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# PARAMETRIC INVESTIGATION OF FIXED-TRAY, SEMI-CONTINUOUS DISTILLATION COLUMN FOR ETHANOL SEPARATION FROM WATER

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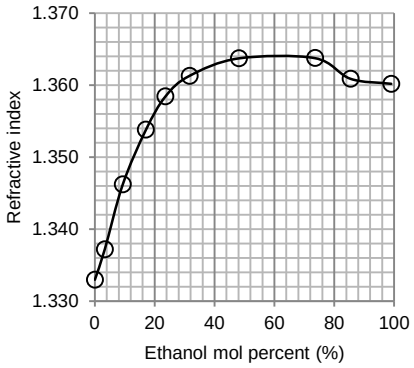
## Graphical abstract




## Abstract

This work was aimed to evaluate the parameters affecting the separation of model fermentation broth (7 mole% ethanol) using 10-tray, semi-continuous distillation column. Ethanol compositions in distillate and bottoms were determined at different reflux ratios and feed locations. Results show that the distillation of lower ethanol concentration is better carried out at higher reflux ratio with feed charged at the middle or bottom tray for good overall tray efficiency. The distillation unit is able to purify the feed to 78 mole% ethanol in distillate. Through trial-and-error stepping off, about 81 mole% was predicted as optimum ethanol purity at reflux ratio of 2.33, while a lower reflux ratio of 1.44 was estimated for 78 mole%. Fixed-tray, semi-continuous distillation is a suitable option to concentrate fermentation broth with sufficient ethanol purity.

*Keywords*: Fixed-tray column; semi-continuous distillation; ethanol-water mixture; fermentation broth

## Abstrak

Kajian ini bertujuan menilai parameter yang mempengaruhi pemisahan model larutan penapaian (7 mol% etanol) menggunakan turus penyulingan 10-dulang, separa berterusan. Kandungan etanol dalam sulingan dan hasil bawah ditentukan pada nisbah refluk dan kedudukan suapan berbeza. Keputusan menunjukkan bahawa penyulingan etanol berkepekatan rendah sesuai dijalankan pada nisbah refluk lebih tinggi dengan suapan pada dulang pertengahan atau bawah untuk meningkatkan kecekapan dulang keseluruhan. Unit penyulingan ini dapat memekatkan suapan kepada 78 mol% etanol dalam sulingan. Melalui cubaan dan jaya berbilang langkah, sekitar 81 mol% diramalkan sebagai kepekatan etanol optimum pada nisbah refluk 2.33, sementara nisbah refluk lebih rendah 1.44 dianggarkan bagi kepekatan 78 mol%. Penyulingan separa berterusan dengan dulang tetap adalah pilihan sesuai untuk memekatkan larutan penapaian dengan kandungan etanol mencukupi.

*Kata kunci*: Turus dulang tetap; penyulingan separa berterusan; campuran etanol-air; larutan penapaian

## 1.0 INTRODUCTION

Alcohol is a hydrocarbon organic compound with the highest priority hydroxyl functional group (—OH) attached to a saturated carbon. Alcohols are produced by reduction of aldehydes or twice reduction of ketones. Methanol and ethanol are the simplest members of saturated aliphatic alcohols. Ethanol, or grain alcohol can be produced by fermenting biomass, commonly corn, sugarcane, switchgrass, potatoes and other starch-rich materials. The other way to produce ethanol is by reversal process of ethanol combustion [1]. Ethanol is a promising alternative fuel or fuel blend as it can be synthesized from renewable resources, and safer to the environment [2]. Nowadays, bioethanol is also widely produced on industrial scale [3].

Ethanol is generally made through the fermentation of plant sugars from agricultural crops and biomass [4]. The most common agricultural crop utilized for ethanol production is corn. Fermentation occurs in anaerobic condition where the oxygen is insufficient for normal cellular respiration. Glucose from biomass materials can be converted into ethanol and carbon dioxide when anaerobic respiration takes place by yeasts in the presence of water.

$$C_6H_{12}O_6 \text{ (fermentation)} \rightarrow 2C_2H_5OH + 2CO_2 \quad (1)$$

The fermentation method is a mature and controllable process. However, ethanol production cost could be escalating due to expensive feedstock plantation [5, 6]. Moreover, the concentration of ethanol produced from fermentation broth is low. Hence, it needs to undergo a subsequent purification process before it can be utilized for fuel, and for other industrial and research purposes. Several purification techniques and technologies such as distillation, extraction, crystallization and so on are feasible for the separation of ethanol from its water-mixture.

Among these, distillation is by far the most widely used method and has a long history in chemical separation technology. The underlying principle of separation by distillation depends upon the distribution of components and relative volatility between individual component in vapor phase and liquid phase [7]. Separation by distillation can be carried though three different modes, namely continuous, semi-continuous and batch.

In continuous distillation, the mixture is continuously fed to column, and the products at column top and bottom are continuously withdrawn. Upon entering the column, feed that is usually introduced as sub-cooled liquid mixture runs down the column while vapour goes up. Vapour is produced by partial vaporization of the mixture which is heated in reboiler (or still). Then, the vapor is condensed to earn back the less volatile compounds (reflux) to the column while the remainder is withdrawn as the distillate product at column top. The remaining liquid in the column is withdrawn as bottom product.

The configuration of semi-continuous distillation is similar to that of batch distillation. In semi-continuous distillation, only feed and distillate flow continuously, while the bottom products can be withdrawn at any time when needed. This mode is suitable for extractive and reactive distillations [8].

Batch distillation is the most frequent separation method in batch processes, and is the oldest operation used for the separation of liquid mixtures [9]. In batch distillation, feed is charged in the reboiler that provides the heat transfer surface. A number of accumulator tanks are connected to the column to collect the distillate fractions [8]. This configuration is also known as rectifying batch column. On the other hand, an inverted or stripping batch column is preferred when the amount of light component in feed is small, and the bottom products are to be recovered at high purity [10]. The feed is normally in saturated liquid, and is charged from the top vessel; so a smaller reboiler can be used for the process.

Semi-continuous and batch distillation are mainly used for the purification of specialty chemicals and pharmaceuticals, whereas continuous distillation is applied in the petrochemical and bulk chemical industries. The semi-continuous or batch distillation is highly preferable over the continuous distillation when it comes to the separation of high-value-added chemicals at low to moderate volume [11]. It is suitable in chemical processing industries where small quantities of materials are to be handled in irregularly or seasonally scheduled periods, especially for the feed composition that varies widely from period to period or handling a completely different feeds [12]. This certainly suits the purification of ethanol from fermentation broth.

This work was aimed at investigating the effect of operating parameters of fixed-tray, semi-continuous distillation for possible separation and purification of ethanol from model fermentation broth. The concentration of ethanol was determined at varying reflux ratios and feed locations. Suitable reflux ratio and distillate composition were also predicted through trial-and-error stepping off.

## 2.0 METHODOLOGY

### 2.1 Materials

Reagent-grade ethanol (purity 96%) was supplied by QRec Chemical. Necessary dilution with water was performed to mimic the model fermentation broth of 0.07 mole fraction of ethanol. A continuous distillation unit (model LS-32203, Lotus Scientific) was used for the distillation process. The schematic representation of the rig is shown in Figure 1.

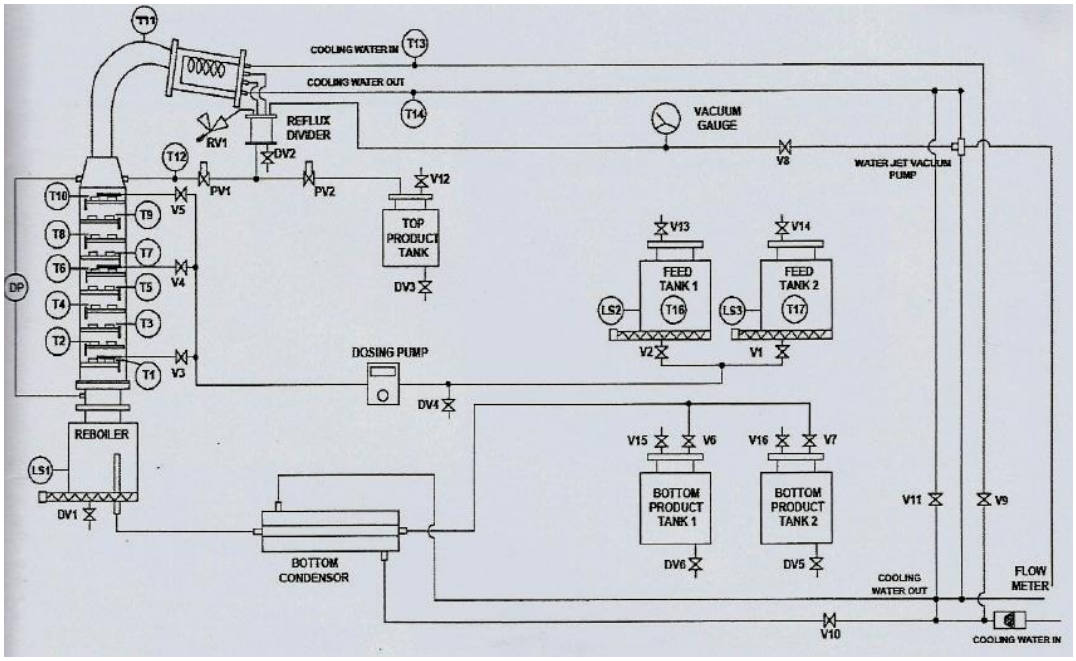



**Figure 1** Fixed tray, semi-continuous distillation unit

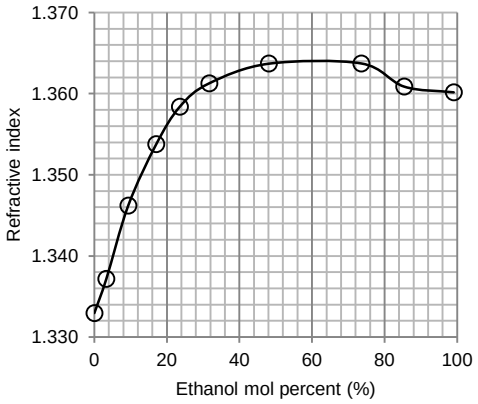



**Figure 2** Calibration of ethanol-water mixture using refractive index

The column consists of 10 trays with three feed locations at trays 1 (bottom), 5 (middle) and 10 (top). The composition of ethanol was determined using refractometer (model RX-5000a, ATAGO). Figure 2 shows the calibration curve of ethanol-water mixture.

### 2.2 Procedures

For semi-continuous mode, valves 6 and 7 leaving the reboiler for continuous operation were closed. A 14 L of ethanol-water mixture of 7 mol% (20% by volume) was charged into the reboiler and feed tank 1 (feed tank 2 was not used). The cooling water was channeled to the condenser through valve 9. The main power and the heater for reboiler were switched on to initiate the distillation process.

Valve 3 was opened, while valves 4 (tray 5) and 5 (tray 10) were closed for feed introduced at tray 1. The reflux ratio (*L/D*) were varied at 0.429 (30%) and 2.33 (70%). The dosage pump was set at 59 mL/min due to equipment constraints. The unit was allowed to stabilize for few minutes after the first drop of distillate appears in the top product tank. The ethanol compositions in distillate and reboiler were recorded at two minutes intervals until the values are consistent. Fresh ethanol-water mixture was added to the reboiler and feed tank for subsequent reflux ratio. The procedures were repeated for the other two feed locations.

## 3.0 RESULTS AND DISCUSSION

### 3.1 Composition of Ethanol at Varying Feed Locations and Reflux Ratios

Table 1 summarizes the composition of ethanol at different feed locations and reflux ratios. An average of 72 mol% of ethanol was able to be purified from an original 7 mol% of ethanol-water mixture by distillation using a 10-tray, semi-continuous column.

Theoretically, sub-cooled feed that is introduced from the column top usually gives the highest distillate purity due to more interfaces for intimate vapour-liquid contact compared to the middle and bottom feed locations. As the feed location is moved lower down the column, the top composition becomes less rich in high volatile component, while

the bottoms contains more of high volatile component.

**Table 1** Ethanol composition at varying parameters

| Feed location | Reflux ratio | *F* (mL/min) | $x_{F,m}$ | *D* (mL/min) | $x_{D,m}$ | $x_{B,m}$ |
|---|---|---|---|---|---|---|
| Tray 1 (bottom) | 0.429 | 59.5 | 0.06 | 18.1 | 0.78 | 0.02 |
| | 2.33 | 58.33 | 0.06 | 21.5 | 0.78 | 0.02 |
| Tray 10 (top) | 0.429 | 58.33 | 0.05 | 55.5 | 0.60 | 0.04 |
| | 2.33 | 59.5 | 0.05 | 30.5 | 0.74 | 0.03 |
| Tray 5 (middle) | 2.33 | 59.5 | 0.07 | 9.9 | 0.78 | 0.01 |

$x_{F,m}$: measured mole fraction of ethanol in feed; $x_{D,m}$: measured mole fraction of ethanol in distillate; $x_{B,m}$: measured mole fraction of ethanol in bottom product

Sorensen and Skogestad [13] also reported that a large amount of heavy component is removed when the mixture is fed at the top of distillation column. However, the highest purity of ethanol in distillate (nearly 80 mol%) was obtained for feed charged at trays 1 and 5, while a lower ethanol composition was recorded for top feed location. This is likely due to lower ethanol composition in feed (~7 mol%), that requires sufficient contact to enrich the ethanol purity before entering the distillate tank. Therefore, bottom or intermediate tray location is preferred for the purification of model fermentation broth.

Moreover, there is also a possibility whereby the sensible heat from the stripped ethanol at the top trays carries together water molecules in the mixture to vaporize upon contact with the water-rich feed. It is supported by a higher distillate flow rate for both reflux ratios for feed at tray 10 as compared to the other two feed locations. A lower reflux ratio (*L*/*D*) for feed at tray 10 exhibits a lower purity of ethanol probably due to large fraction of water discharged from the column top as compared to that returned (refluxed) back to the column.

In general, a higher reflux ratio would result in a decrease of flow rate at the distillate. If the comparison is made based on reflux ratio, it can be seen that a higher reflux ratio gives a higher composition of ethanol.

A greater fraction of refluxed liquid usually improves the efficiency of vapour-liquid separation because of a higher interfaces between the two phases. For a tower with fixed-tray, reflux ratio is commonly adjusted to control the purity of the distillate: the higher the reflux ratio the purer the distillate [14]. Normally, time needed to distill a large quantity of ethanol from a water-rich mixture is longer at higher reflux ratio.

Nevertheless, the ethanol concentration in distillate remains higher for a longer time because the vapor formed inside the column is enriched in more volatile component [15]. From Table 1, the compositions of ethanol in the bottom product are between 1 and 5 mol%. It was also found that the feed at tray 5 gave the smallest amount of ethanol in the bottom product.

### 3.2 Theoretical Number of Trays and Tray Efficiency

Constant pressure vapor-liquid equilibrium (VLE) data for binary (two-component) system was obtained from the boiling point diagram. The VLE plot expresses the bubble-point and the dew-point of a binary mixture at constant pressure. The curved is called the equilibrium line that describes the compositions of the liquid and vapour in equilibrium. The *y* = *x* diagonal line was included for reference. The VLE diagram is often used to stepping off number of theoretical trays and to determine the overall tray efficiency.

Figure 3 shows the stepping off number of ideal trays for different parameters studied, and the results are summarized in Table 2. The feed section operating line (also known as *q* line) was determined as,

$$y = \frac{q}{q-1}x - \frac{x_F}{q-1} \quad (2)$$

where the line intersects the mole fraction of feed ($x_F$) at the 45° diagonal line. The value of *q* was calculated as,

$$q = \frac{C_{p,m}\Delta T + \lambda_F}{\lambda_F} \quad (3)$$

**Table 2** Enriching operating line and theoretical number of trays

| Feed | Reflux ratio | *q* | Enriching line | Stepping off | [1]Feed tray | $x_{B,e}$ | Tray efficiency (%) |
|---|---|---|---|---|---|---|---|
| Tray 1 | 0.429 | 110 | y = 0.3x + 0.546 | 1 step; 0 tray | - | 0.71 | 0 |
| | 2.33 | 110 | y = 0.7x + 0.234 | 8 steps; 7 trays | Still | 0.05 | 70 |
| Tray 10 | 0.429 | 122 | y = 0.3x + 0.420 | 3 steps; 2 trays | - | 0.13 | 20 |
| | 2.33 | 111 | y = 0.7x + 0.222 | 6 steps; 5 trays | Still | 0.04 | 50 |
| Tray 5 | 2.33 | 105 | y = 0.7x + 0.234 | 9 steps; 8 trays | 8 | 0.04 | 80 |
| | Total reflux | - | y = x | 5.5 steps; 4.5 trays | 5 | - | 45 |

[1]Estimated feed tray location from column top; $x_{B,e}$: estimated mole fraction of ethanol in bottom product

where $C_{p,m}$ is the constant pressure heat capacity of the mixture in feed, $\Delta T$ is the temperature difference between the feed temperature and its dew point, and $\lambda_F$ is the latent heat of the mixture in feed. The enriching section operating line is given by the following expression,

$$y = \frac{R}{R+1}x + \frac{x_D}{R+1} \quad (4)$$

where $R$ is the reflux ratio and $x_D$ is the mole fraction of ethanol in distillate. The stripping section operating line was not drawn in the VLE diagrams because the mode of operation is in semi-continuous, by which the bottom product is not continuously withdrawn from the distillation unit. The overall tray efficiency, $E$ was calculated as,

$$E = \frac{number\ of\ ideal\ trays}{number\ of\ actual\ trays} \quad (5)$$

The column consist of 10 trays and one reboiler (11 actual steps). In general, a higher reflux ratio gives a higher tray efficiency and reasonable estimate of ethanol mole fraction in the bottom product (4-5 mole%). The highest tray efficiency of 80% was recorded by feed at tray 5 and reflux ratio of 2.33 (70%). At reflux ratio of 2.33, all three feed locations exhibit the number of trays higher than the minimum one (4.5 trays at total reflux). It implies that the purification of fermentation broth is suitable to be performed at higher reflux ratio. The stepping off also predicts that the feed is better charged at the bottom tray or directly to the reboiler (still). Nevertheless, the state of the feed (sub-cooled, saturated, etc.) and its composition may also affect the operating lines, hence the number of stages required for separation.

### 3.3 Optimum Distillate Composition and Reflux Ratio

Attempts have been made to predict the optimum distillate composition and reflux ratio through trial-and-error methods. Two modes of batch distillation were employed. The first method is by varying the distillate composition at constant reflux ratio, and the second one by varying the reflux ratio at constant distillate composition. Stepping off was performed so as to satisfy the actual number of trays (11 steps).

Tables 3 and 4 summarize the optimum values of reflux ratio and ethanol mole fraction in distillate using a 10-tray, semi-continuous distillation column. Some of the associated VLE-stepping off figures are illustrated in Figures 4 and 5, respectively.

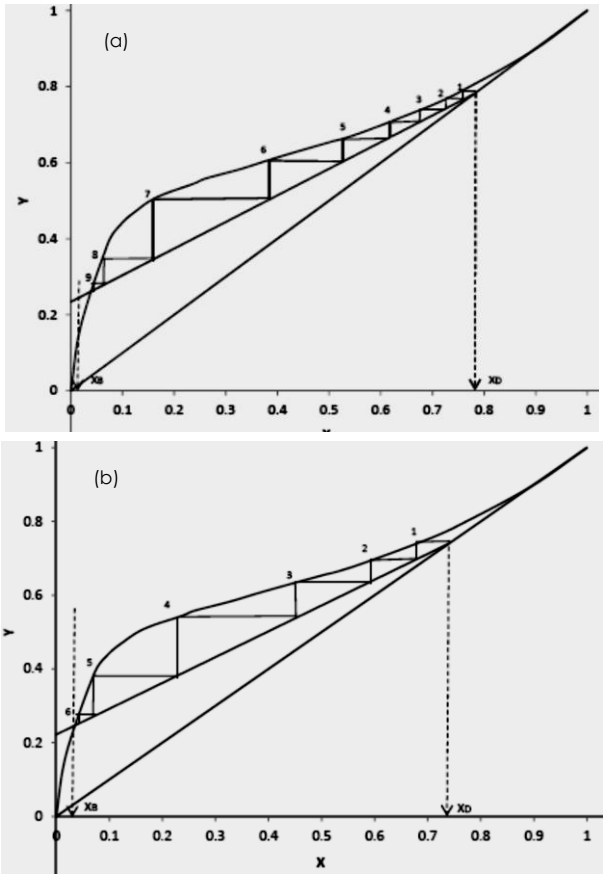
At constant reflux, the slope of the operation line is fixed and is given by the $L/V$ ratio, i.e., the molar flow rates of reflux and boilup. Initially, the distillate composition is $x_D$. Drawing downwards the number of stages gives the bottoms concentration of the light component, $x_B$. In order to satisfy the desired number of trays (or steps), the $x_D$ ordinate was adjusted along the 45° diagonal line with enriching section operating line ended at $x_D/(R+1)$ on the y-intercept.

**Table 3** Optimum ethanol composition in distillate at fixed reflux ratio

| $R$ | $x_D/(R+1)$ | $x_{B,p}$ | $x_{D,p}$ | Stepping off | $E$ (%) |
|---|---|---|---|---|---|
| 0.429 | 0.455 | 0.19 | 0.65 | 5 steps; 4 trays | 40 |
| 2.33 | 0.243 | 0.06 | 0.81 | 11 steps; 10 trays | 100 |
| 2.33 | 0.246 | 0.05 | 0.82 | 13 steps; 12 trays | 120 |

$R$: reflux ratio; $x_D/(R+1)$: intercept of enriching section operating line; $x_{B,p}$: predicted ethanol composition in bottom product; $x_{D,p}$: predicted ethanol composition in distillate; $E$: overall tray efficiency

In general, the purity of distillate depends on the reflux flow rate and number of trays. As shown in Table 3, for distillation operated at fixed reflux ratio of 2.33, a 100% overall tray efficiency could be achieved with 81 mole% and 6 mole% of ethanol in distillate and bottoms, respectively. The values are close enough and comparable to those obtained experimentally. As opposed to classical batch distillation, the distillate purity remains unchanged due to continuous supply of feed. If higher purity and recovery are desired, the tower (column) should have sufficient number of trays for separation from the beginning.



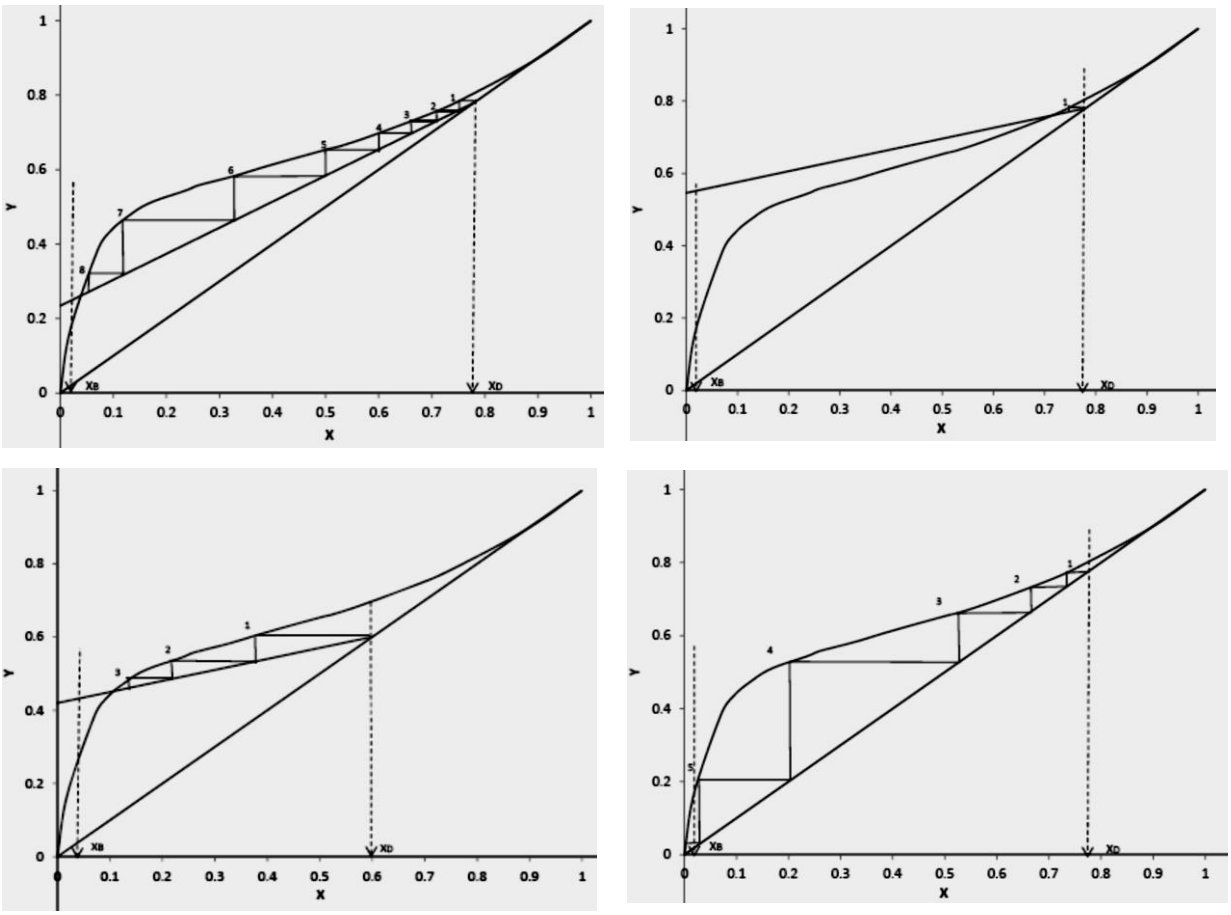


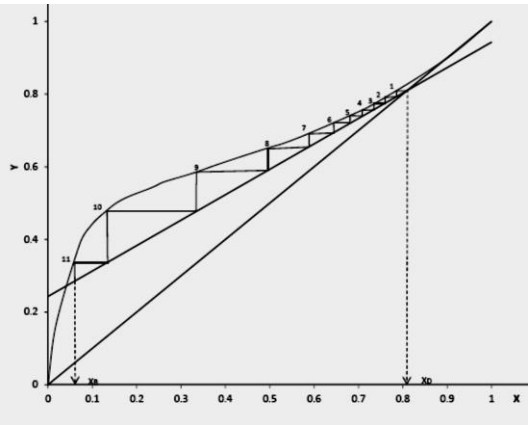

**Figure 3** Stepping off number of theoretical trays for different feed locations at reflux ratio of 2.33: (a) Tray 5; (b) Tray 10; (c) Tray 1, reflux ratio of 0.429: (d) Tray 10; (e) Tray 1, and (f) total reflux

**Table 4** Optimum reflux ratio at fixed ethanol composition in distillate

| $R_p$ | $x_D/(R_p+1)$ | $x_{D,f}$ | $x_{B,p}$ | Stepping off | E (%) |
|---|---|---|---|---|---|
| Total | - | 0.78 | 0.02 | 5.5 steps; 4.5 trays | 45 |
| 19 | 0.039 | 0.78 | 0.01 | 6 steps; 5 trays | 50 |
| 4.0 | 0.156 | 0.78 | 0.03 | 7 steps; 6 trays | 60 |
| 1.5 | 0.296 | 0.74 | 0.05 | 7 steps; 6 trays | 60 |
| 1.5 | 0.312 | 0.78 | 0.08 | 9 steps; 8 trays | 80 |
| 1.44 | 0.320 | 0.78 | 0.08 | 11 steps; 10 trays | 100 |
| 1.33 | 0.335 | 0.78 | 0.07 | 12 steps; 11 trays | 110 |
| 1.0 | 0.300 | 0.60 | 0.05 | 3 steps; 2 trays | 20 |

$R_p$: predicted reflux ratio; $x_{B,p}$: predicted ethanol composition in bottom product; $x_{D,f}$: target ethanol composition in distillate

At variable reflux ratio, the ethanol concentration in distillate ($x_D$) is aimed to be constant by increasing continuously the slope of the enriching section operation line. From Table 4, the optimum reflux ratio for $x_D$=0.78 is 1.44, with the predicted composition of ethanol in bottoms is 8 mole%. The sensitivity analysis suggests that the unit could also obtain similar ethanol purity at lower reflux ratio. If high recovery is desired to satisfy the required number of trays, the reflux should grow considerably to the end, hence raising proportionally the utility consumption [16].



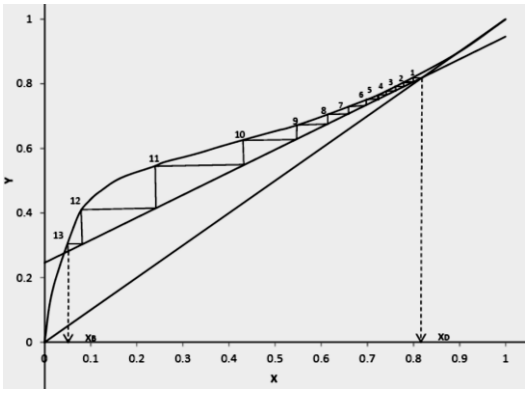
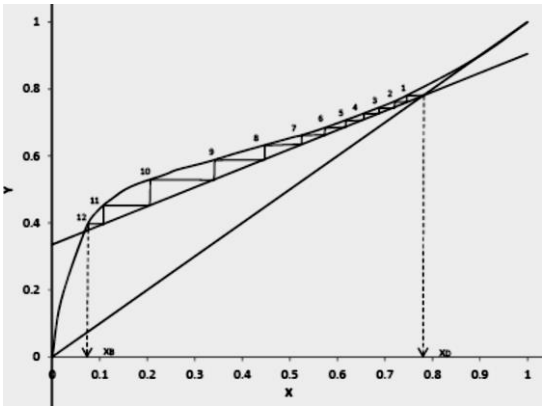


**Figure 4** Stepping off for optimum ethanol compositions in distillate and bottom product: (a) *E*=100%; (b) *E*=120%



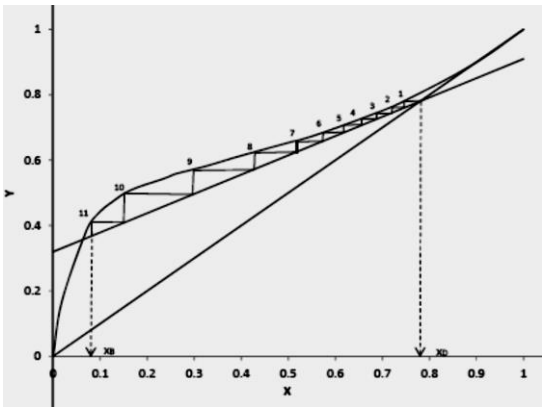


**Figure 5** Stepping off for optimum reflux ratio: (a) E=110%; (b) E=100%

## 4.0 CONCLUSION

Semi-continuous distillation of model fermentation broth (~7mol% ethanol) was carried out using a 10-tray tower. The ethanol compositions in distillate and bottoms are 78 and 2 mole%, respectively. For a higher overall tray efficiency, the unit is better operated at higher reflux ratio and feed is charged at the middle or bottom tray. In distillation process, number of trays and reflux ratio play important roles in the purification of ethanol. The predicted optimum ethanol composition in distillate is 81 mole%, and the column could also be operated at lower reflux ratio for 78 mole% of ethanol. Fixed-tray, semi-continuous distillation is a suitable option to concentrate fermentation broth with sufficient ethanol purity.

## Acknowledgement

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