corresponding to operational phase 1 of the direct or indirect sequences need not be identical. Hence, to establish a uniform comparison, the marginal N_{min} per unit recovery is obtained by dividing the marginal N_{min} by the corresponding recovery value. Let us denote this as the specific marginal N_{min} (SMN_{min}). Hence, the overall specific marginal N_{min} for direct and indirect sequences are given as,

$$SMN_{min,direct} = \frac{MN_{min}(A/BC)}{R_A} \tag{13}$$

and,

$$SMN_{min,indirect} = \frac{MN_{min}(AB/C)}{R_C} \tag{14}$$

The overall specific marginal N_{min} for both the sequences is compared, and the sequence, which is least influenced by the presence of non-keys, i.e., has the smallest SMN_{min} value, is considered the optimal separation sequence.

III. Case study

Let us consider a ternary mixture consisting of A - Pentane, B - Hexane, and C - Heptane [7] to illustrate the proposed approach. The feed compositions and relative volatility for the mixture are given in the Table II. The initial feed (F = 1000 mol) is allocated to the distillate vessel (D), the bottom vessel (B), and the tray holdup (T). For this case study, the tray holdup is set at 5% of the total feed, and the desired purity of products is considered to be 99%.

TABLE II: Ternary mixture details

Component	Feed (x_F)	α (Relative to C)
Pentane	0.25	7.1352
Hexane	0.50	2.6292
Heptane	0.25	1

For the operational phase A/BC of the direct sequence, $x_{DA} = 0.99$, $x_{DB} = 0.01$, $x_{DC} = 0$. The recovery values of the key components (R_A and R_B) are taken as 0.9401, and the recovery of a non-key component (R_C) is taken as 0.97. Using the proposed approach, as mentioned in section II, we get $x_{BA} = 7.1583 \times 10^{-5}$, $x_{BB} = 0.6596$. Using the Fenske equation, we get

$$N_{min}(A/BC) = \frac{\log\left[\left(\frac{x_{DA}}{x_{BA}}\right)\left(\frac{x_{BB}}{x_{DB}}\right)\right]}{\log\left(\frac{\alpha_A}{\alpha_B}\right)} = 13.7462$$

Now, for split A/B in the absence of non-key component C, Feed (F) = $x_{FA} \times 1000 + x_{FB} \times 1000$ = 750 mol and Tray holdup (T) = 0.05F = 37.5 mol. The same purity specs $x_{DA} = 0.99$ is used for A/B split, and the same recovery values (R_A and R_B) = 0.9401 are taken. Accordingly, we get $x_{DB} = 0.01$, $x_{BA} = 0.0106$, and $x_{BB} = 0.9894$. Using the Fenske equation, we get

$$N_{min}(A/B) = \frac{\log\left[\left(\frac{x_{DA}}{x_{BA}}\right)\left(\frac{x_{BB}}{x_{DB}}\right)\right]}{\log\left(\frac{\alpha_A}{\alpha_B}\right)} = 9.1434$$

Hence,

$$MN_{min}(A/BC) = N_{min}(A/BC) - N_{min}(A/B) = 4.6028$$

and,

$$SMN_{min,direct} = 4.8960$$

Similarly, the overall SMN_{min} for the indirect sequence is obtained as 5.0565. Hence, based on these values, it can be inferred that the direct sequence is least influenced by the presence of non-key component and thus is considered as the optimal sequence.

To verify the proposed approach, dynamic simulations are carried out for both the direct and indirect sequences for the given feed mixture. In these simulations, the vapor rate (V), tray holdup (T), and number of trays (N) are maintained constant across all the operational phases to provide a uniform basis for comparison. The initial feed (1000 mol) is distributed among the distillate (D), bottom holdup (B), and tray holdup for operational phase 1 of both the direct and indirect sequences. The distillate and bottom vessel holdups are maintained at constant values proportional to the initial feed composition. The corresponding column specifications are given in Table III.

TABLE III: Operating conditions for operational phase 1 of direct and indirect sequence

	Phase 1	
Operating conditions	**Direct (A/BC)**	**Indirect (AB/C)**
N	42	42
V (mol/min)	20	20
T (mol)	50	50
D (mol)	237.5	712.5
B (mol)	712.5	237.5

The batch time for each operational phase is taken as the time required to achieve the desired product purity and recovery. The overall batch time for a sequence is obtained by summing the batch times of its individual operational phases. The simulations to get the batch time for each sequence are performed using MATLAB version R2023b by solving the unsteady-state material balance equations for tray, distillate, and bottom compositions. The corresponding composition profiles and the batch time are depicted in Fig 3. The overall batch time for both sequences is listed in the Table IV

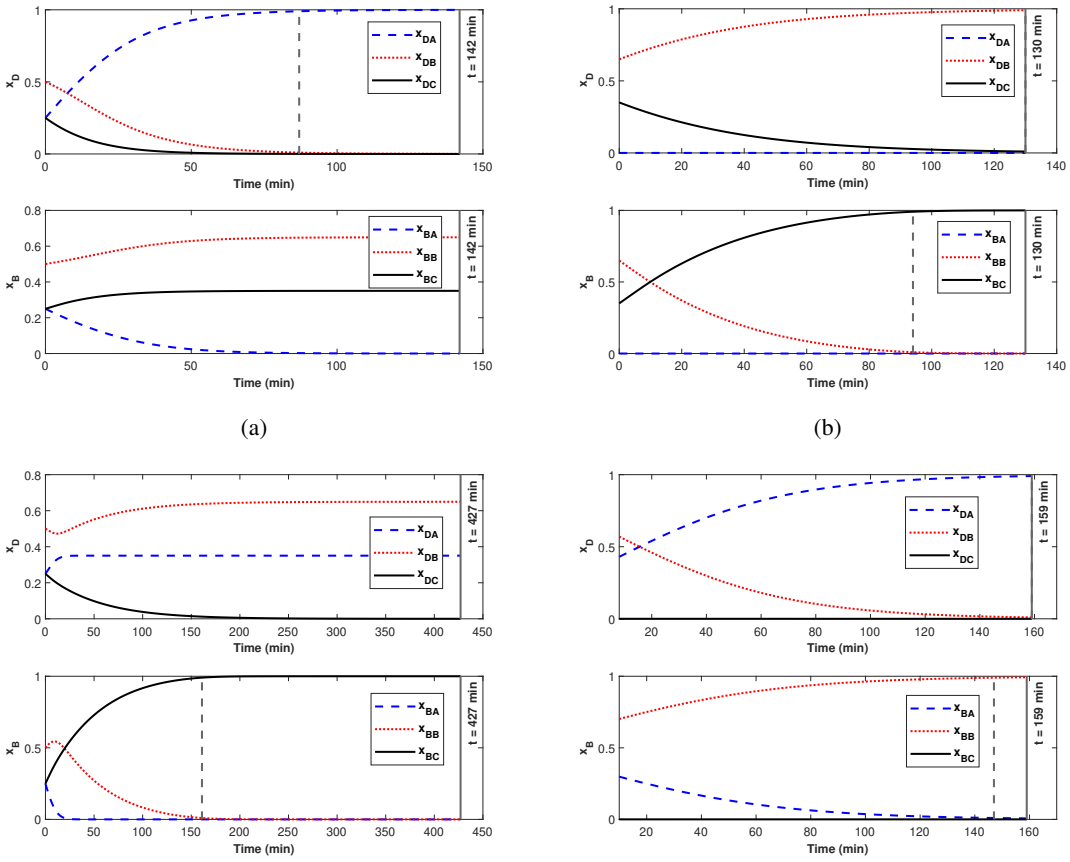

Fig. 3: Concentration profile for operational phase: (a) A/BC (direct sequence) (b) B/C (direct sequence) (c) AB/C (indirect sequence) (d) A/B (indirect sequence)

TABLE IV: Comparison of proposed approach and dynamic simulations

Sequence	**SMN_{min}**	**Batch time (min)**
Direct	4.8960	272
Indirect	5.0565	586

From the table, it can be noted that the overall batch time for the direct sequence is lower than for the indirect sequence, and thus the direct sequence can be considered as the best sequence. This is consistent with the proposed N_{min} based approach.

IV. CONCLUSIONS

In this article, a novel quantitative approach for separation sequencing for batch column operating under total reflux is proposed. The optimal sequence is identified based on a novel concept of marginal minimum number of stages (marginal N_{min}). The proposed quantitative approach is efficient and does not require rigorous simulations. The methodology is illustrated using ternary mixture separation and is verified using dynamic simulations.

In this article, the proposed approach is developed for a ternary mixture. The use of this approach to more general multicomponent mixtures, as well as complex column configurations, is currently pursued in our group.

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