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**Link to publisher version:** <https://doi.org/10.1016/j.cep.2017.08.012>

**Citation:** Aqar DY, Rahmanian N and Mujtaba IM (2017) Feasibility of Integrated Batch Reactive Distillation Columns for the Optimal Synthesis of Ethyl Benzoate. *Chemical Engineering & Processing: Process Intensification*. 122:10-20.

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# Feasibility of Integrated Batch Reactive Distillation Columns for the Optimal Synthesis of Ethyl Benzoate

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## Abstract

The synthesis of ethyl benzoate (EtBZ) via esterification of benzoic acid (BeZ) with ethanol in a reactive distillation is challenging due to complex thermodynamic behaviour of the chemical reaction and the difficulty of keeping the reactants together in the reaction zone (ethanol having the lowest boiling point can separate from the BeZ as the distillation proceeds) causing a significant decrease in the conversion of BeZ in a conventional reactive distillation column (batch or continuous). This might be the reason of not reporting the use of reactive distillation for EtBZ synthesis although the study of BeZ esterification reaction is available in the public literature. Our recently developed Integrated Conventional Batch Distillation (i-CBD) column offers the prospect of revisiting such reactions for the synthesis of EtBZ, which is the focus of this work. Clearly, i-CBD column outperforms the Conventional Batch Distillation (CBD) column in terms of product amount, purity and conversion of BeZ and eliminates the requirement of excess use of ethanol. For example, compared with CBD column, the i-CBD operation can yield EtBZ at a much higher purity (0.925 compared to 0.730) and can convert more benzoic acid (93.57% as opposed to only 74.38%).

Keywords: Conventional batch distillation; Integrated conventional batch distillation; Modelling; Optimization; Batch Time, Ethyl benzoate

## 1. Introduction

The worldwide demand for benzoic acid and its derivatives receives increasing attention (Gaifutdinova and Beresnev, 2002). Ethyl benzoate (EtBZ) is an organic ester and a colorless transparent liquid having a pleasant odor (described as fruity, wintergreen, medicinal, cherry,

and grape) that is almost insoluble in water, but miscible with organic solvents. Ethyl benzoate is a vastly used as solvents of cellulose, heat resistant lubricants, plasticizers for synthetic resins, laboratory reagent, flavoring agent in various substances including API drug, rubbers, paper, food, and personal-cares and cosmetics (foot powders and sprays) (Li et al., 2008; and Wu et al., 2013). This can also be used in perfumery, and for the preparation of artificial flavors, and tobacco due to its low toxicity (Paul and Newman, 1978; Lewis, 2007;; and Lin and Pang, 2016).

There are commonly two main methods, which can be employed to synthesise ethyl benzoate as documented in Table 1.

Table 1. Two proposed reaction methods for EtBZ production.

Reaction Method	Reference
The acidic esterification of BeZ with EtOH to produce EtBZ (main product) and H <sub>2</sub> O (by-product) using a heterogeneous reaction system.	(Plazl, 1994; Pipus et al., 2000; and Lee et al., 2005)
The ozonolysis of styrene in the presence of EtOH, and then followed by heating decomposition of the intermediate ozonolysis products.	(Gaifutdinova and Beresnev, 2002)

The esterification process is an equilibrium-limited reaction, which is regulated by the chemical equilibrium in the presence of water as by-product. The esterification reaction of benzoic acid with ethanol to yield ethyl benzoate is not a new process. For instance, this esterification was investigated by using conventional and microwave heating in a stirred tank reactor by (Plazl, 1994). Pipus et al. (2000) studied the same method to produce EtBZ in a tubular flow reactor heated by microwaves, catalyzing with Amberlyst-15. They used an irreversible quasi-homogeneous model to describe the kinetic model. The highest conversion obtained was about 38% for homogeneously catalysed esterification at the lowest flow rate. Lee et al. (2005) developed three kinetic models (such as the quasi-homogeneous (QH), Eley-Rideal (ER), and Langmuir-Hinshelwood-Hougen-Watson (LHHW) models to study experimentally the kinetic behavior of the synthesis of ethyl benzoate over Amberlyst-39 using a fixed-bed reactor at the atmospheric pressure. They found out that the LHHW model gives the best representation for the ethyl benzoate production. However, they achieved a conversion of BeZ into EtBZ of 90.20% with EtOH to BeZ feed molar ratio of 5. Recently, Wu et al. (2013) prepared an acid catalyst of SO<sub>4</sub><sup>2-</sup> over Ti<sub>3</sub>AlC<sub>2</sub> ceramic to examine the esterification of benzoic acid with ethanol but their study illustrated that the resulting catalyst

exhibited only 80.40% conversion of benzoic acid under 120 °C at the reaction time of 34 hr. They extended the reaction time of batch reactor to achieve a maximum conversion of benzoic acid (80.40%).

Traditionally, in many chemical industries, the reaction and distillation are carried out separately in a reactor followed by a non-reactive batch distillation column as depicted in Figure 1 (Charalambides et al., 1994). Therefore, the separation of desired product cannot affect the conversion of reaction reactants in the fixed bed reactor. However, batch distillation with chemical reaction (the combination of reaction and separation into single apparatus, which is referred to as batch reactive distillation operation) is recommended when one of the reaction species is either the lightest or the heaviest component in the reactive mixture (Edreder, 2010; and Edreder et al., 2011).

In the case of reversible reaction system, the removal of specified products by distillation (either as the distillate or as the bottom product) favours the forward reaction and thus can yield a higher conversion of reactants than the traditional approach.

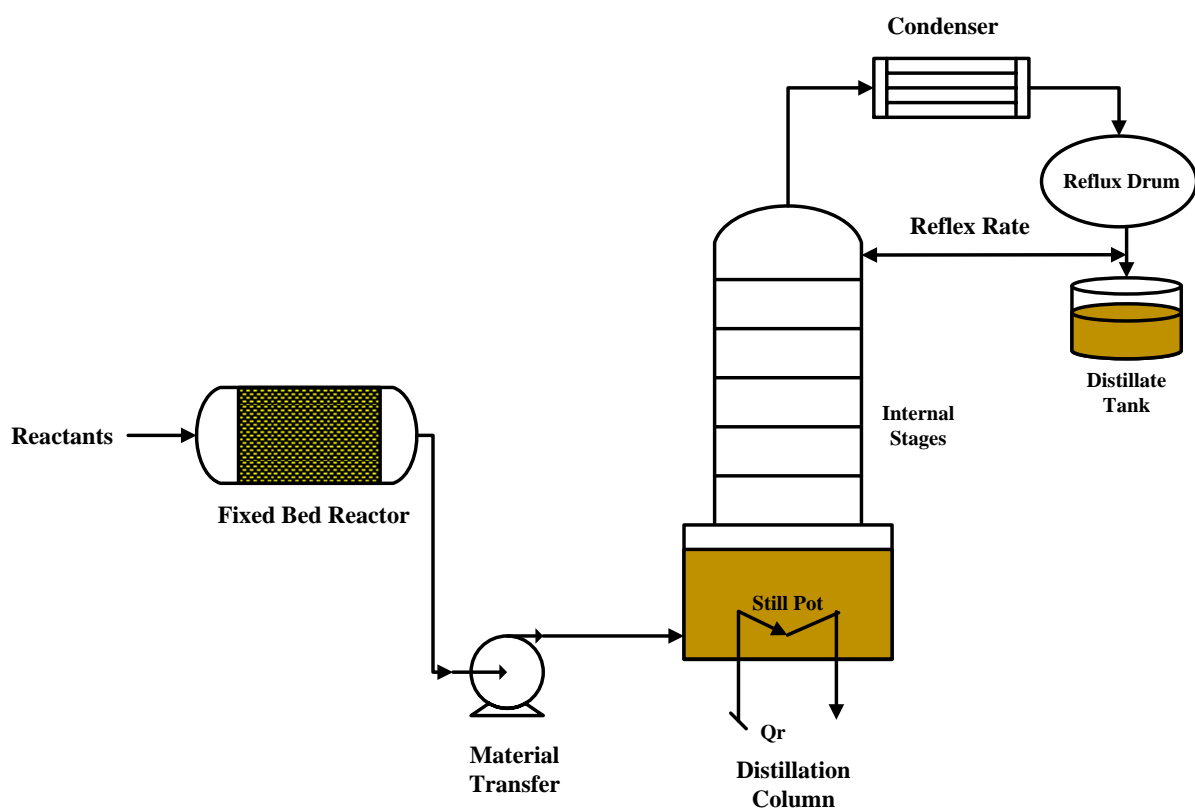


Figure 1: Traditional Batch Reactor-Batch Distillation (TRBD) Operation.

However, to the best of our knowledge, all the previous studies considered synthesis of EtBZ via esterification of benzoic acid with ethanol using different types of reactors only. To increase the conversion of acid to EtBZ excess ethanol has been used (as described earlier). However, no reported work in literature has addressed use of either batch or continuous distillation columns for the separation of EtBZ from the reaction mixture.

In this study, for the sake of comparison, first the traditional batch reactor-batch distillation approach (TRBD) is considered to establish the maximum amount and purity of EtBZ that can be obtained via batch distillation. Then batch reactive distillation is considered to explore whether an improved conversion level of BeZ, and maximum achievable purity and yield of product are possible. For this purpose, the application of a conventional batch distillation column (CBD) and the integrated conventional batch distillation column (i-CBD) recently proposed by Aqar et al. (2016b) are used in this work. Note, Aqar et al. (2016b) demonstrated the superiority of i-CBD column over CBD column for the synthesis of methyl lactate via esterification of lactic acid with methanol. Note, the boiling point differences between the components of methyl lactate synthesis are significantly different from those of EtBZ synthesis problem considered in this work making the separation of the desired product (EtBZ) challenging. For the synthesis of methyl lactate system, the boiling points of reactants; lactic acid and methanol are 490.15 K and 337.15 K respectively, for the products; methyl lactate and water are 417.15 K and 373.15 K respectively. While for the synthesis of ethyl benzoate system, the boiling points of reactants; benzoic acid and ethanol are 523.0 K and 351.40 K respectively, for the products; ethyl benzoate and water are 485.90 K and 373.15 K respectively. Seemingly, use of i-CBD could significantly increase reaction conversion of BeZ and thus product purity for the EtBZ but is subject to investigation and is therefore the focus of this work.

The optimum operations of CBD and i-CBD columns are presented in terms of minimum operating time. The reflux ratios, and ethanol recycled rate (for i-CBD) are employed in the dynamic optimization study which are discretized using Control Vector Parameterization (CVP) technique as already described by Mujtaba (2004). A rigorous dynamic model for each of these configurations is incorporated within the optimization framework. The dynamic optimization problem is transformed into non-linear programming (NLP) problem, which is solved using a SQP-based technique within gPROMS software (2015).

## 2. Column Configurations and Process Model

Figure 2 shows the schematics of the CBD and i-CBD columns. The detailed descriptions of these columns and the detailed dynamic models (except the kinetics and vapour liquid equilibrium for BeZ esterification reaction) for these two configurations can be found elsewhere; i.e. Mujtaba (2004) and Aqar et al (2016a, b). The detailed dynamic models are based on the following assumptions:

- Negligible vapour hold-up
- Adiabatic trays
- Perfect mixing on plates
- Fast energy dynamics
- Constant operating pressure (atmospheric pressure)
- Total condensation (no sub-cooling)
- Chemical reaction on the stages, in the total condenser, and in the still pot
- Ideal vapour phase

However, for the convenience of the readers the model equations are presented in the Appendix A.

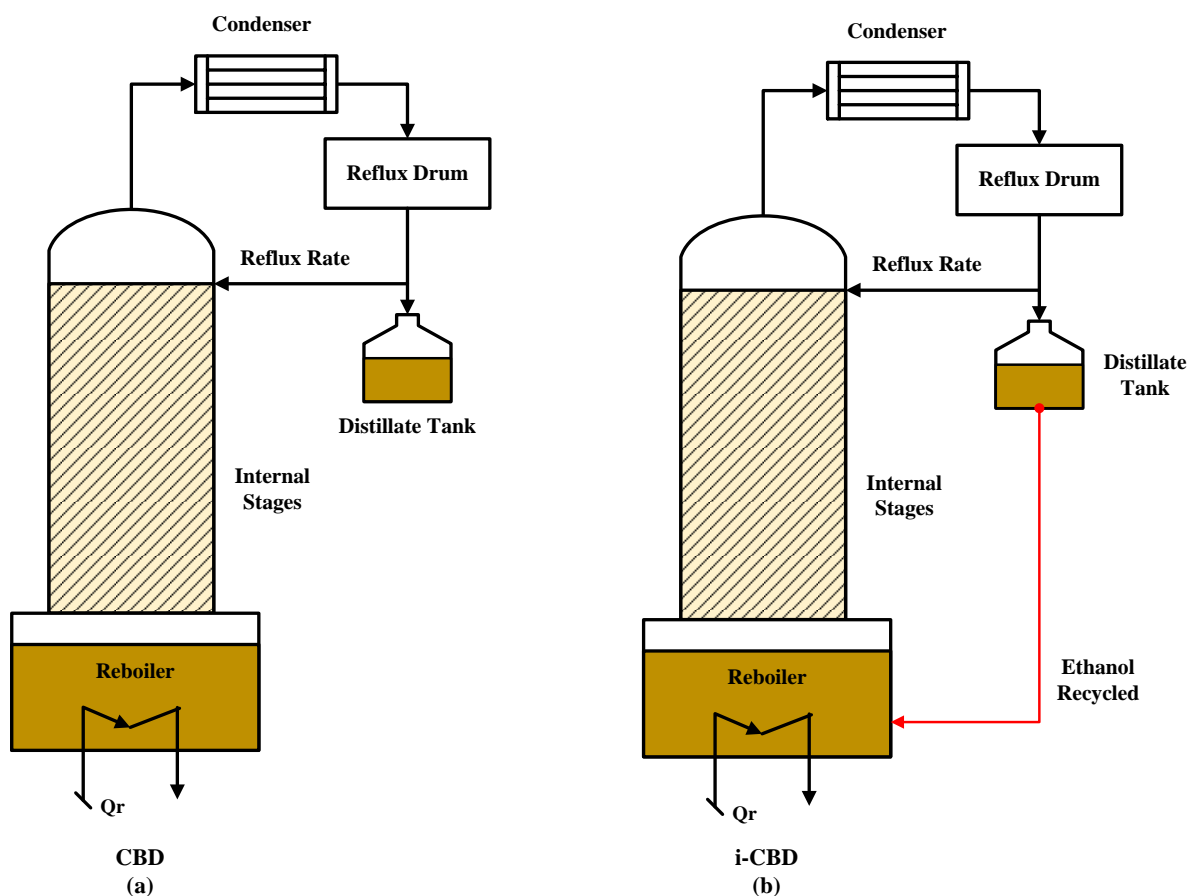
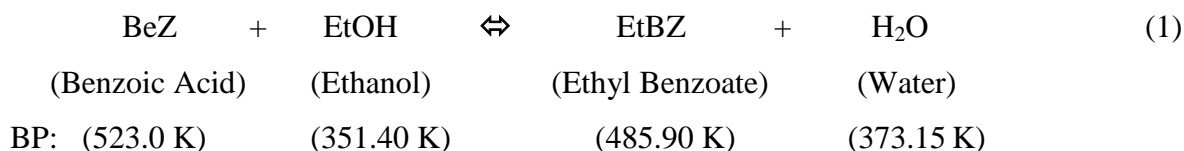


Figure 2: Schematic diagram of three column configurations for producing ethyl benzoate: (a) conventional (CBD) and (b) integrated conventional (i-CBD).

## 2.1 Kinetic modelling and phase equilibrium (VLE) for benzoic acid esterification

### 2.1.1 Kinetic reaction

Lee et al. (2005) investigated experimentally the kinetic behaviour of the liquid-solid catalytic synthesis and hydrolysis of ethyl benzoate. The formation of ethyl benzoate (EtBZ) was implemented through esterification of benzoic acid (BeZ) with ethanol (EtOH) over an acidic cation-exchange resin (Amberlyst-39) via the reversible kinetic reaction as shown in Equation 1. The boiling point (BP) temperature of each reacting species is also shown below.



For the synthesis of ethyl benzoate, a Langmuir-Hinshelwood-Hougen-Watson (LHHW) activity ( $a_i = \gamma_i x_i$ ) based kinetic model is used which can be written as:

$$-r_{\text{BeZ}} = m_{\text{cat}} \left\{ \frac{3.0532 \times 10^{13} \exp\left(\frac{-9620}{T}\right) \left[ a_{\text{BeZ}} a_{\text{EtOH}} - 0.01908 \exp\left(\frac{541.48}{T}\right) a_{\text{EtBZ}} a_{\text{H}_2\text{O}} \right]}{\left[ 1 + 0.08154 a_{\text{BeZ}} + 1.6308 a_{\text{EtOH}} + 0.3793 a_{\text{EtBZ}} + 9.1747 a_{\text{H}_2\text{O}} \right]^2} \right\} \quad (2)$$

This kinetic model yields the best representation for the kinetic behaviour of the global system (Lee et al., 2005) and therefore, this reaction model is employed in this work.

### 2.1.2 Vapour-liquid equilibrium (VLE)

According to some studies (Hong et al., 2003; and Horsley, 1952), two binary azeotropes can be formed in the ethanol + water, and in the ethyl benzoate + water systems. Hong et al. (2003) measured the vapour-liquid equilibrium (VLE) properties for binary (ethyl benzoate + ethanol) by determining experimentally their saturated pressures and the compositions. They found out that no azeotrope was formed in binary mixture (ethyl benzoate + ethanol). However, according to DeGarmo et al. (1992), the azeotrope formation in reactive distillation (RD) processes is generally overcome due to their ability to improve the conversion level by removing the products instantaneously from the reaction region, and by consuming the azeotrope forming constituents in chemical reaction. Probably this could be the reason why azeotropes were not considered by a number of authors (Plazl, 1994; Pipus et al., 2000; Lee et al., 2005; Wu et al., 2013). Based on these observations, we have decided not to include azeotropes in this study.

Note, the calculations of liquid and vapour enthalpies and thermodynamic properties for the synthesis of ethyl benzoate are similar to those shown in our previous work (Aqar et al., 2016 a). The saturation pressure of the vapour ( $P_i^{\text{sat}}$ ) of the pure components has been calculated as a function of temperature through the Antoine's equation:

$$\text{Log}_{10} P_i^{\text{sat}} = A + \frac{B}{T} + C \log_{10} T + DT + ET^2$$

(3)

Where A, B, C, D, E are the regression parameters (with appropriate units) for the Antoine's equation and T is the temperature in Kelvin. All parameters for the Antoine's equation utilised in the present work were taken from (Yaws, 1997) and are summarised in the Appendix B. The NRTL model was applied to compute the liquid-activity coefficients (the vapour-liquid equilibrium) with the binary constants are given in Lee et al. (2005). The vapour phase is assumed to be ideal gas mixture. Note also, the vapour enthalpy and the





$$B = B^* + \varepsilon \quad (\text{Inequality Constraints})$$

$$x_{\text{EtBZ}} = x_{\text{EtBZ}}^* + \varepsilon \quad (\text{Inequality Constraints})$$

Where  $B$ , and  $x_{\text{EtBZ}}$  are the amount of bottom product and purity of EtBZ at the end of batch time  $t_p$  in the reboiler ( $B^*$ , and  $x_{\text{EtBZ}}^*$  are specified).  $R_{\text{CBD}}$  and  $R_{\text{i-CBD}}$  are the time dependent reflux ratios,  $S_{\text{EtOH}}$  is the recycle rate of ethanol (in case of i-CBD) which are optimized and  $\varepsilon$  is small positive numbering in the order of magnitude of  $10^{-3}$ . Note, the model equations of the i-CBD system are characterized by the set of highly nonlinear differential-algebraic equations (DAEs) which acts as equality constraints to the optimization framework.

## 4. Results and Discussions

### 4.1 Traditional Batch Reactor-Batch Distillation (TRBD) System

In a small laboratory fixed bed reactor, Lee et al. (2005) used a feed rate of  $9.15 \times 10^{-6}$  kmol/hr with molar ratio of (5: 1) for (Ethanol: Benzoic Acid) resulting in feed composition of 0.167 (BeZ), 0.833 (EtOH), 0.0 (EtBZ), and 0.0 (H<sub>2</sub>O) mole fraction. They achieved 90.20% conversion of BeZ resulting in the reactor outlet molar composition of 0.016 (BeZ), 0.683 (EtOH), 0.150 (EtBZ), and 0.150 (H<sub>2</sub>O). The residence time for the reactor was 13.23 hr. For the TRBD system in this work, we scaled up the total quantity of feed to the reactor (5 kmol) and the total catalyst loading (3886 kg), and assumed that with the same residence time of 13.23 hr the batch reactor will also convert 90.20% of the acid resulting in the same final product composition as obtained by Lee et al. (2005) in the fixed bed reactor.

For the conventional batch distillation part (Figure 1), therefore, we used this composition as the initial feed composition. Note, in TRBD mode, no further reaction takes place in the distillation column. The separation of ethyl benzoate (EtBZ) is carried out in a batch column with ten theoretical trays (including both total condenser and reboiler) with (2.5 kmol/hr) of overhead vapour condenser load at the atmospheric pressure. The column plates are numbered from the top to the bottom, indicating condenser as 1<sup>st</sup> stage and reboiler as 10<sup>th</sup> stage. The total column holdup is considered to be 4% of the total feed charge. Fifty percent of total column holdup is taken for condenser and the rest for the trays (equally divided). These distributions of holdup were utilized by a number of authors in the past as reported by Aqar et al. (2016a). Note also, the same strategy is used for the catalyst distribution in the reactive distillation column (described later in sections 4.2 and 4.3).

The condenser and the trays compositions are assumed to be the same composition as the initial feed charge at the beginning of process. Then, the batch column is operated at total

reflux operation during initial start-up mode until it reaches a steady-state condition and the composition profiles of column are thus established. The production period for all cases shown later in the next sections begins from this point (designated  $t = 0$ ) onward. Similar policy of column initialization was employed previously by Cuille and Reklaitis (1986).

Ideally, if all of the EtBZ (desired product) in the feed could be recovered at 100% purity, the maximum desired product amount would be 0.75 kmol. However, this will not be possible as the benzoic acid is the heaviest in the mixture. Therefore, ideally if all the water and ethanol are removed by distillation and no water remains in the reboiler after the removal of ethanol, 0.830 kmol of bottom product will be left with purity of 90.36% (mol %) of EtBZ.

The optimization results in terms of optimum reflux ratio, column batch time, and reactor time, as well as the total operating time for a range of desired product purity specifications (0.855 mole fraction onward) are tabulated in Table 2. For both cases, the bottom product amount to be achieved is set as 0.83 kmol (to see if EtBZ purity of 90.36% is possible to achieve). The results of Table 2 show that all reflux ratio and batch time, increase progressively with increasing the EtBZ mole fraction in the reboiler. It is noted also from Table 2 that no results were obtained at product purity beyond 0.86 mole fraction due to the loss of some of the EtBZ in stages above the reboiler due to distillation.

Table 2. Optimal Operation results for the EtBZ production for TBRD system at  $\langle \text{BeZ} = 0.016, \text{EtOH} = 0.683, \text{EtBZ} = 0.150, \text{H}_2\text{O} = 0.150 \rangle$ .

Product Quality, $x_{\text{EtBZ}}^*$	Optimal Reflux Ratio (-----)	Column time, $t_{\text{CBD}}$ , (hr)	Reactor time, $t_{\text{FBR}}$ , (hr)	Total Batch time, $t_{\text{tot}}$ , (hr)
0.855	0.202	1.99	13.23	15.22
0.860	0.285	2.22	13.23	15.45
> 0.870	--- <sup>a</sup>	--- <sup>a</sup>	--- <sup>a</sup>	--- <sup>a</sup>

<sup>a</sup> Infeasible.

#### 4.2 The performance of CBD and i-CBD columns for EtBZ synthesis with excess ethanol in the feed

Having studied the TRBD in section 4.1, it will now be interesting to evaluate effectiveness of reactive distillation for the reaction system concerned. In all cases, the feed composition (0.167 BeZ, 0.833 EtOH, 0.0 EtBZ, and 0.0 H<sub>2</sub>O mole fraction) is kept the same as in Lee et

al. (2005) and the amount of product in the reboiler is kept constant at 0.83 kmol (same as the traditional batch operation) for making useful comparison.

#### 4.2.1 Case 1: CBD column

The purity of EtBZ is varied and several scenarios are generated and discussed here. Table 3 presents the optimal operation results for CBD column in terms of reflux ratio, minimum batch time, the total heat usage, and the BeZ conversion for a range of product purity constraints (mole fraction of 0.860 to 0.925). It can be seen from Table 3 that, in all cases, the reflux ratio, batch time, and the thermal energy consumption reduce gradually with increasing the desired purity specifications. The reason for this decrease is that the column is trying to get rid of ethanol and water faster and in a large amount to satisfy the product purity in the reboiler. Reduced reflux ratio helps removing water (as it is being produced) thus pushing the reaction more forward. Although, ethanol will also be removed with water, as it is the lightest component, but due to excess ethanol being used, the remaining ethanol in the reboiler is sufficient to convert more of the benzoic acid and thus improves the purity of the desired product (benzoate). It can be noticed from the results that the conversion level of BeZ into EtBZ during the batch increase progressively and thus increases the product compositions. This is obvious as higher purity of EtBZ orders more conversion of benzoic acid. A comparison of the results between the conversion of BeZ using CBD column and the TRBD process conversion indicates that for the same amount of bottom product (0.83 kmol) CBD process can produce more ethyl benzoate at a much higher purity (0.925 compared to 0.860), can convert more benzoic acid (96.11% as opposed to only 90.20%).

The mode of constant vapour load to condenser is considered here to operate both i-CBD and SBD columns (as used by Aqar et al., 2016a, b). Note, the reboiler heat duty ( $Q_{\text{heat}}$ ) rises gradually in this strategy to keep the constant vapour load to the condenser drum. This leads to the following form for the computing of energy consumption rate.

$$Q_{\text{tot}} = \int_0^{t_p} Q_{\text{heat}} dt \quad (5)$$

Alternatively, the differentiation of Equation (5) gives:

$$\frac{dQ_{\text{tot}}}{dt} = Q_{\text{heat}} \quad (6)$$

The above differential equation is inserted to the model equation presented later in Appendix A. The  $Q_{\text{tot}}$  at the final operating time ( $t_p$ ) will result the total heat usage of both batch distillation operations.

Table 3. Optimal Operation results for the production of EtBZ for CBD <math>C\_{BeZ} = 0.167, C\_{EtOH} = 0.833</math>.

Product Quality, $X_{EtBZ}^*$	Optimal Reflux Ratio, $R_{CBD}$	Final Batch time, $t_p$ , hr	Energy Usage, $Q_{tot}$ , GJ	Conversion of BeZ (%)
0.860	0.735	6.00	0.577	89.44
0.875	0.713	5.53	0.530	90.93
0.900	0.672	4.84	0.462	93.51
0.925	0.623	4.22	0.401	96.11

Table 4 shows the optimization results, the reboiler and accumulator tank compositions, respectively for different product purities at the end of the operating batch time. It can be seen that ethyl benzoate is only remained in the bottom tank, whereas, the distillate tank contains mainly a mixture of ethanol and some amount of water at 0.925 of EtBZ purity. The concentration of benzoic acid (the heaviest component) expands as the product EtBZ quality increases (by mass-balance). The compositions of both BeZ and EtBZ in the distillate receiver were found to be very small (as they are heavier components).

Table 4. The bottom and distillate compositions at several purities of EtBZ using CBD column.

Purity of EtBZ	$X_{BeZ}$	$X_{EtOH}$	$X_{H2O}$	$X_{BeZ}^*$	$X_{EtOH}^*$	$X_{EtBZ}^*$	$X_{H2O}^*$
0.860	0.105	0.030	0.005	$5.85 \times 10^{-7}$	0.830	$7.38 \times 10^{-13}$	0.170
0.875	0.090	0.031	0.004	$5.83 \times 10^{-7}$	0.827	$9.08 \times 10^{-13}$	0.173
0.900	0.065	0.031	0.003	$5.61 \times 10^{-7}$	0.821	$1.16 \times 10^{-13}$	0.179
0.925	0.039	0.034	0.002	$5.85 \times 10^{-7}$	0.815	$1.22 \times 10^{-13}$	0.185

\*The composition in the distillate accumulator (mole fraction)

#### 4.2.2 Case 2: i-CBD column

The integrated conventional batch distillation process (i-CBD), where part of the distillate is recycled to the still pot, which is recently suggested by Aqar et al. (2016b), is used in this work for the production of ethyl benzoate as presented in Figure 2b. Note, the column specifications and operating conditions of i-CBD operation, and the holdup distribution assumptions are the same as those for the CBD system (see section 4.2.1).

The optimum results for the i-CBD system are displayed in Table 5, including the optimal recycle rate of ethanol, optimal reflux ratio, minimum operation time, total energy usage, and total amount of ethanol recycle, as well as the BeZ conversion for four product quality constraints. It can be noticed from these results that the all reflux ratio, batch time and energy requirement, amount of recycled EtOH, and the conversion level of BeZ gradually increase with increasing EtBZ purity considerations (unlike those observed in a CBD process in section 4.2.1). Table 6 also shows the bottom and distillate composition profiles for each case. Clearly, the recycled stream has considerable amount of water with ethanol, which pushes the reaction backward. Thus, it takes considerably more time (compared to CBD) to produce the same amount of product for a given purity. Increasing the production time can significantly lead to rise the overall reaction conversion. Note, there is a sharp increase in operating time and thus energy usage rate as well as the total amount of ethanol recycled (Table 5) to increase the quality of EtBZ from 0.900 to 0.925 (mole fraction). The distillation column requires to operate at higher reflux ratio and higher recycle rate of ethanol to suppress the move of EtBZ up to the top of column, and thus needs a longer processing batch time to satisfy the product constraint.

Note, comparison of the results in Table 5 with those in Table 3 shows that the use of CBD operation is more beneficial for the synthesis of EtBZ than the i-CBD column in terms of batch time and thermal heat consumption. As an example, with 0.925 mole fraction of EtBZ purity, the significant reductions in the operating batch time and the energy usage rate are almost 64.50%, and 65.51% as compared to those obtained by the i-CBD process. However, the i-CBD column is better than CBD operation in terms of maximum achievable conversion due to the ethanol recycled to the pot tank, which can have further reaction with the unreacted benzoic acid (Table 6). It is realized that 2.53% of conversion rate of BeZ can be improved at 0.925 of product purity as compared to that of the CBD system.

Table 5. Optimal Operation results for the production of EtBZ for i-CBD  $\langle \text{BeZ} = 0.167, \text{EtOH} = 0.833 \rangle$ .

Product Quality, $x_{\text{EtBZ}}^*$	Optimal Recycle Rate, kmol/hr	Optimal Reflux Ratio, $R_{i\text{-CBD}}$	Final Batch time, $t_p$ , hr	Energy Usage, $Q_{\text{tot}}$ , GJ	EtOH Recycle Amount, kmol	Conversion of BeZ (%)
0.860	1.67	0.045	5.55	0.535	9.28	98.39
0.875	1.69	0.059	5.95	0.574	10.02	98.41
0.900	1.63	0.092	6.23	0.601	10.17	98.52
0.925	1.73	0.172	11.88	1.162	20.61	98.53

Table 6. The bottom and distillate compositions at several purities of EtBZ using i-CBD column.

Purity of EtBZ	$X_{\text{BeZ}}$	$X_{\text{EtOH}}$	$X_{\text{H}_2\text{O}}$	$X_{\text{BeZ}}^*$	$X_{\text{EtOH}}^*$	$X_{\text{EtBZ}}^*$	$X_{\text{H}_2\text{O}}^*$
0.860	0.015	0.122	0.003	$1.90 \times 10^{-6}$	0.796	$1.80 \times 10^{-5}$	0.204
0.875	0.015	0.108	0.003	$7.44 \times 10^{-7}$	0.796	$2.80 \times 10^{-6}$	0.204
0.900	0.014	0.084	0.002	$5.30 \times 10^{-7}$	0.797	$1.21 \times 10^{-7}$	0.203
0.925	0.014	0.059	0.001	$5.15 \times 10^{-7}$	0.798	$1.38 \times 10^{-9}$	0.202

\*The composition in the distillate accumulator (mole fraction).

Some researchers ignored the influences of azeotrope formation for the synthesis of isopropyl palmitate system due to higher conversion of palmitic acid of 99.40 % achieved in their work (Chen et al., 2012, Zhang et al., 2015). Note that, although both EtOH-H<sub>2</sub>O and EtBZ-H<sub>2</sub>O form minimum-boiling azeotropes, their impacts are neglected also in our work due to higher product purity of EtBZ and higher conversion level of BeZ into EtBZ are achieved (see Tables 3 and 5).

### 4.3 Optimal operations of CBD, and i-CBD for EtBZ synthesis at equimolar feed

Lee et al (2005) used excess ethanol in their reactor, the mass balance will show that it reduces the amount of desired product significantly (as can be seen in section 4.1 and 4.2). The question arises here is whether it is essential to have excess ethanol and whether there is a scope for improving the amount of desired product for the same product purity. In this section, therefore, equimolar reactant ratio (BeZ: EtOH) of 5 kmol of initial feed charge to the still pot is investigated in all batch reactive configurations (CBD, and i-CBD). For all cases, we set the 2.4 kmol as the desired product amount.

#### 4.3.1 Case 2: CBD column

Table 7 presents the optimization results (reflux ratio, minimum batch time, total energy consumption, and the conversion of BeZ into EtBZ) for each bottom product (EtBZ) purity. As before, the results of Table 7 indicate that for all cases, reflux ratio, batch time, and the total energy usage decrease gradually with increasing the purity of the product. However, although the conversion of BeZ increases with the increasing the EtBZ purity compared to CBD with excess ethanol (Table 3), the maximum purity of benzoate that could be achieved is 0.73 mole fraction, which is much lower than those of CBD with excess ethanol. This is due to the fact that although reduction in reflux ratio helps removing ethanol (as it is being lightest component) thus pushing the reaction more forward as shown in Figure 3. However,

since there is no excess ethanol in this case, the remaining ethanol in the reboiler is not sufficient to convert more of the benzoic acid and thus cannot improve the purity of the desired product (ethyl benzoate) (Figure 4 reboiler composition). As it can be noticed, the distillation column operates with a low reflux ratio to achieve the maximum possible the product composition of 0.73 mole fraction. Also, it can be seen that it is hard to achieve a high BeZ conversion using a CBD column at the equimolar feed ratio.

Table 7. Optimal Operation results for the production of EtBZ for CBD column with equimolar feed ratio.

Product Quality, $x_{\text{EtBZ}}^*$	Optimal Reflux Ratio, $R_{\text{CBD}}$	Final Batch time, $t_p$ , hr	Energy Usage, $Q_{\text{tot}}$ , GJ	Conversion of BeZ (%)
0.700	0.227	1.24	0.170	71.47
0.710	0.186	1.18	0.164	72.41
0.720	0.130	1.10	0.157	73.42
0.730	0.022	0.98	0.145	74.38
> 0.730	--- <sup>a</sup>	--- <sup>a</sup>	--- <sup>a</sup>	--- <sup>a</sup>

<sup>a</sup> Infeasible.

The accumulator and the the reboiler composition profiles for product purity ( $x_{\text{EtBZ}}^* = 0.73$ ) are given in Figures 3 and 4. The composition of water (2<sup>nd</sup> boiling component) increases from zero and reaches the highest value and then drops down to almost zero. This is thought to be due to its removal in the distillate tank, see Figure 3. Ethanol reactant as the lightest boiling component is progressively depleted through the chemical reaction with benzoic acid at the bottom of the column and resulting a higher enhancement in the conversion of BeZ at the end of the operation (as shown in Figure 4, Table 7). As long as the reaction continues, the concentration of ethanol gradually reduces in the still tank due to its lowest boiling point, which accumulated at the top of column (see Figure 3). More ethyl benzoate is yielded as the time proceeds and remains in the still pot (as the intermediate boiling point component).



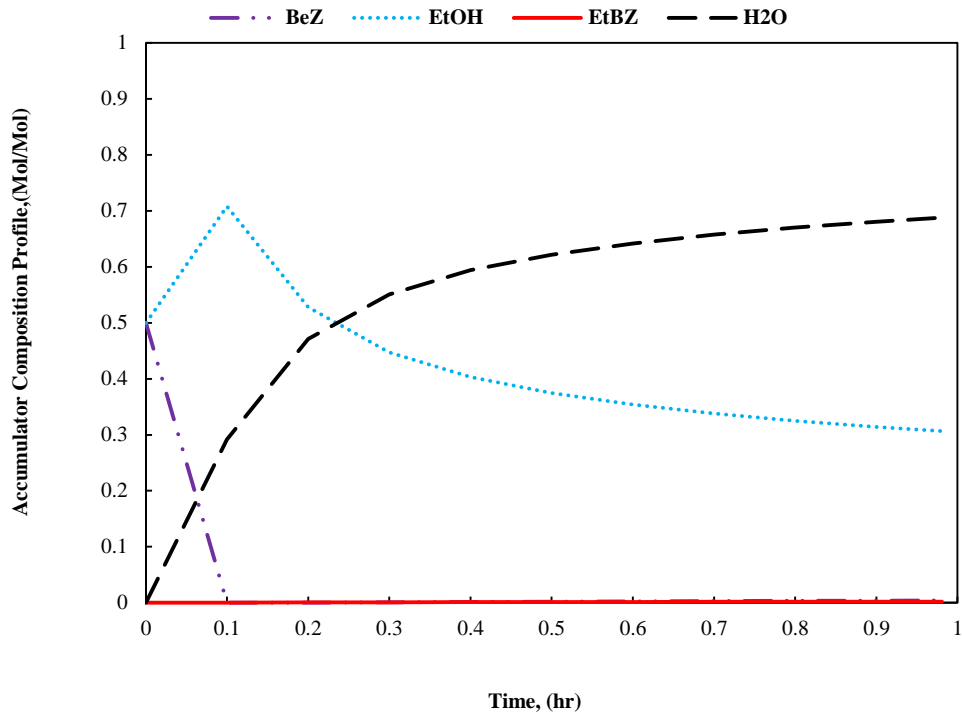


Figure 3: The accumulator composition of CBD column ( $x_{EtBZ}^* = 0.73$ ).

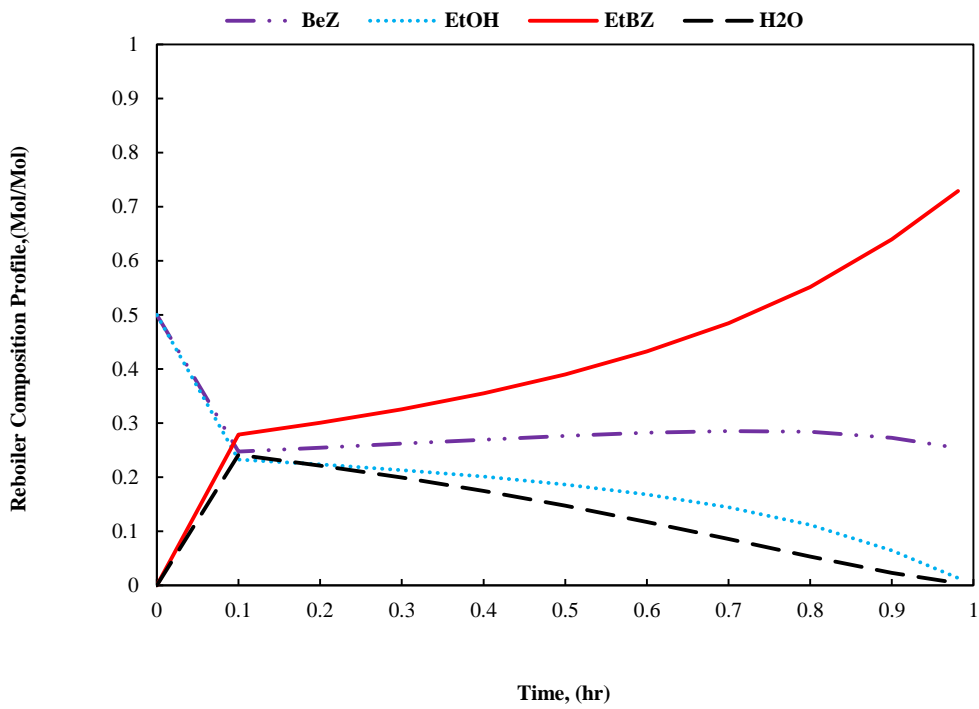


Figure 4: The reboiler composition of CBD column ( $x_{EtBZ}^* = 0.73$ ).

### 4.3.2 Case 2: i-CBD column

The operational and economic feasibility of the i-CBD operation as a prospective candidate for the EtBZ production is investigated. As mentioned before in sections 4.1 and 4.2, the use of excess ethanol in the feed can only enhance the conversion rate of benzoic acid, which decreases the desired bottom product amount significantly. Here, the i-CBD process is examined to improve the product amount in the reboiler at the equimolar ratio. Two scenarios are examined here, Scenario-A with one control interval policy of operation (NCI=1), and Scenario-B with two-control intervals (NCI=2). Note that the EtBZ product specification is increased starting from 0.730 onward in each scenario whilst the product amount in the bottom tank remains the same at 2.4 kmol.

#### 4.3.2.1 Scenario-A: Use of One-Reflux Interval (NCI=1)

The optimum operating results (optimum ethanol recycle rate, reflux ratio, minimum batch time together with the total energy usage, the total amount of ethanol recycled over the production time, and the conversion of BeZ into EtBZ) for different bottom product purities of EtBZ are summarized in Table 8. Unlike CBD case (Table 7), the results in Table 8 evidently indicate that i-CBD can produce higher quality product (0.925 mole fraction of EtBZ). To achieve this, the reflux ratio has to increase. This is due to the fact that the recycled stream has considerable amount of water to enhance the reverse reaction. To reduce the amount of water in the recycled stream, higher reflux ratio is required to enhance the forward reaction by converting more benzoic acid into ethyl benzoate (thus increasing conversion rate as shown in Table 8). This consequently increase the batch time and the energy consumption. As anticipated, an increase in the batch time results in the increase of BeZ conversion. It is obvious from Table 8 that the higher reflux ratio, and the higher processing-batch time demands the higher energy consumption at 0.925 of EtBZ purity compared to the others to suppress the move of EtBZ up the distillation column further and to fulfill the product purity requirement (Figure 8). The mixture composition profiles in the distillate tank and in the still pot are shown in Figure 5, and 6 for the EtBZ purity ( $x_{\text{EtBZ}}^* = 0.730$  mole fraction) and in Figure 7 and 8 for the EtBZ purity ( $x_{\text{EtBZ}}^* = 0.925$ ). Note that there is a sharp increase in minimum batch time and thus total heat usage (Table 8) to increase the EtBZ purity from 0.730 to 0.925 (mole fraction). For this case (0.925 mole fraction), the column needs to operate at higher reflux ratio and higher operating batch time to reduce the removal of ethanol from the top of column and to enhance the conversion of BeZ into EtBZ to satisfy the product constraint as presented in Table 8. It is clearly indicated

from the results of Table 8 that i-CBD system can produce ethyl benzoate at a much higher purity (0.925 mole fraction), and can convert more benzoic acid (93.57%) as compared to those obtained (74.38%) by using the CBD column (see Table 7). Note, the i-CBD with equimolar feed (Table 8) demanded higher operating time and more energy usage compared to the i-CBD case with excess ethanol (Table 5). A higher quantity of total ethanol recycling was needed for the i-CBD with equimolar feed compared to that for i-CBD with excess ethanol. Since a higher product amount of 2.4 kmol was specified to be obtained in the i-CBD at the equimolar feed case, the removal of higher amount from the still pot tank in this case needed a longer production batch time.

Table 8. Optimal Operation results for the production of EtBZ for i-CBD column at equimolar ratio using  $NCI = 1$ .

Product Quality, $X_{EtBZ}^*$	Optimal Recycle Rate, kmol/hr	Optimal Reflux Ratio, $R_{i-CBD}$	Final Batch time, $t_p$ , hr	Heat Usage, $Q_{tot}$ , GJ	EtOH Recycle Amount, kmol	Conversion of BeZ (%)
0.730	0.03	0.048	1.02	0.149	0.03	74.45
0.860	1.50	0.296	9.07	0.973	13.56	87.41
0.875	1.63	0.275	12.75	1.351	20.72	89.05
0.900	1.42	0.392	24.02	2.496	34.11	91.27
0.925	1.18	0.504	41.20	4.221	48.71	93.57

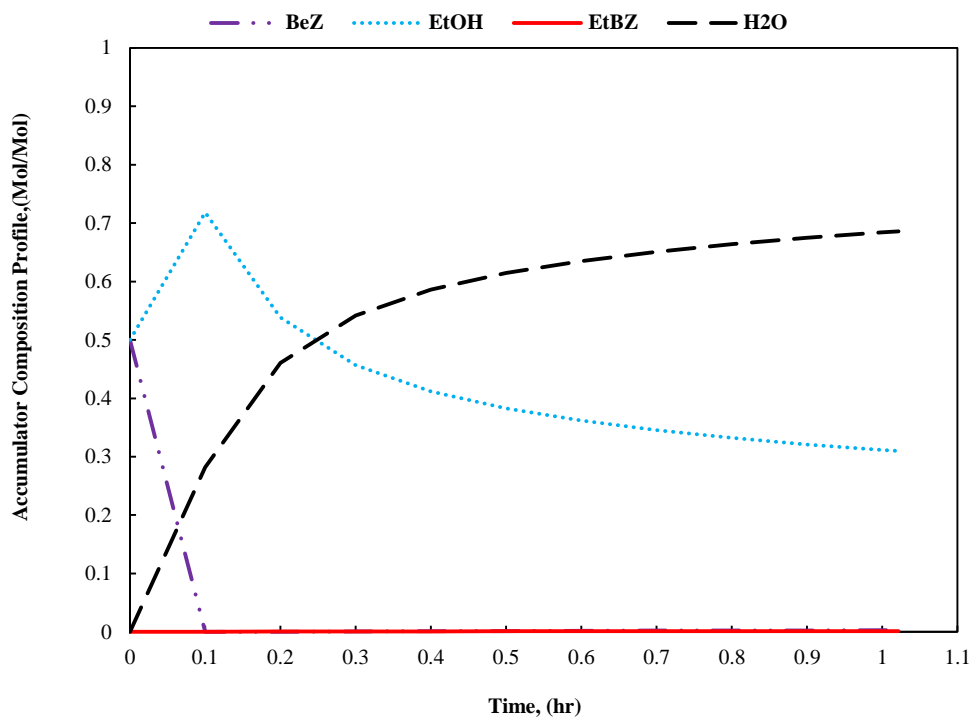


Figure 5: The accumulator composition of i-CBD column ( $x_{EtBZ}^* = 0.730$ ).

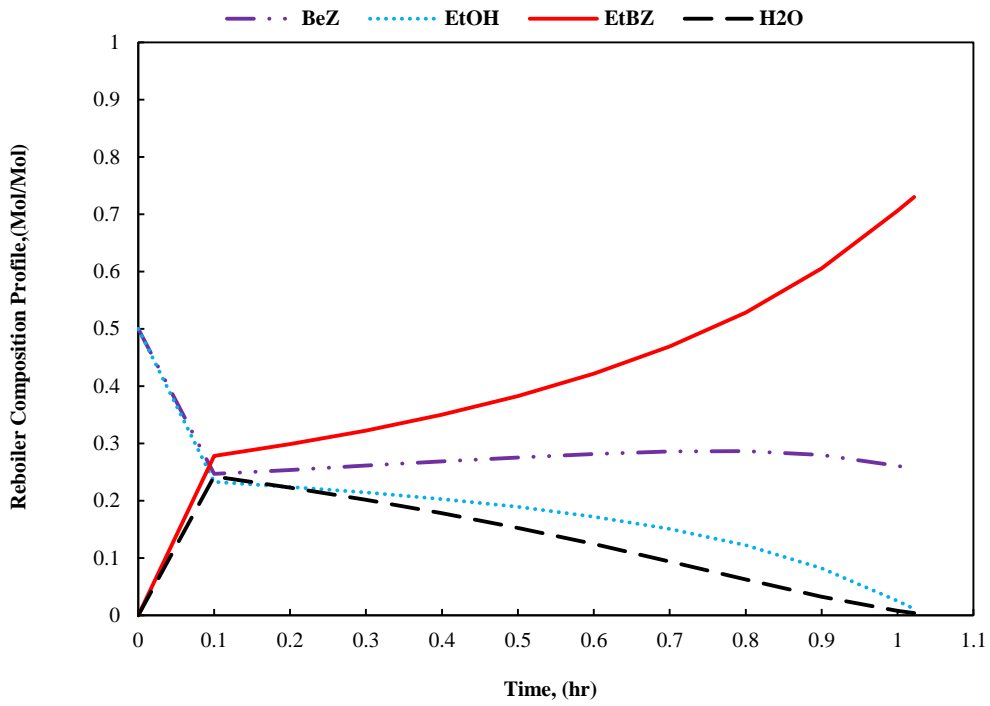


Figure 6: The Reboiler composition of i-CBD column ( $x_{EtBZ}^* = 0.730$ ).

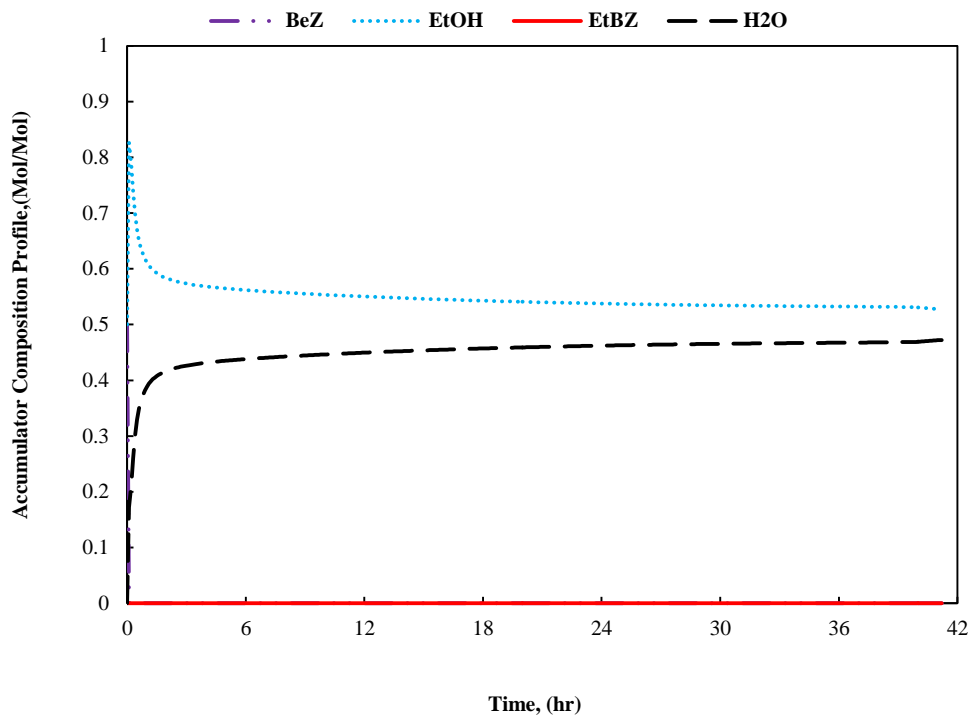


Figure 7: The accumulator composition of i-CBD, Single Control Interval ( $x_{EtBZ}^* = 0.925$ ).

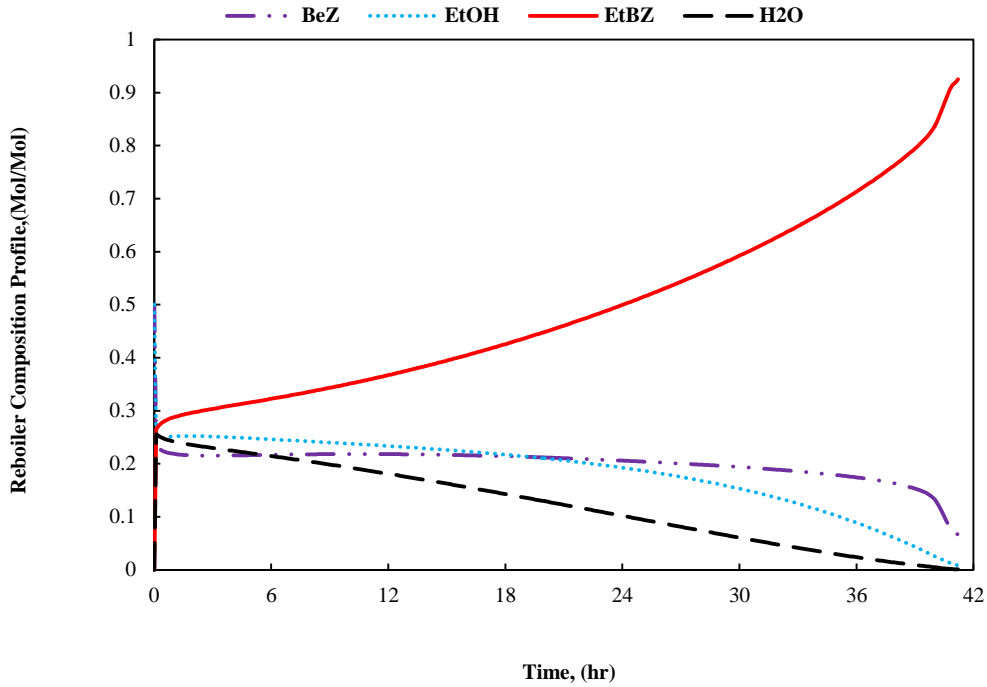


Figure 8: The Reboiler composition of i-CBD, Single Control Interval ( $x_{EtBZ}^* = 0.925$ ).

#### 4.3.2.2 Scenario-B: Use of Two-Reflux Intervals (NCI=2)

The optimal operating strategy for the i-CBD column is presented in Table 9, including the optimal recycle rate and reflux ratio, optimal switching time for each interval, final batch time, minimum energy consumption, total amount of EtOH recycle, and the maximum conversion of BeZ for different product purity considerations. It can be observed from Table 9 that the potential savings in the final production time (by about 81.12%), and the total energy required (by almost 80.25%), and maximum enhancement in the conversion of BeZ is by 1.97%, respectively at the 0.925 more fraction of EtBZ using multi-reflux intervals compared to single-reflux interval i-CBD operation (scenario-A). It is evident from Table 9 that two-reflux operation caused a significant reduction in the operating batch time and the heat demand compared to one reflux policy. This clearly shows the advantage of utilizing multi-control intervals strategy. It can be also noted that, total recycled ethanol can be reduced at using two control operation (reduction by about 75.55% compared to the single control interval policy). Multi-control strategy for the i-CBD process is found to have ability to secure more time and energy savings, and to enhance the maximum achievable conversion compared to one-control for the i-CBD operation (scenario-A).

It can be seen from Table 9 that the column operates at higher reflux ratio and lower operating batch time for the first-time interval to drive the water up to the distillate receiver

and then at low reflux ratio and high recycle rate of ethanol in the second interval to maintain both reactants (BeZ and EtOH) in the still drum to have further chemical reaction to satisfy the required product (EtBZ) quality. More ethanol is removed from the bottom of distillation column at high purity in the first-time interval but is not recycled leading to some amount of benzoic acid in the still pot and possibly having reverse reaction (see Figure 10, Table 9). While, in the second-time intervals ethanol is recycled converting most of the BeZ and producing EtBZ. Note that, although in this work only single and two-control intervals are employed, more than two-reflux intervals can be considered and optimization techniques can be used (Mujtaba, 2004) to determine suitable control intervals and further reductions in both production batch time and energy consumption are expected in such cases.

Table 9. Optimal Operation results for the production of EtBZ for i-CBD column at equimolar ratio using  $NCI = 2$ .

Product Quality, $x_{EtBZ}^*$	Optimal Recycle Rates $S_1, S_2$	Optimal Reflux Ratios $R_1, R_2$	Batch Time Intervals $t_1, t_2, \text{hr}$	Final Batch time, $t_p, \text{hr}$	Heat Usage, $Q_{tot}, \text{GJ}$	EtOH Recycle Amount, $\text{kmol}$	Conversion of BeZ (%)
0.730	0, 0.12	0.033, 0.000	0.62, 0.38	1.00	0.147	0.05	74.51
0.860	0, 1.47	0.641, 0.061	0.56, 2.16	2.72	0.326	3.17	88.42
0.875	0, 1.53	0.660, 0.067	0.71, 2.25	2.96	0.352	3.45	90.07
0.900	0, 1.67	0.704, 0.085	1.49, 2.10	3.59	0.42	3.50	92.90
0.925	0.2, 1.77	0.633, 0.199	1.16, 6.62	7.78	0.834	11.91	95.45

The mixture composition profiles in the distillate tank and the still pot drum of i-CBD operation at product purity requirement ( $x_{EtBZ}^* = 0.925$ ) are displayed in Figure 9 and 10 for two-control intervals. In the still pot, as the chemical reaction progresses, initially the concentrations of reactants (benzoic acid and ethanol) reduce gradually, whereas, the composition of ethyl benzoate rises. It can be seen from Figure 10 that although the concentration of benzoic acid increases in the first-time interval and then reduces in the second interval due to its consumption by reaction with ethanol resulting in higher BeZ conversion level at the end of reaction (see Table 9), the concentration of ethanol remains on decreasing due to big difference between the boiling point of the feed mixture. The ethyl benzoate reached the desired purity at the lower batch time for two-reflux strategy than the single-reflux case (Figure 8).

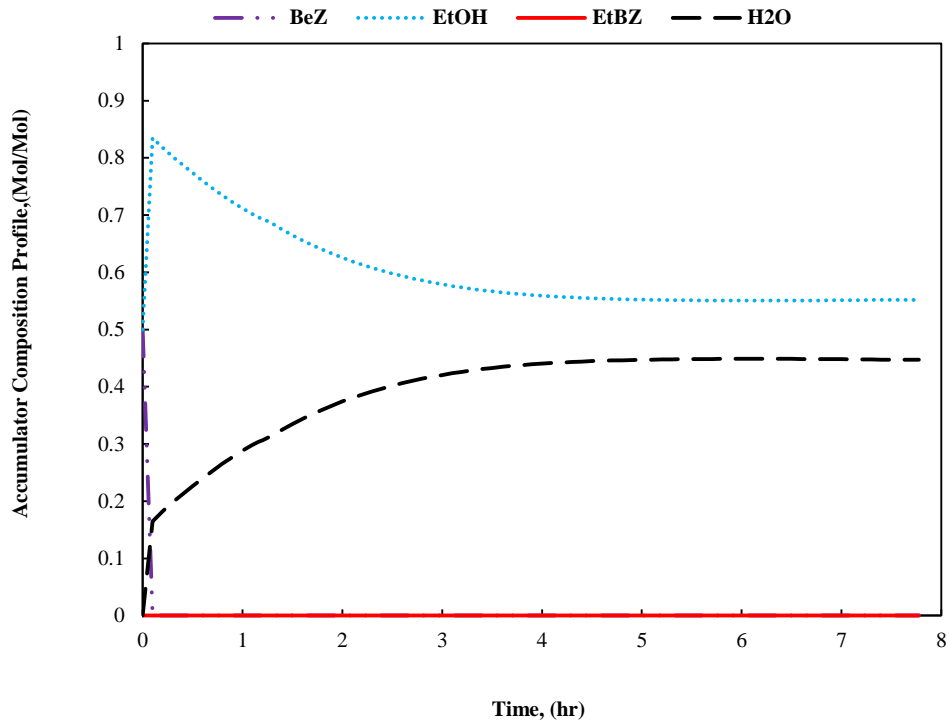


Figure 9: The accumulator composition of i-CBD, multi-control intervals ( $x_{EtBZ}^* = 0.925$ ).

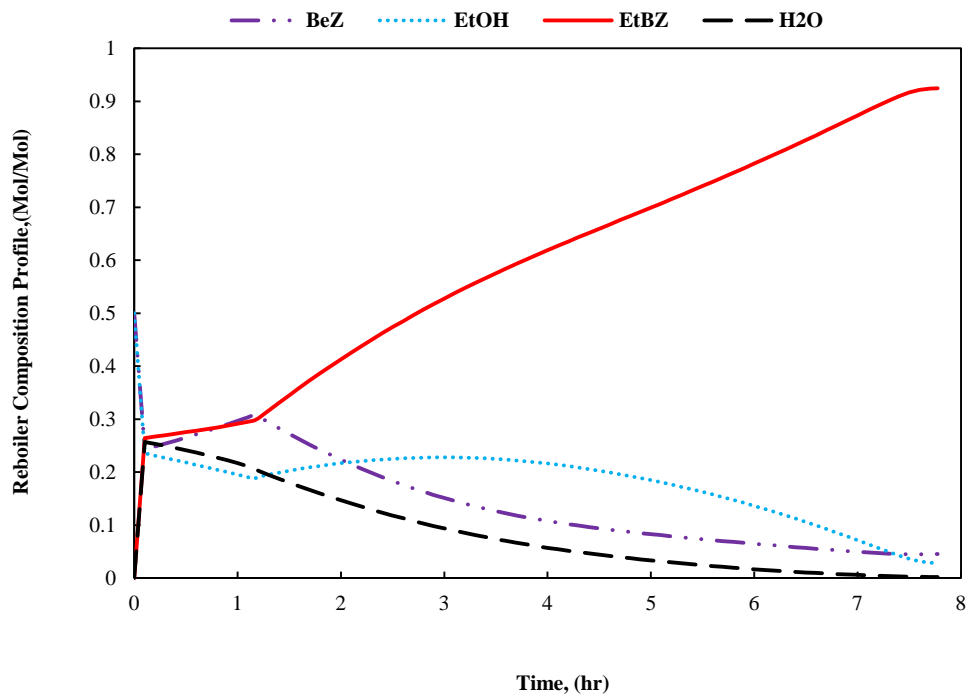


Figure 10: The Reboiler composition of i-CBD, multi-control intervals ( $x_{EtBZ}^* = 0.925$ ).

## 5. Conclusions

The production of ethyl benzoate (EtBZ) via esterification of benzoic acid with excess ethanol has only been reported in the past using reactors but the use of reactive distillation has not been reported. In this work, for the first time, the optimal operations of Conventional and Integrated (CBD and i-CBD) Batch Distillation columns are evaluated using model based techniques for the synthesis of EtBZ via the esterification of benzoic acid and ethanol. However, first, the traditional batch reactor-batch distillation (TRBD) operation is investigated to find the maximum possible amount and purity of EtBZ that can be obtained by using non-reactive batch distillation column. It is found that the effectiveness of employing the TRBD approach is very limited in terms of product amount and purity. Next, the reactive distillation columns (CBD and i-CBD) are investigated with excess ethanol to study if the conversion of the limiting reactant (BeZ) and the product amount purity can be improved.

Clearly, the reactive distillation system is found to outperform the classical TRBD mode by achieving higher ethyl benzoate purity with shorter production time and higher conversion rate. With excess ethanol, the performance of CBD mode was superior to the i-CBD process in terms of product purity, batch time, conversion of acid and energy consumption. Interestingly, with equimolar reactants ratio in the feed, the use of i-CBD column significantly improves the process efficiency in terms of batch time, energy consumption and conversion of the acid compared to those obtained by using CBD operation. In addition, equimolar feed ratio improves the amount of product significantly. This is only true when using two control intervals.

Note also, the optimization results for a given separation task indicate that multi-control intervals policy can significantly improve the process efficiency compared to that obtained by using single-control interval for the i-CBD column. For example, an overall operating time reduction of 81.12%, energy consumption reduction of 80.25%, and BeZ conversion enhancement of 1.97% at EtBZ composition of 0.925 mole fraction are possible by applying two-reflux interval policy instead of one reflux interval policy.

## Nomenclature

DAEs	Differential algebraic equations
$Q_{\text{tot}}$	The energy usage rate (mkJ)
$F_{\text{EtOH}}$	Ethanol feed rate (kmol/hr)
$S_{\text{EtOH}}$	Ethanol recycle rate (kmol/hr)



CBD	Conventional batch distillation column
i-CBD	Integrated conventional batch distillation column
OP1	Optimisation
D	Distillate rate (kmol/hr)
$H_L, H_V$	Liquid, vapor enthalpy (kJ/kmol)
K	Vapour-liquid equilibrium constant
$k_e$	Pre-exponential factor for the esterification reaction
L	Liquid rate in the column (kmol/hr)
$H_a, H_C$	Accumulator and condenser holdup respectively (kmol)
$H, H_N$	Stage and reboiler holdup respectively (kmol)
N	Number of stages
$Q_C, Q_{heat}$	Condenser or reboiler duty (kJ/hr)
$R_{i-CBD}, R_{CBD}$	Reflux ratio for i-CBD and CBD columns
$-r_{BeZ}$	Reaction rate of benzoic acid (mol/min.kg)
$m_{cat}$	The catalyst loading (kg of catalyst)
NCI	Number of control intervals
$S_1, S_2$	Recycled ethanol rate in time interval 1, and 2 for i-CBD (kmol/hr)
$F_1, F_2$	Ethanol feed rate in time interval 1, and 2 for SBD (kmol/hr)
SQP	Successive quadratic programming algorithm
$t_P$	Final batch time (hr)
$t_1, t_2$	Length of interval 1, and 2 and (hr)
$V_C$	Vapor load to the condenser (kmol/hr)
T	Temperature (K)
TRBD	Traditional batch reactor-batch distillation system
x	Liquid composition (mole fraction)
$x_a$	Accumulated distillate composition (mole fraction)
$x_D$	Instant distillate composition (mole fraction)
y	Vapor composition (mole fraction)

### **Greek Letters**

#### *Superscripts and subscripts*

$\epsilon$	Small positive numbering the order of $10^{-3}$
i	Component number
j	Stage number
$\Delta n$	Change in moles due to chemical reaction

## Abbreviations

BeZ	Benzoic Acid
EtBZ	Ethyl Benzoate
EtOH	Ethanol
H <sub>2</sub> O	Water

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## Appendix A

### A. Process Model for the CBD Column

#### 2.1. Condenser System and Distillate Tank: j=1

- Distillate Accumulator Total Mass Balance:

$$\frac{dH_a}{dt} = D \quad 7$$

- Component Mass Balance:

a) Distillate Accumulator:

$$H_a \frac{dx_{ai}}{dt} = D (x_{Di} - x_{ai}) \quad 8$$

b) Condenser Holdup Tank:

$$H_c \frac{dx_{ci}}{dt} = V_2 y_{2i} - (V_2 + \Delta n_1 H_c) x_{Di} + r_{1i} H_c \quad 9$$

- Energy Balance:

$$0 = V_2 H_2^V - (V_2 + \Delta n_1 H_c) H_1^L - Q_c \quad 10$$

- Physical Properties and other equations:

$$H_1^L = H_1^L(x_{D1}, T_1, P) \quad 11$$

$$T_1 = T_1(x_{D1}, P) \quad 12$$

$$r_{1j} = r_{1j}(k_e, x_{Di}) \quad 13$$

$$\Delta n_1 = \sum r_{1j} \quad 14$$

$$L_1 = R (V_2 + \Delta n_1 H_c) \quad 15$$

$$D = (1 - R) (V_2 + \Delta n_1 H_c) \quad 16$$

#### 2.2. Intermediate plates: j= 2 to N-1

- Total Mass Balance:

$$0 = L_{j-1} + V_{j+1} - L_j - V_j + \Delta n_j H_j \quad 17$$

- Component Balance:

$$H_j \frac{dx_j}{dt} = L_{j-1} x_{j-1} + V_{j+1} y_{j+1} - L_j x_j - V_j y_j + H_j r_{ji} \quad 18$$

- Energy Balance:

$$0 = L_{j-1} H_{j-1}^L + V_{j+1} H_{j+1}^V - L_j H_j^L - V_j H_j^V \quad 19$$

- Equilibrium:

$$K_{j,i} = \frac{y_{j,i}}{x_{j,i}} \quad 20$$

- Restrictions:

$$\sum y_{j,i} = 1 \quad 21$$

- Relations Defining Physical Properties and Chemical Reactions:

$$K_{j,i} = K_{j,i}(y_{j,i}, x_{j,i}, T_j, P) \quad 22$$

$$H_{j,i}^L = H_{j,i}^L(x_{j,i}, T_j, P) \quad 23$$

$$H_{j,i}^V = H_{j,i}^V(y_{j,i}, T_j, P) \quad 24$$

$$r_{j,i} = r_{j,i}(k_e, x_{j,i}) \quad 25$$

$$\Delta n_j = \sum r_{j,i} \quad 26$$

### 2.3. Partial Reboiler: j=N

- Total Mass Balance:

$$\frac{dH_n}{dt} = L_{n-1} - V_n + \Delta n_n H_n \quad 27$$

- Component Mass Balance:

$$H_n \frac{dx_n}{dt} = L_{n-1}(x_{n-1} - x_n) - V_n(y_n - x_n) + H_n r_n \quad 28$$

- Energy balance:

$$0 = L_{n-1}(H_{n-1}^L - H_n^L) - V_n(H_n^V - H_n^L) + Q_{\text{heat}} \quad 29$$

## B. Process Model for the i-CBD Column

The i-CBD process model is exactly same as the CBD column presented above except that the additional terms added to the process model to serve for the recycled ethanol from the distillate tank as presented below.

### 2.4. Distillate Tank:

- Distillate Accumulator Total Mass Balance:

$$\frac{dH_a}{dt} = D - S_{\text{EtOH}} \quad 30$$

- Component Mass Balance:

a) Distillate Accumulator:

$$H_a \frac{dx_{ai}}{dt} = (D - S_{\text{EtOH}}) \times (x_{Di} - x_{ai}) \quad 31$$

### 2.5. Partial Reboiler: j=N

- Total Mass Balance:

$$\frac{dH_n}{dt} = L_{n-1} - V_n + S_{\text{EtOH}} + \Delta n_n H_n \quad 32$$

- Component Mass Balance:

$$H_n \frac{dx_n}{dt} = L_{n-1}(x_{n-1} - x_n) - V_n (y_n - x_n) + S_{\text{EtOH}} (x_{\text{ai}} - x_n) + H_n r_n \quad 33$$

- Energy balance:

$$0 = L_{n-1} (H_{n-1}^L - H_n^L) - V_n (H_n^V - H_n^L) + S_{\text{EtOH}} (H^a - H_n^L) + Q_{\text{heat}} \quad 34$$

## Appendix B

Table 10. Antoine Parameters for Eq 3 (Yaws, 1997)

Antoine Coefficients	BeZ	EtOH	EtBZ	H <sub>2</sub> O
A [--]	-140.0388	23.8442	40.8047	29.8605
B [K]	8.0479E+1	-2.8642E+3	-3.9985E+3	-3.1522E+3
C [K <sup>-1</sup> ]	6.2611E+1	-5.0474	-1.1793E+1	-7.3037
D [K <sup>-1</sup> ]	-6.5321E-2	3.7448E-11	4.0697E-3	2.4247E-9
E [K <sup>-2</sup> ]	2.4596E-5	2.7361E-7	-1.2372E-13	1.8090E-6

A, B, C, D, E are the regression coefficients for chemical component.