Modelling and Optimization of Conventional and Unconventional Batch Reactive Distillation Processes

Investigation of Different Types Batch Reactive Distillation Columns for the Production of a Number of Esters such as Methyl Lactate, Methyl Decanoate, Ethyl Benzoate, and Benzyl Acetate using gPROMS

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Abstract

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Keywords: CBD, i-CBD, SBD, i-SBD, i-DWCBD, IBD, MVD, Modelling, Optimization, Esterification

The synthesis of a number of alkyl esters such as methyl lactate, methyl decanoate, and ethyl benzoate via esterification in a reactive distillation is quite challenging. It is due to the complexity in the thermodynamic behaviour of the chemical species in the reaction mixture in addition to the difficulty of keeping the reactants together in the reaction section. One of the reactants (in these esterification reactions) having the lowest boiling point can separate from the other reactant as the distillation continues. This can result in a significant drop in the reaction conversion in a conventional reactive distillation whether it is a batch or a continuous column.

To overcome this challenge, new different types of batch reactive distillation column configurations: (1) integrated conventional (2) semi-batch (3) integrated semi-batch (4) integrated dividing-wall batch distillation columns have been proposed here.

Four esterification reaction schemes such as (a) esterification of lactic acid (b) esterification of decanoic acid (c) esterification of benzoic acid (d) esterification of acetic acid are investigated here. A detailed dynamic model based on mass, energy balances, chemical reaction, and rigorous thermodynamic (chemical and physical) properties is considered and incorporated in the optimisation framework within gPROMS (**g**eneral **PRO**cess **M**odelling **S**ystem) software.

It is found that for the methyl lactate system, the i-SBD operation outperforms the classical batch operations (CBD or SBD columns) to satisfy the product constraints. While, for the methyl decanoate system, the i-DWCBD operation outperforms all CBD, DWBD and sr-DWBD configurations by achieving the higher reaction conversion and the maximum product purity. For the ethyl benzoate system, the performance of i-CBD column is superior to the CBD process in terms of product quality, and conversion rate of acid. The CBD process is found to be a more attractive in terms of operating time saving, and annual profit improvement compared to the IBD, and MVD processes for the benzyl acetate system.

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Nomenclature and Abbreviation

AA	Acetic Acid	-
AC	Annualised Capital Cost	($/year)
AgCL	Silver Chloride	-
AM	Acetamide	-
AgL	Silver Lactate	-
AmL	Ammonium Lactate	-
BeZ	Benzoic Acid	-
BzAC	Benzyl Acetate	-
BzOH	Benzyl Alcohol	-
CBD	Convectional batch distillation	-
CH_3CL	Methyl Chloride	-
CVP	Control Vector Parameterisation	-
D	Distillate flow rate	(kmol/hr)
DAE	Differential Algebraic Equations	-
DeC	Decanoic Acid	-
DHA	Dihydroxyacetone	-
DWBD	Divided-wall batch distillation	-
ET	Ethyl Lactate	-
EtBZ	Ethyl Benzoate	-
EtOH	Ethanol	-
F_1, F_2	Methanol feed rate in time interval 1, and 2	(kmol/hr)
FAME	Fatty Acid Methyl Ester	-

FFA	Free Fatty Acid	-
F_{MeOH}	Methanol feed rate	(kmol/hr)
GLA	Glyceraldehyde	-
H_a, H_c	Accumulator and condenser holdup	(kmol)
H_j, H_N	Plate and reboiler holdup respectively	(kmol)
H_L, H_V	Liquid, and vapour enthalpy respectively	(kJ/kmol)
HC	Hemiacetal	-
H_2O	Water	-
IBD	Inverted batch distillation	-
i-CBD	Integrated conventional batch distillation	-
i-DWCBD	Integrated divided-wall batch distillation	-
i-SBD	Integrated semi-batch distillation	-
K	Vapour-Liquid Equilibrium Constant	-
ke	Pre-exponential factor for the esterification	-
L	Liquid rate in the column	(kmol/hr)
L_2	Reflux side rate for sr-DWBD column	(kmol/hr)
L^{DW}	Liquid sent back to divided-wall column	(kmol/hr)
LA	Lactic Acid	-
m_{cat}	The catalyst loading	kg
MeDC	Methyl Decanoate	-
MeOH	Methanol	-
ML	Methyl Lactate	-
MVD	Middle-vessel batch distillation	-
N	Number of column plates	-

N_B	Number of Batches/year	(batch/year)
nc	Number of components	-
NCI	Number of Control Intervals	-
NLP	Nonlinear Programming Problem	-
OC	Operating cost	($/year)
OP	Optimisation	-
P	Operating pressure	(bar)
P^{sat}	Vapour pressure of pure component *i*	-
Q_C, Q_{Heat}	Condenser or reboiler duty	kJ/hr
Q_{tot}	Total Energy Consumption	(mkJ)
r	reaction rate	-
R, R_{max}	Reflux ratio and maximum reflux ratio	-
R_1, R_2	Reflux ratio in time interval 1, and 2	-
r_L	Liquid Split Ratio	-
r_V	Vapour Split Ratio	-
S_{MeOH}	Recycled Methanol rate	(kmol/hr)
S_1, S_2	Recycled Methanol rate in interval 1, and 2	(kmol/hr)
SBD	Semi-batch distillation	-
sr-DWBD	Split reflux divided-wall batch distillation	-
SQP	Successive Quadratic Programming	-
T	Temperature	(K)
t_f, t_s	Batch time and setup time	(hr)
t_1, t_2	Length of interval 1, and 2	(hr)
TAG	Tri-alkyl Glycerides	-

TRBD	Traditional Reactor-Batch Distillation System	-
u(t)	Control variable	-
V	Vapour flow rate in the column	(kmol/hr)
V^{DW}	Vapour sent back to the DWC	(kmol/hr)
x, y	Liquid or vapour composition	(mole fraction)
x_a	Accumulated distillate composition	(mole fraction)
x_D	Instant distillate composition	(mole fraction)

Superscripts and subscripts

ε	Small positive numbering the order of 10^{-3}	-
i	Component number	-
j	Stage number	-
γ_i	Activity coefficient of component *i*	-
λ_i	Latent heat of vaporisation of component *i*	(kJ/kmol)
Δn	Change in moles due to chemical reaction	-

Chapter One

Introduction

Batch distillation processing is a vital technique for separation of liquid mixtures into two or more products having different boiling points. The distillation operation can be categorized into two main types based on their application: continuous and batch distillation. Continuous distillation is mostly used in the petrochemical and bulk chemical industries, whereas, batch distillation is primarily used in specialty product, pharmaceutical, and biotechnological industries. Additionally, the semi-continuous mode (semi-batch) is used also as a distillation process. All these processes can be executed with or without chemical reactions. The batch process is an especially attractive option for low-scale production and high-value added such as polymers, pharmaceuticals, and biochemical or specialty chemicals. Shah (1992) presented several reasons of using batch processing such as increasing the global competition in the bulk products sector; manufacturing consumer specific products, and seasonal requirements of specific products. It is economically more desirable to produce small amounts of different products in a facility such as multiuse batch process, instead of operating single plant per product. This chapter displays the general background of distillation column, the brief characterization of the different distillation configurations, and their significance and applications.

Next, the scope of the research, and its aim and objectives are summarized. Finally, the organization of this thesis work is outlined.

1.1 Continuous Distillation Column

The continuous distillation column is classified into two main sections: rectifying, and stripping sections as shown in Figure 1.1 (Perry and Green, 1997).

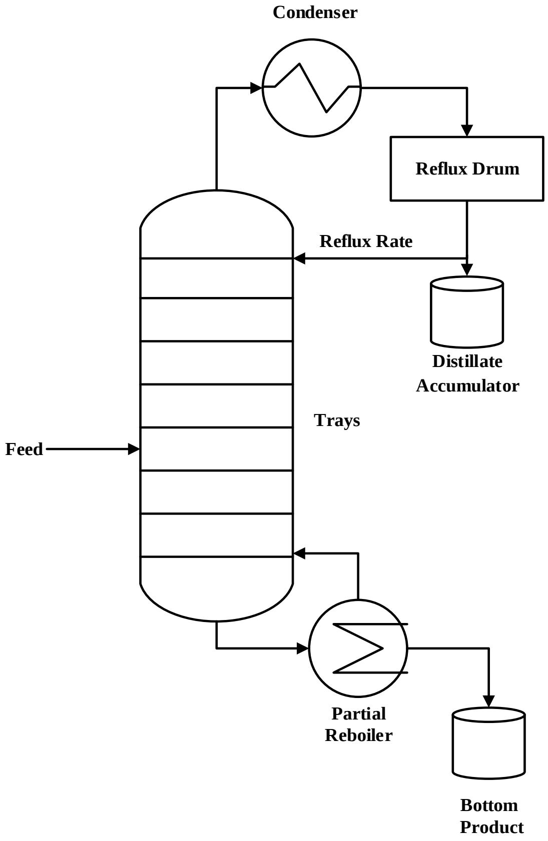

Figure 1.1 Continuous Distillation Column Configuration

In this type of column, the feed mixture is injected into the distillation column at one or more stages along the column shell, which is separated into fractions. The vapour flows up the distillation column while liquid flows down the column contacting vapour at each equilibrium plate due to the large difference in gravity between them.

The liquid reaching the bottom of column is partially vaporized in a still pot to offer the boil-up, which is returned to the main column. The remaining liquids are taken out from the bottom stream as heavy bottom product.

The vapour reaching the top of the column is partially or fully condensed to liquid in overhead condenser. Part of the condensed liquid is refluxed back to the column in order to provide liquid overflow. The remaining liquid is withdrawn from the top of the column as the distillate product.

In general, continuous distillation operations run at fixed reflux ratio and re-boil ratio during the processing periods, whereas, the optimum values of both reflux and re-boil ratios are basically estimated at the design stage. The continuous distillation technology is vastly employed in oil refineries to distillate high amounts of liquids.

The mixture of crude oil can be refined into valuable fractions (e.g. light overhead gases, light and heavy naphtha, kerosene and diesel, and residue in a multiple product column (Gary and Handwerk, 1984). Figure 1.2 illustrates schematic diagram of crude oil distillation tower.

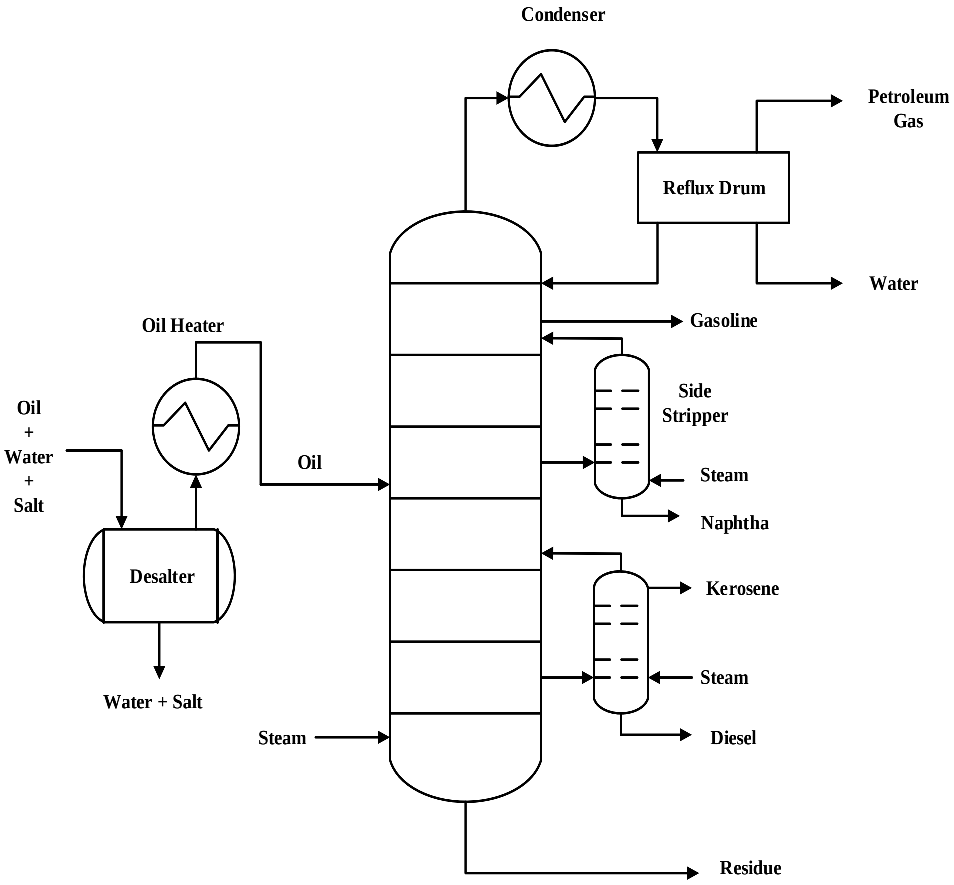

Figure 1.2 Scheme of Atmospheric Distillation Unit

1.2 Batch Distillation Column

Batch distillation is the oldest process used for separation of liquid mixtures, particularly for seasonal demand and/or low-volume production. It is extensively utilised in many applications such as the production of fine, specialized products such as alcoholic beverages, perfume, pharmaceutical and petroleum products. Batch distillation operations have received more considerable acceptance due to increasing seasonal demands for high-value-added fine products, specialty chemicals, food and pharmaceuticals, and biochemical products. Compared with the continuous distillation operation, it is a more flexible operation with lower annual investment cost and suitable for lower volume production. When the batch-wise operation is compared with continuous reactive distillation unit, the batch distillation is more efficient and appropriate for low scale production and high-added value such as fine and specialty chemicals industries. Many researchers (Mujtaba, 2004; Kao and Ward, 2015 a; Kao and Ward, 2015 b; Orozco et al., 2016; Safdarnejad et al., 2016; Reddy et al., 2017; and Stojkovic et al., 2018) recommended the use of the batch-wise process in many chemical industries where the small volume products are handled in different scheduled periods (regular or seasonal demands).

1.2.1 Conventional Batch Distillation

The conventional (regular) batch column (CBD) is typically the most famous type of batch distillation column. In a CBD column, the total amount of initial feed is loaded into the reboiler drum at the beginning of operation and heated up to its boiling point temperature. The CBD consists of a rectifying section (plate or packed column) placed over the partial reboiler and linked by a total/partial condenser system and accumulator tank. The vapour flows up the column and condensed at the top. A part of the condensed liquid is collected continuously at the distillate tank while the rest is refluxed down to the rectifying section (intermediate trays). The reflux rate and reflux ratio can be considered as vital keys in determining the distillate/bottom purity and the operation batch time. The liquid with lower boiling point compounds in the in the bottom tank is progressively exhausted. As the total amount of liquid in the pot drum reduces, the composition of heavier component increases. A schematic diagram of regular batch distillation column is given in Figure 1.3. The CBD process typically runs at three aspects of operating modes: constant reflux ratio with varied distillate mole fraction, fixed distillate composition with variable reflux ratio, and total reflux mode. Hence, these above basic modes of operation can be combined to optimize the process of a given separation task.

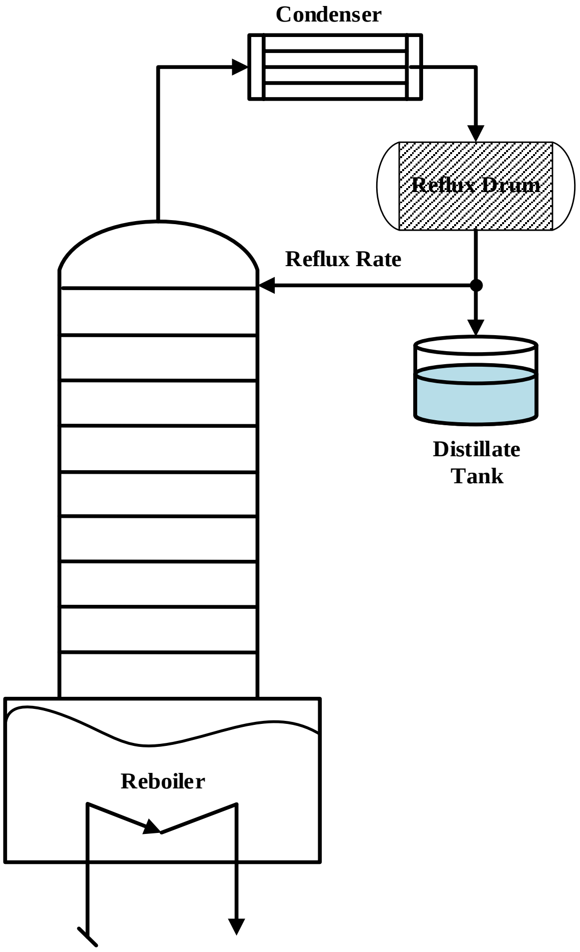

Figure 1.3 Schematic Diagram of Conventional Batch Column

1.2.2 Divided-Wall Batch Distillation Column

A common characteristic of batch and continuous distillation columns is high energy requirement. To overcome this challenge, the divided-wall distillation column (DWDC) was employed by Petlyuk et al. (1965). The dividing-wall distillation column (DWDC) is a special process accomplished by inserting a vertical-partition wall inside a single-distillation column. The divided-wall distillation system was patented by Kaibel (1987) as presented in Figure 1.4b. It is thermodynamically equivalent to the Petlyuk distillation system explored by Petlyuk et al. (1965) when there is no heat transfer from the dividing wall.

Since then, the divided-wall distillation operations are extensively utilised for liquid separations in chemical industries, thereby reduction up 30% in total annualized costs and saving total operating costs by up to 40% due to avoiding the remixing impact of liquids and improving the thermodynamic proficiency (Asprion and Kaibel, 2010; Dejanović et al., 2010; Harmsen, 2010; and Yildirim et al., 2011).

The divided-wall operations offer a better performance in terms of higher process efficiency, higher product purities, lower energy usage rate, and lower total equipment costs, as well as lower installation space as compared with continuous and batch distillation configurations. Since the heating vapour and the cooling liquid-divided streams from the main column to the the side column (prefractionator) in the reactive divided-wall distillation configuration are provided by prefractionator, there is no need to utilize a condenser and pot drum (Figure 1.4a). In general, the Petlyuk distillation and the dividing wall (DWDC) systems are examples of the thermally-coupling distillation column.

A high degree of remixing of intermediate component can happen in conventional distillation systems, whose effect can cause wastage of a portion of the required thermal energy used in order to purify the component with the intermediate boiling temperature from the light component. The dividing-wall distillation configuration can be used to minimize the energy demand due to the decrease in the degree of remixing in the prefractionator. The condenser and the reboiler of the prefractionator are omitted through the thermal linking of the two columns in contrast to conventional distillation processes. The dividing-wall distillation system is the integration of the main column and side column of Petlyuk configuration into the same vessel (Figure 1.4b).

The batch reactive distillation column with a divided wall placed inside a single-shell vessel is split into the left and right sections, and the prefractionator section is located in the left part of batch column. There are two interlinking streams between the main column and prefractionator. Since the side column (prefractionator) has no condenser and reboiler drum with a consequent reduction in energy usage rate, the dividing-wall distillation configuration can be considered thermodynamically an equivalent to a Petlyuk distillation system. The liquid split stream is at the top of the liquid distributor tray where interconnection liquid split ratio (r_L) defined as the fraction of the liquid sent back to the prefractionator to the total flow rate of liquid coming down from the first tray of main column. While, at the bottom of the vapour distributor tray, there is an interconnection vapour split ratio (r_V) defined as the proportion of the vapour fed to the prefractionator to the vapour coming down from the last tray of main column.

It has been stated before that the thermal energy consumption relies strongly on the liquid and vapour split ratios as the vital parameters. The thermal energy proficiency of divided-wall batch distillation column can be considerably reduced by a small deviation in either the liquid or the vapour split ratio from the optimal operating conditions. Hence, it is important to find the optimal values for both liquid and vapour split ratios to minimize the total energy demand (Hernandez and Jimenez, 1999; Delgado-Delgado et al., 2012; Ge et al., 2014; Li et al., 2016; and Ge et al., 2017). The vertical-wall fitted into the batch distillation column can be employed to prevent the chemical and physical contacts of lift with the right-side stream. Therefore, this technique can lead to savings in both the processing-batch time and energy usage rate and thus enhance the system efficiency.

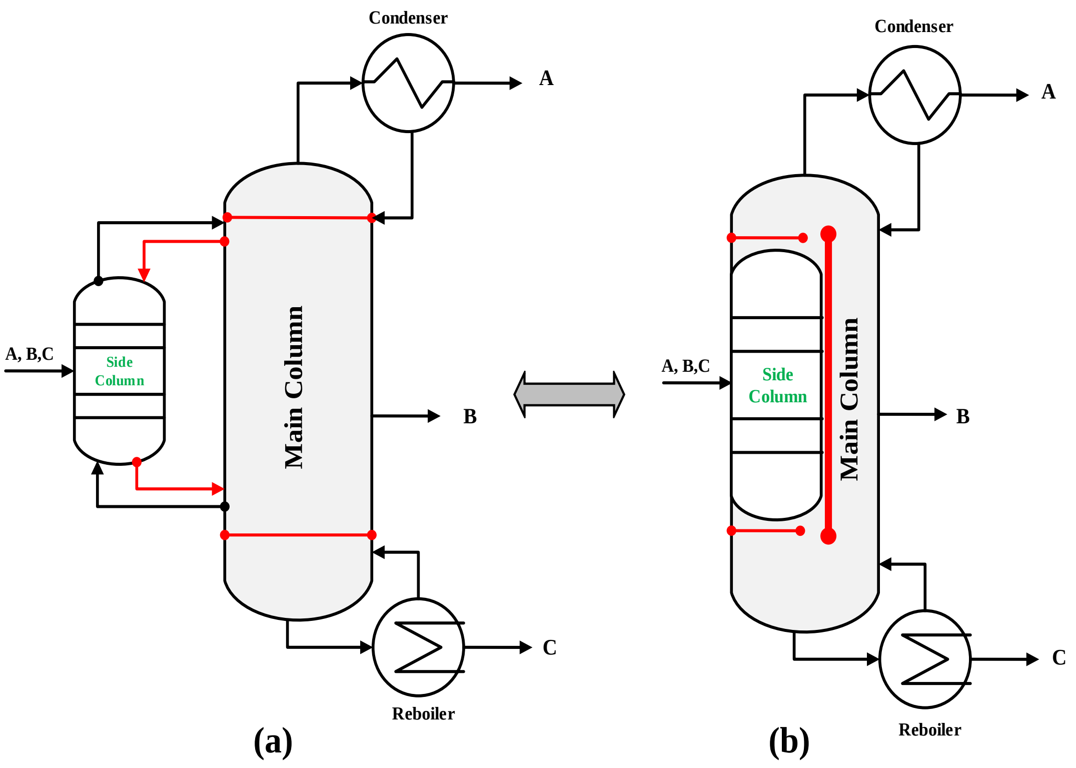

Figure 1.4 (a) Petlyuk system; (b) Dividing-wall distillation column

1.2.3 Semi-Batch Distillation Column

Figure 1.5 displays a representative semi-batch (semi-continuous) distillation process (SBD). The SBD is the same as the CBD system except that a feed is charged continuously to the distillation column via a side stream, whereas in CBD, all chemical species are loaded initially to the reboiler drum.

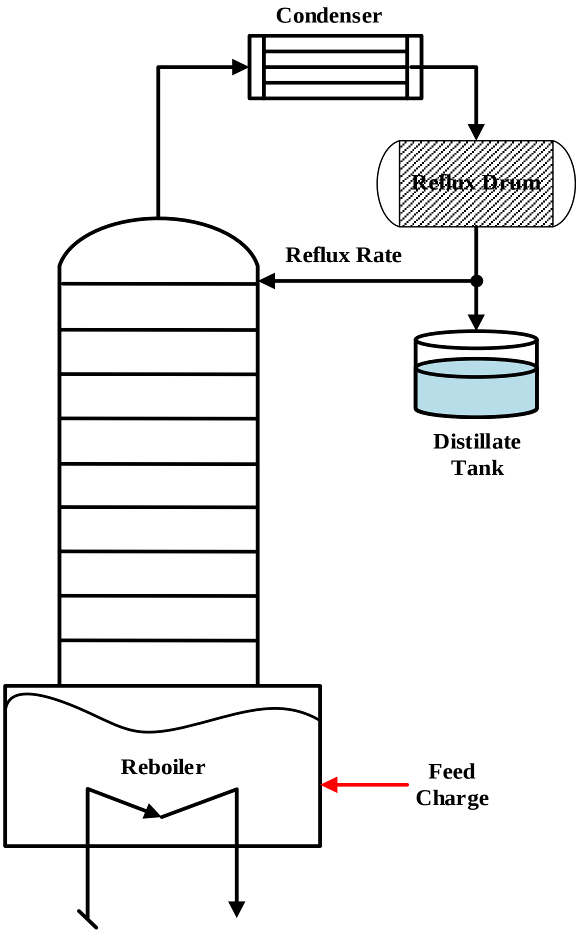

Figure 1.5 Schematic Diagram of Semi-Batch Column

This type of the column configuration is more convenient for batch reactive distillation, extractive distillation, etc. (Lang and co-workers, 1994; Li et al., 1998; Mujtaba 1999, Fernholz et al., 2000; Adams and Seider, 2008; Thotla and Mahajani, 2009; Edreder, 2010; Qi and Malone, 2010; Wijesekera and Adams, 2015a; Wijesekera and Adams, 2015b; Meidanshahi and Adams, 2016; and Lee et al., 2016).

A number of features of distillation systems are used to compare batch with semi-batch (semi-continuous) and continuous distillation columns and were outlined by Edreder (2010) as shown in Table 1.1.

Table 1.1 Comparisons of Distillation Operations

Feature	Batch	Semi-Batch	Continuous
Investment	Low	Intermediate	High
Flexibility	More Flexible	More Flexible	Less Flexible
Single column for ternary mixture	Yes	Yes	No
Heat integration	No	No	Yes
Automatic control	Unusual	Possible	Often
Throughput	Low	Middle	High

1.2.4 Inverted Batch Distillation

Figure 1.6 shows the inverted batch distillation column (IBD) originally suggested by Robinson and Gilliland (1950) which integrates the feed tank and the reflux drum and operates in an all-stripping aspect with low amount of holdup in the reboiler. The liquid flowing down the column is evaporated in the still pot and the fraction is removed as the distillate product. The products are withdrawn with the heavier component first, based on their boiling points. The operation of IBD configuration is exactly similar to CBD process except the desired products are taken out from the bottom tank. For this type of batch system, the reboil ratio is usually defined as the produced vapour flow rate over the withdrawn bottom flow rate where the reboiler ratio is one of the important keys in estimating the desired product purity specification with the final time.

Mujtaba and Macchietto (1994); Sorensen and Skogestad (1996); Masoud and Mujtaba (2009); Edreder et al. (2011); and Kao and Ward (2015 a) reported further the use of inverted batch columns.

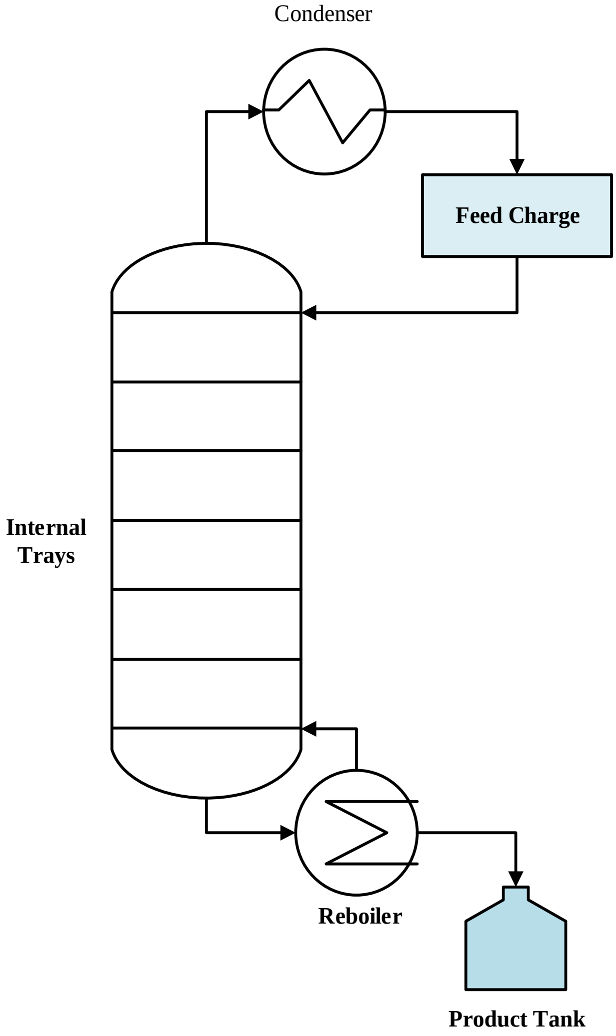

Figure 1.6 Schematic Diagram of Inverted Batch Column

1.2.5 Middle Vessel Batch Distillation

The middle-vessel batch column (MVD) is the integration of conventional and inverted batch distillation column as shown in Figure 1.7. The separation section in MVD is divided into rectifying and stripping sections when the feed is introduced into the middle of column, as in the usual continuous distillation process. There are several advantages of this type of batch distillation, which include injecting the feed into an appropriate location, keeping the reboiler holdup to the minimum, recycling the liquid mixture from the feed plate to the feed tank and withdrawing the lighter and heavier fractions simultaneously from top and bottom of column by pushing the reaction further to the right (Mujtaba, 2004).

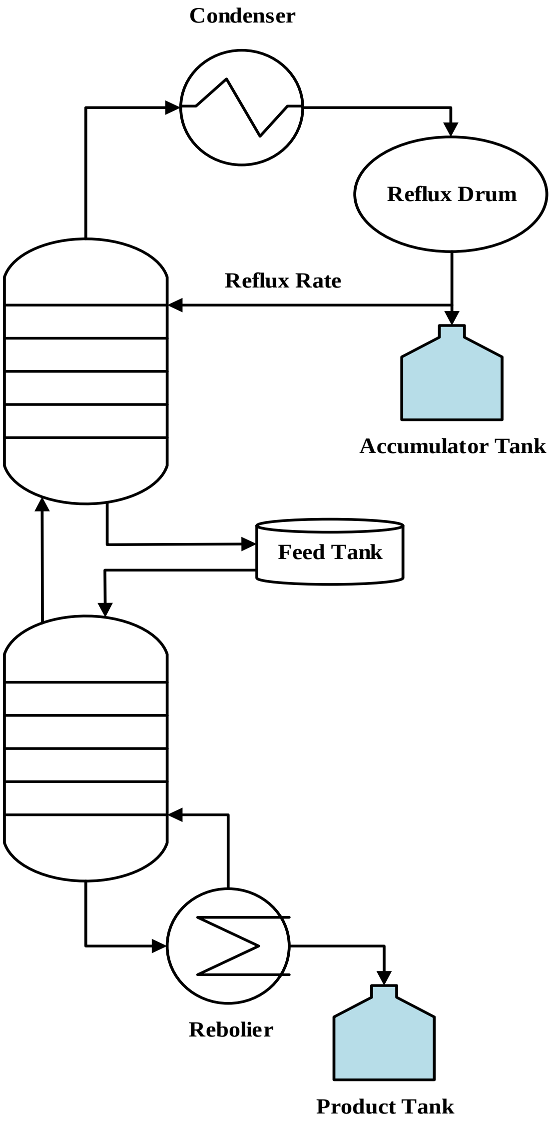

Figure 1.7 Schematic Diagram of Middle Vessel Batch Column

MVD can be used where some of the reaction products have lower and some higher boiling point rankings than those of the reactants. This MVD scheme was initially proposed by Robinson and Gilliland (1950) and was first applied to evaluate the column performance for binary mixture by Bortolini and Guarise (1970). Further investigations on MVD column were carried out by many authors (Hasebe et al., 1992; Barolo et al., 1996; Mujtaba and Macchietto, 1992, 1994; Warter and Stichlmair, 2000; Warter et al., 2004; Kao and Ward, 2014b; and Kao et al., 2017).

1.3 Traditional Batch Reactor-Batch Distillation Approach

Usually, for a number of chemical industries, chemical reactions and distillation have been carried out separately in a reactor followed by a non-reactive batch distillation operation as displayed in Figure 1.8 (Charalambides et al., 1993). Therefore, the separation of desired product in cannot affect the conversion of limiting reactant in the fixed bed reactor. Batch distillation with reaction is the combination of chemical reaction and separation into a single vessel, which is referred to as batch reactive distillation system. However, it is a highly recommended when one of the reaction species is either the heaviest or the lightest component in the reaction mixture (Edreder, 2010; and Edreder et al., 2011). In the case of reversible reaction system (A+B <==> C+D), the removal of desired products by distillation process (either as the top or as the bottom product) favours the forward reaction and thus can produce a higher conversion of reaction reactants than the traditional batch reactor-batch distillation system.

The mixture feed (A and B) is injected to the equilibrium reactor at the beginning, where the chemical reaction is carried out in the liquid phase in the presence of a catalyst and reached equilibrium point (the rate of forward reaction = the rate of backward reaction). After that, a distillation column is needed to separate the products reaction (C and D), whereas the unreacted compounds can be returned back to the reactor. Although, the benefits of reactive distillation technology are well known in the chemical industry specifically with the esterification reaction regimes since 1921, the improvement and successful application of integration of reaction and distillation in single apparatus has attracted growing interest in last years (Backhaus, 1921). Taylor and Krishna (2000) outlined a number of advantages by using batch reactive distillation column: a) significant reductions in capital investment and operating costs through the simplification of separation system, b) higher benefit in reduced recycling costs can be achieved by increasing the reaction conversion, c) the formation of by-product can be decreased, d) no azeotropes can be formed, e) the reboiler heat duty can be decreased and the heat of vaporization can be provided from the reaction heat as the heat integration benefits if the overall reaction occurred in the batch column is exothermic.

The batch reactor as shown previously in Figure 1.3 can be integrated with the multistage separator in one single unit and named as batch reactive distillation column where this integrated process is very helpful for such chemical reaction for which equilibrium reaction limits the conversion level. With continuous separation of products from reactants, whilst the chemical reaction is in progress, the reaction can continue to a much higher conversion of limiting reactant. The feed is loaded into the still pot or batch rectifier at the bottom of the rectification section. The yields of the equilibrium reactions in the reactor can be improved by increasing the reaction temperature up to the boiling point of the mixture.

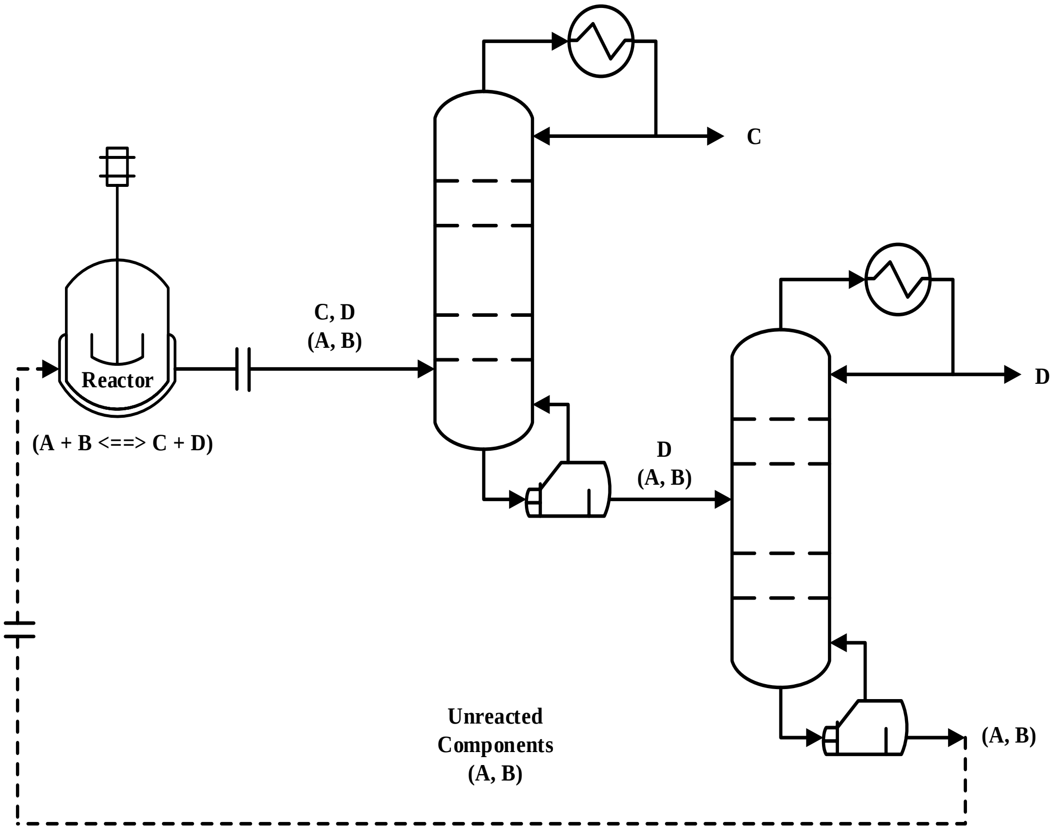

Figure 1.8 Traditional Reaction Distillation Process

1.4 Scope of This Research

This research is focused on the optimization of different batch distillation systems for a number of reaction schemes, such as (a) esterification of lactic acid with methanol (b) esterification of decanoic acid with methanol (c) esterification of benzoic acid with ethanol and (d) esterification of acetic acid with benzyl alcohol. The main issues in batch reactive distillation column processes are:

- Minimizing the operating batch time for a given product amount and product purity in a given column.
- Minimizing the total energy consumption for a defined separation task.
- Maximizing the profitability of operation for given product constraints.

The purification of impure lactic acid in the past has been conducted in reactive distillation (batch or continuous) as a two-step operation: esterification of impure lactic acid into methyl lactate followed by hydrolysis of methyl lactate into pure lactic acid (Choi and Hong, 1999; Kim et al., 2002; Ma et al., 2005; and Kumar et al., 2006 a, b). However, the main focus of their work was the synthesis of lactic acid and not the methyl lactate. On the other hand, very limited studies in the existing literature have reported the dynamic simulation and modelling of methyl lactate synthesis in semi-continuous and continuous distillation modes (Thotla and Mahajani, 2009; Chen et al., 2013; Zhang et al., 2015; Chen et al., 2016; and Cao et al., 2017). Although some of these studies mentioned the importance of removal of large quantity of water in the esterification reaction (due to dilute lactic acid feed and subsequent production of water) before the separation of methyl lactate for the hydrolysis reaction, no one took into account the difficulty of keeping both lactic acid and methanol together in the reboiler to enhance the conversion of lactic acid.

The esterification of decanoic acid with methanol to synthesize methyl decanoate has been considered only in continuous reactive distillation by a limited number of scholars (Steinigeweg and Gmehling, 2003; and Machado et al., 2011). Inferior performances of product purity and conversion level of decanoic acid were obtained in their study. The use of batch reactive distillation for the synthesis of methyl decanoate is non-existent and is considered here to see if an improved conversion of decanoic acid and product purity are possible.

The esterification process of benzoic acid with ethanol producing ethyl benzoate was conducted previously by using different types of reactors (Plazl, 1994; Pipus et al., 2000; Lee et al., 2005; and Wu et al., 2013). However, to the best of author’s knowledge, no reported work in literature has addressed to date the use of either batch or continuous distillation columns for the synthesis of ethyl benzoate from the reaction mixture.

Kinetic studies of the esterification of acetic acid with benzyl alcohol to produce benzyl acetate explored only in batch reactor in the past (Roy and Bhatia, 1987, Ali and Merchant, 2009, and Kirumakki et al., 2004). In fact, to author’s knowledge, no investigations have been reported to present on the employing of either batch or continuous distillation systems for the synthesis of benzyl acetate.

Obviously, there is much scope of further research in batch reactive distillation process when the current work (with all the four kinetic systems in different sorts of batch column configurations) is compared with the issue highlighted at the beginning of this section.

From the foregoing, this research is focused on the following:

- Enhance the production and recovery of methyl lactate rather than focusing on the purification of lactic acid which has already received quite a bit of attention in recent years (Edreder et al., 2011; Mujtaba et al., 2012).
- Recovery and recycling of methanol in an integrated manner by proposing two new integrated column configurations (i-CBD and i-SBD) for the optimal synthesis of methyl lactate in terms of maximum annual revenue via the minimization of batch time.

- Minimize the energy consumption rate for the synthesis of methyl decanoate using both integrated conventional (i-CBD) and semi-batch distillation reactive operations.
- Minimize the energy consumption rate for the synthesis of methyl decanoate using different types of divided-wall batch reactive distillation columns (DWBD, sr-DWBD, i-DWCBD). A detailed dynamic model for the process is constructed and used in the optimization framework.
- Minimize the batch time for the synthesis of ethyl benzoate using the application of a conventional (CBD) and the integrated (i-CBD) conventional batch distillation columns.
- Maximize the profitability for the synthesis of benzyl acetate using middle-vessel (MVD), inverted (IBD), and conventional (CBD) batch distillation columns. A rigorous dynamic model incorporating the kinetic model of Ali and Merchant (2009) is developed and utilized into the dynamic optimization problem.

In all case studies, rigorous dynamic models are characterized by the set of highly nonlinear differential-algebraic equations (DAEs) which act as equality constraints to the optimization framework.

The dynamic optimization problem is converted to a nonlinear programming problem (NLP) and solved by Control Vector Parameterization (CVP) method using efficient SQP-based technique (Mujtaba, 2004) within gPROMS software (general PROcess Modelling System, 2017).

1.5 The Aim and the Objectives of the Work

The aim of this work is to propose novel batch configurations and to study the optimization of different batch reactive column configurations with application to the several reaction systems, including esterification of lactic acid, decanoic, benzoic acid, and acetic acid with different alcohol (methanol, ethanol, and benzyl alcohol). The different problem of optimization frameworks is formulated and solved.

The objectives of the thesis can be summarized as follows:

- To carry out literature review on the modelling, simulation and optimization of different batch column configurations (conventional and unconventional). Reaction kinetics and thermodynamic aspects of esterification schemes.
- To achieve the best operational strategy of semi-batch reactive system for the optimal synthesis of methyl lactate and this strategy to enhance the process performance. The performance of a semi-batch column is evaluated in terms of minimum batch time. The piecewise-constant strategy for the optimization parameters (reflux ratios, and methanol feed rate) are used in the optimization study. Additional constraints are posed into the optimization problem to prevent the overloading of reboiler due to continuous feeding of methanol.
- To maximize the profitability via the minimum operating batch time for the production of methyl lactate in both i-CBD and i-SBD systems. The reflux ratio and methanol recycle rate for i-CBD and methanol feed charge for i-SBD are chosen as control variables which are optimized

(as piecewise constants) for a given desired product purity and its amount in the bottom.

- To minimize the total energy usage for the optimal formation of methyl decanoate (MeDC) using different types of batch distillation processes (i-CBD and SBD) with varying feed concentration subject to a given amount of MeDC and its quality.
- To minimize the energy consumption for the optimal synthesis of methyl decanoate (MeDC) using both sr-DWBD and i-DWCBD. The piecewise-constant policy for the optimization (reflux ratio, liquid, and vapour split ratios, as well as the refluxed rate of side stream (for sr-DWBD) and methanol recycled rate (for i-DWCBD) are employed in the optimization study.
- To minimize the batch time for the synthesis of ethyl benzoate by using both CBD and i-CBD operations. Different cases with varying quantity of reactants (excess feed and equimolar feed) are utilized to improve the process efficiency. The effect of excess feed composition on the process is also considered in this work.
- To maximize the profitability via minimization of batch time for the benzyl acetate production using different batch distillation columns (middle-vessel, inverted, and regular batch columns). For a defined separation task, the reboil ratio for IBD and reflux ratio for MVD, and CBD are selected as optimization parameters.

This thesis will highlight the following contributions (Table 1.2) for the synthesis of a number of esters such as methyl lactate, methyl decanoate, ethyl benzoate, and benzyl acetate via esterification processes in terms of different optimisation problems using different novel column configurations.

Table 1.2 Contributions of this Research Work

Type of Columns	System	Optimization
CBD, SBD	Methyl Lactate	Min. Batch Time
i-CBD, SBD, i-SBD		Max. Profitability
CBD, i-CBD, SBD	Methyl Decanoate	Min. Energy Usage
DWBD, sr-DWBD, i-DWCBD		Min. Energy Usage
TRBD, CBD, i-CBD	Ethyl Benzoate	Min. Batch Time
MVD, IBD, CBD	Benzyl Acetate	Max. Profitability

1.6 The Thesis Outline

This thesis focuses on the dynamic optimisation of several distillation column configurations involving a number of esterification reactions. The organization of this thesis is shown as follows:

Chapter 1: Introduction

Chapter one shows an overview on batch distillation in general, brief introduction, feasibility and their applications of conventional and unconventional batch distillation modes. The scope of this research, aim and objectives has been presented.

Chapter 2: Literature Survey

Chapter Two takes a look at the previous work on conventional and unconventional distillation columns with chemical reaction. The knowledge gap in the research is identified which sets the scene for this thesis. This chapter also describes the relevance of early work to the current work.

Chapter 3: New Reactive Distillation Configurations and Their Applications

Chapter Three presents in detail different types of batch reactive distillation systems such as i-CBD, i-SBD, sr-DWBD, and i-DWCBD. This chapter also shows the applications of these batch configurations for the production of a number of esters such as methyl lactate, methyl decanoate, and ethyl benzoate through the esterification reactions.

Chapter 4: Process Modelling and Optimization using gPROMS Software

Chapter Four illustrates in detail mathematical models with relevant assumptions, which have been employed in this work. Some of the earlier studies on optimization problems of batch distillation column using gPROMS tool are discussed at the end of the chapter.

Chapter 5: Optimisation of Lactic Acid Esterification Process

Chapter Five is based on the study of esterification of lactic acid and methanol to produce methyl lactate using conventional (CBD), integrated conventional (i-CBD), semi-batch (SBD), and integrated semi-batch (i-SBD) reactive distillation processes. Different case studies are presented with/without considering recovery and recycling stream of methanol with an objective function to minimize the operating batch time for given product considerations.

Chapter 6: Optimisation of Decanoic Acid Esterification Process

In Chapter Six, different types of batch reactive distillation configurations (such as CBD, i-CBD, SBD, DWBD, sr-DWBD, and i-DWCBD) are considered for the decanoic acid esterification reaction. The influence of excess amount of methanol in the feed on the overall performance is also considered in this work. Different cases are investigated with different feed concentrations and with objective function to minimize the energy expense.

Chapter 7: Optimisation of Benzoic Acid Esterification Process

Chapter Seven presents the feasibility of regular (CBD) and integrated (i-CBD) batch distillation systems for the optimal synthesis of ethyl benzoate via the esterification reaction of benzoic acid with ethanol. The batch-processing time employed as the measure to compare the performance of such columns. The effect of excess ethanol in the feed mixture on the batch time to achieve maximum possible conversion level and product quality is also considered in this research.

Chapter 8: Optimisation of Acetic Acid Esterification Process

Chapter Eight addresses the optimal operation of middle-vessel (MVD), inverted (IBD), and regular (CBD) batch distillation configurations involving the esterification of acetic acid and benzyl alcohol to form benzyl acetate at high purity. For a defined separation task, the profitability is used as the performance measure to compare the performances of these distillation columns. Middle-vessel, inverted, and conventional batch columns will be compared in terms of maximum profit function at the end of this chapter.

Chapter 9: Conclusions and Future Work.

Chapter Nine presents highlights what have been accomplished during this course of study and suggests some recommendations for future work.

Chapter Two

Literature Survey

2.1 Introduction

This chapter reviews in detail the past work on the continuous reactive distillation and conventional, semi-batch, divided-wall, inverted, and middle vessel reactive distillation operations for the synthesis of a number of esters such as methyl lactate, methyl decanoate, ethyl benzoate, and benzyl acetate via esterification process. More literature survey on these are provided in later chapters for convenience.

2.2 Continuous Reactive Distillation Process

Reactive distillation (RD) technology has been successfully employed and applied in various existing chemical industries in the past for several reaction systems such as etherification, esterification, polymerization, hydrodesulphurization, acetalization and hydrogenation. Some published works in the literature reviewed the esterification of impure lactic acid with methanol to obtain methyl lactate and then the distillated methyl lactate hydrolyzed back into pure lactic acid using a reactive distillation application (batch or continuous) as two-step separation techniques (Kim et al., 2000; Kim et al., 2002; Kumar et al., 2006 a; and Kumar et al., 2006 b). However, a number of works have been published on continuous reactive distillation for the synthesis of methyl lactate in the recent years (Thotla and Mahajani, 2009; Chen et al., 2013; Zhang et al., 2015; Chen et al., 2016; and Cao et al., 2017).

Thotla and Mahajani (2009) proposed a reactive distillation system with side draw for the production of methyl lactate through the esterification of lactic acid and methanol to overcome the water removal in order to improve the conversion of acid. However, they also did not appreciate the challenging of retaining both methanol and the lactic acid together in the system, which could further improve the conversion of lactic acid.

Chen et al. (2013) presented a reactive distillation with a top-bottom external recycle column for the same reaction scheme. Their outcomes demonstrated sharp reductions in both total annual costs and energy requirement. However, the product purity specification is very low (0.497 mole fraction).

Zhang et al. (2015) proposed a continuous distillation process with two reactive sections and feed splitting strategy for the synthesis of methyl lactate. They indicated from their results that this configuration is more favourable for enhancing the internal mass and energy consumption between the reaction and separation involved. However, they achieved a lower purity of methyl lactate of 0.497 mole fraction.

Recently, Chen et al. (2016) developed a reactive distillation column with two reactive sections: feed splitting plus external recycle for the synthesis of methyl lactate to improve the process proficiency. They found out that this system can reduce the energy usage rate significantly, but a lower purity of product was obtained.

Very recently, Cao et al. (2017) presented a reactive distillation column with double reactive sections at the top and bottom of the column for the production of methyl lactate. Their dynamics and control are studied in detail, with special attention given to the impact of the feed splitting strategy on the process dynamics and controllability. All of the obtained results have confirmed that the new column configuration significantly enhanced the tracking performance with even improved the disturbance rejection capabilities.

Limited investigations have considered the esterification reaction of decanoic acid with methanol to synthesize methyl decanoate employing only continuous reactive distillation operation in the past (Steinigeweg and Gmehling, 2003; and Machado et al., 2011). Steinigeweg and Gmehling (2003) proposed a heterogeneously catalysed reactive distillation system for the formation of methyl decanoate via the esterification of decanoic acid with methanol based on experimental and simulation studies at a feed molar ratio of (fatty acid : methanol) = <0.341:0.659>. However, they achieved a lower conversion of acid and product quality (fatty acid methyl ester) of 42.99% and 0.314 mole fraction, respectively.

Recently, Machado et al. (2011) simulated a reactive distillation operation for the esterification of decanoic acid with methanol using Amberlyst-15 catalyst and the stoichiometric feed ratio of reactants same as used by Steinigeweg and Gmehling (2003). The simulation results were validated and compared with the experiential data available in literature and achieved 42.99% of decanoic acid conversion and 0.386 mole fraction of methyl decanoate. Also interestingly, although their work considered the importance of synthesys of methyl decanoate in the esterification reaction, they did not achieve higher composition of the fatty acid methyl ester and conversion rate of decanoic acid even with an excess of methanol. This is due to the fact that they did not take into consideration the difficulty of keeping both reactants (the decanoic acid and methanol) together in the pot drum to enhance the conversion of acid.

2.3 Batch Reactive Distillation in Conventional Column

The application of conventional batch reactive system is common practice in the chemical and bio-chemical industries (Egly et al., 1979, Cuille and Raklaties, 1986; Wilson, 1987; Logsdon et al., 1990; Albet et al., 1991; Mujtaba and Macchietto, 1992; Mujtaba and Macchietto, 1997; Mujtaba, 2004; Edreder et al., 2011; Kao and Ward, 2014a; and Banerjee and Jana, 2018).

2.3.1 Esterification of Lactic Acid and Methanol

The production of methyl lactate was carried out through the esterification of lactic acid with methanol over the cation-exchange resin (Amberlyst-15) via the reversible reaction. The boiling point temperature of each component is provided by the following stoichiometric equation:

	Lactic acid +	Methanol <=>	Methyl lactate +	Water	(2.1)
B.P (K)	490.15	337.15	417.15	373.15	

The chemical reaction will start with the beginning of the operation, and methyl lactate and water will be formed. Having water as the next boiling component after methanol, water will start moving up the distillation column after methanol. Methyl lactate will tend to be near the vicinity of the still pot due to the higher boiling point temperature. Methyl lactate in the distillate tank after the separation of methanol and water (Edreder et al., 2011) or it can be remained in the reboiler drum and it can be purified to the desired specification by converting more and more of the lactic acid (as considered in this work).

2.3.2 Esterification of Decanoic Acid and Methanol

The formation of methyl decanoate is a reversible kinetic reaction, which involves the esterification of decanoic acid with methanol over the resin catalyst (Amberlyst-15). The boiling point temperature of each component was considered in a reversible reaction system using the following stoichiometric form:

Decanoic acid + Methanol <=> Methyl decanoate + Water (2.2)

B.P (K) 543.15 337.15 505.13 373.15

The esterification of fatty organic acids (such as decanoic, oleic, and dodecanoic acids) with a number of alcohols, ranging from methanol, ethanol, and propanol to 2-ethyl hexanol using reactive distillation column are common practices in the chemical and petrochemical industries. For instance, the studies on esterification reaction of oleic acid with methanol to produce methyl oleate were investigated by several researchers (Thotla and Mahajani, 2009; Kusmiyati and Sugiharto, 2010; Machado et al., 2011; and Karacan and Karacan, 2015).

In the past, the esterification of lauric (dodecanoic) acid with methanol has been conducted in thermally-coupled reactive distillation columns by a limited number of investigators (Hernandez et al., 2010; and Nguyen and Demirel, 2011) to synthesize methyl dodecanoate. However, others have previously discussed the reaction of decanoic acid with methanol to yield methyl decanoate using a continuous reactive distillation process (Steinigeweg and Gmehling, 2003; and Machado et al., 2011).

More recently, Lamba et al. (2018) produced methyl decanoate in a small batch reactor through the esterification reaction of decanoic acid and methanol on solid acid catalyst Amberlyst-15 using Eley-Rideal model. They also studied the influence of different reaction parameters such as amount of catalyst, temperature of reaction, molar ratio of reactants, speed of stirrer, and concentration of water on catalyst pellets for optimization of rate of conversion.

2.3.3 Esterification of Benzoic Acid and Ethanol

The production of ethyl benzoate was carried out via the esterification of benzoic acid with ethanol over an acidic cation-exchange resin (Amberlyst-39) through the reversible kinetic reaction. The boiling point (B.P) temperature of each reacting species is also presented below.

	Benzoic acid +	Ethanol <=>	Ethyl Benzoate +	Water	(2.3)
B.P (K)	523.0	351.40	485.90	373.15	

The esterification process of benzoic acid with ethanol to produce ethyl benzoate is not new. As in the example, this esterification operation was investigated by using microwave heating and conventional in a stirred tank reactor by (Plazl, 1994).

Pipus et al. (2000) investigated the same method to form ethyl benzoate in a tubular flow reactor heated by microwaves, catalyzing with Amberlyst-15. They utilized an irreversible quasi-homogeneous model to characterize the kinetic model. The highest conversion of acid achieved was about 38% for homogeneously catalysed esterification at the lowest flow rate.

Lee et al. (2005) proposed three kinetic models (such as the quasi-homogeneous (QH), Eley-Rideal (ER), and Langmuir-Hinshelwood-Hougen-Watson (LHHW) models) to examine experimentally the kinetic behavior of the production of ethyl benzoate over an acidic-cation exchange resin (Amberlyst-39) using a fixed-bed reactor at the atmospheric pressure. Their study showed that the LHHW model gives the best representation for ethyl benzoate formation. However, they obtained a conversion of benzoic acid of 90.20% with ethanol to benzoic acid feed molar ratio of five.

Recently, Wu et al. (2013) prepared an ionic acid catalyst of SO_4^{2-} over Ti_3AlC_2 ceramic to study the esterification of benzoic acid with ethanol but their study demonstrated that the resulting catalyst exhibited only 80.40% conversion rate of benzoic acid under 393.15 K at the reaction time of 34 hours. They extended the reaction time of the batch reactor to achieve a highest conversion level of benzoic acid (80.40%).

The kinetics of esterification of benzoic acid and isoamyl alcohol catalyzed by P-toluenesulfonic acid as a catalyst was studied recently by Xue et al. (2018) in the temperature range of 353.15–383.15 K. The impacts of the catalyst concentration, reaction temperature, and initial acid to alcohol molar ratio on reaction kinetics were examined in their study.

Very recently, Pečar and Goršek (2018) explored the esterification reaction of benzoic acid with methanol to produce methyl benzoate using two types of solid acid catalysts (S_1 and S_3) in batch reactor. They found that a higher conversion of benzoic acid of 60% was achieved using the catalyst S_1.

2.3.4 Esterification of Acetic Acid and Benzyl Alcohol

The reversible reaction schemes together with the boiling points (K) of the components for esterification of acetic acid and benzyl alcohol to produce benzyl acetate and water are:

Acetic acid + Benzyl Alcohol <=> Benzyl Acetate + Water (2.4)

B.P (K) 391.05 477.85 486.65 373.15

The investigations on esterification reaction of acetic acid with benzyl alcohol to produce benzyl acetate were studied by a number of researchers (Roy and Bhatia, 1987; Kirumakki et al., 2004; and Ali and Merchant, 2009).

Roy and Bhatia (1987) considered the kinetic of esterification of acetic acid with benzyl alcohol catalysed by a cation-exchange resin (Amberlyst-15) in the temperature range 328–359 K and at atmospheric pressure using a batch system.

Kirumakki et al. (2004) studied the esterification of acetic acid with benzyl alcohol over zeolites Hβ, HY and HZSM5 in a batch reactor. They found that the conversion rate of benzyl alcohol using the zeolite Hβ was higher as compared to other catalysts. The resulting catalyst exhibited only 75% conversion of benzyl alcohol into benzyl acetate under 403 K, catalyst weight of 0.5 g, and 2:1 of molar ratio of acid: alcohol at the reaction time of 1 hour.

Ali and Merchant (2009) proposed three kinetic models (such as the pseudo-homogeneous model (PH), Eley-Rideal (ER), and Langmuir-Hinshelwood-Hougen-Watson (LHHW) models) to study experimentally the kinetic behavior of the production of benzyl acetate over Dowex using a batch reactor at atmospheric pressure. They concluded that the LHHW model offers better performance for the benzyl acetate formation. However, they obtained a lower conversion of acetic acid of 35.50% with the equimolar amount of feed, and 30 g of dry cat. /L at the reaction time of 4 hours.

It can be seen that the research work concerning the use of a batch reactive distillation to form benzyl acetate is non-existent compared to that by using batch reactor system. This work will focus into the optimization of different column configurations (such as MVD, IBD, and CBD) for production of benzyl acetate in terms of maximum process profitability.

2.3.5 Dynamic Modelling and Optimization

To the author’s best knowledge, no studies have been carried out concerning modelling and optimization of esterification of lactic and decanoic acid with methanol or esterification of benzoic acid with ethanol, and esterification of acetic acid with benzyl alcohol in the past using batch reactive distillation system in a conventional column. This thesis will focus in detail on the optimization of different batch reactive configurations for the production of a group of esters such as methyl lactate, methyl decanoate, ethyl benzoate, and benzyl acetate.

2.3.6 Other Reaction Systems in Batch Column

Choi et al (1996) studied both esterification of lactic acid and its reverse hydrolysis processes in batch system using acidic resins as a homogenous catalyst. They also compared the activity of acidic resins with that of sulphuric acid catalyst. Their study showed that the activity of resins catalyst was less than the sulphuric acid catalyst, but it was easily removed and reused.

Choi and Hong (1999) examined a batch reactive operation for the esterification of impure lactic acid and hydrolysis reactions in two reactors and two distillation columns. They investigated the recovery of pure lactic acid and found that the total investment cost was high. To overcome these problems, the batch distillation with simultaneous reaction was suggested.

Seo et al. (1999) developed an apparatus with two batch distillation columns, esterification followed by hydrolysis for recovery of lactic acid by batch reactive process using cation exchange resin (Dowex-50, SIGMA co.) as a catalyst. The influences of some operating conditions such as catalyst mass, reactant molar ratio, the mixture feed composition, type of alcohols and the temperature of partial reboiler were analyzed. The reaction products of the esterification step (methyl lactate and water) were further separated and fed to the hydrolysis step for recovery of pure lactic acid. They stated that as the catalyst mass increased, the recovery of pure acid also increased with reducing feed lactic acid concentration and reaction feed mole ratio. Also, it was found that methanol as a reactant offered higher productivity than any other alcohol.

Kim et al. (2002) studied the dynamic behaviour of batch reactive distillation system for the recovery of lactic acid. They concluded that the rate of reaction increased by control of boilup rate and process batch time during the operation by manipulating both methanol feeding rate and methanol recycle rate. In their work, the semi-batch column was also compared with the batch distillation column. They concluded that the continuous feeding of methanol increased the recovery of lactic acid.

Elgue et al. (2002) presented the dynamic optimisation of methyl acetate synthesis. They formulated two types of dynamic optimisation problems: the first minimising the operating batch time necessary to accomplish the maximum reaction conversion and the second minimising an objective function which is a combination of conversion and operating time. They indicated that a considerable total reflux mode time (more than 15 min) is needed for higher conversion of limiting reactant in the first type. While, for the second type, it was shown that a total reflux time of around 23 min is needed if more operating batch time would allow reaching higher conversion rate.

Kumar et al. (2006b) proposed a batch reactive distillation system including experimental esterification and hydrolysis reaction to recover pure lactic acid. The impact of operating variables such as feed composition, molar ratio, catalyst weight, and boil-up rate on the recovery yield of lactic acid were investigated. Their results demonstrated that the pure lactic acid could be recovered from its aqueous solution by using this type of column configuration.

Delgado et al. (2007) studied the kinetic equations for esterification of lactic acid with ethanol and the hydrolysis of the ethyl lactate in liquid-phase using an acid catalyst (Amberlyst-15). They also investigated the impact of different operating parameters such as reaction temperature, catalyst loading, stirrer speed, catalyst particle size, and initial reactant molar ratio.

Patel et al. (2007) developed a detailed model and simulation of batch reactive distillation operation for ethyl acetate production using a MATLAB program. They found out that for given ethyl acetate product concentration of 0.500 mole fraction, the optimal reflux ratio was found to be around 0.875 with an operating batch time of 8.3 hours.

Kumar and Mahajani (2007) studied the synthesis of n-butyl lactate through the esterification of lactic acid with n-butanol in the presence of cation-exchange resins as catalyst. A pseudo-homogeneous (PH) model was utilized to calculate the reaction rate. They compared the experimental results with the simulation results using both continuous and batch reactive distillation processes. They also examined the influences of operating variables such as feed molar ratio, catalyst loading, and boil-up rate on the conversion rate of lactic acid in batch distillation system.

Rahman et al. (2008) presented a theoretical study on optimization of a reactive distillation column along with CSTR reactor for the recovery of lactic acid using differential evolution algorithm, a robust global optimization technique. They found that the generalized differential evolution algorithm could be successfully used for optimizing CSTR and reactive distillation process simultaneously in terms of lower total annual cost.

Jiang et al. (2010) presented the kinetic study of methyl lactate hydrolysis over cation exchange resin catalyst using the pseudo-homogeneous (PH) model to correlate the experimental data. The influences of the reaction temperature, catalyst loading, initial reactant molar ratio, and the reusability of the resin catalyst were also investigated. The PH model was found to provide a good agreement with the experimental kinetic data.

Kathel and Jana (2010) presented a dynamic simulation and nonlinear generic control of a high-purity batch reactive distillation system for the formation of butyl acetate. They inferred that the control scheme along with the effective distillate strategy yielded a maximum reaction conversion and highest product purity.

Edreder (2010) studied different reaction schemes involving the esterification of methanol and ethanol with acetic acid, and hydrolysis of methyl lactate into lactic acid using a conventional batch distillation process. Several optimization objectives were considered to fulfil the product requirements.

Mujtaba et al. (2012) studied a significant thermal energy reduction in lactic acid production using a batch reactive distillation column. The thermal energy saving was accomplished by minimizing the operating batch time by carefully optimizing the reflux ratio but without compromising the product consideration. It was noted that 56% of total energy consumption rate can be saved to a product with a certain specification and 0.950 mole fraction of lactic acid quality were not achieved with a single reflux ratio strategy.

Edreder et al. (2015) studied the performance of batch reactive distillation process for the production of methyl acetate in terms of maximum conversion rate of methanol. The reflux ratio was selected as a control variable into optimization study. Two cases were studied with/without excess feed amount. The excess acetic acid case resulted in a higher operation temperature and maximum reaction conversion compared to those obtained by using the equimolar feed ratio case.

Kao and Ward (2015a) developed a batch reactive distillation with off-cut recycling strategy for the optimal production of lactic acid, and methyl formate in terms of maximum batch capacity. They applied the pseudo-steady-state concept batch processing to simplify the optimization problem. They found that the recycling off-cut could save the trouble of processing the off-cut and make the operation more economical.

Kao and Ward (2015b) investigated the simultaneous optimization of design (e.g. a total number of trays and vapour boil-up rate) and operating variables (reflux ratio and catalyst loading) of batch distillation operation for two reaction systems: hydrolysis of methyl lactate and esterification of formic acid. The influence of equipment design and operating variables on the total annualised cost problem was studied.

Jiang et al. (2017) proposed three kinetic models (such as the pseudo-homogeneous (PH), Eley-Rideal (ER), and Langmuir-Hinshelwood-Hougen-Watson (LHHW) models) to investigate the kinetic behaviour of the production of isoamyl lactate via the esterification between lactic acid and isoamyl alcohol over a silica gel-supported sodium hydrogen sulphate. The effects of the internal mass transfer, external mass transfer, catalyst loading, initial reactant molar ratio and reaction temperature were studied. Their study showed that the ER model based on adsorbed alcohol gave a better agreement with the experimental data compared with other models.

More recently, Talnikar* et al. (2017) explored the recovery of trifluroacetic acid from dilute aqueous solutions by both batch and continuous distillation modes. They concluded that higher conversion and recovery of acid were achieved in both reactive distillation systems compared to those obtained by a batch reactor.

2.4 Batch Reactive Distillation in Semi-Batch Column

As mentioned earlier in chapter one, the difference between the conventional batch (CBD) distillation and semi-batch (SBD) distillation is that in the SBD operation, one or more components are charged continuously to the distillation column via a side stream, whereas in CBD, all chemical species are loaded initially to the reboiler drum.

2.4.1 Esterification of Lactic Acid and Methanol

Reactive distillation (RD) with side draw of water using both continuous and semi-continuous distillation modes for the formation of lactic acid was suggested by Thotla and Mahajani (2009). They inferred that RD with side draw not only increases the conversion rate of acid but also avoids possible methyl lactate hydrolysis leading to polymerization reactions. However, the difficulty of retaining both reactants together in reaction zone to have further reaction was not considered in their work.

Adams and Seider (2008) proposed a semi-batch (semi-continuous) distillation process for the production of ethyl lactate from ethanol and lactic acid. In their work, a rigorous simulation and total annual cost estimation were considered. They found that the feasibility of using semi-batch distillation process is a more effective option to both continuous and batch operations.

2.4.2 Other Reaction Systems in Semi-Batch Column

Kreul et al. (1998) studied previously the esterification of acetic acid and methanol to yield methyl acetate in a semi-batch operation. The dynamic component material and energy balances, as well as the rigorous thermodynamic properties were used. The column hydraulics, reaction kinetics and mass transfer relationship parameters were experimentally derived. They concluded that there was close match between simulation and experimental results.

Fernholz et al. (2000) presented work on the optimisation of semi-batch distillation processing for methyl acetate production. Two different optimization problems, minimum batch time and maximum productivity of ester problems were examined. They found that the productivity based optimal problem formulation leads to higher conversion of acetic acid for identical operating times. They also concluded that the operation is quite restricted by reaction kinetics rather than by the separation.

Qi and Malone (2010) used a semi-batch distillation column for isopropyl acetate synthesis with acetic acid charged continuously to the top of the column to decrease the concentration of the alcohol in the top product. They showed that semi-batch processing can offer 20% higher production efficiency than conventional batch process. However, they did not use non-reactive inverted batch distillation column for separating isopropyl acetate (the main product) from water (by-product).

Edreder et al. (2009) developed a dynamic model for semi-batch distillation operation for the synthesis of ethyl acetate via the esterification of acetic acid and ethanol using gPROMS software. Acetic acid was fed continuously to the batch column, in addition to the initial feed of acetic acid and ethanol. Their optimization study showed that the amount of ethyl acetate product and the conversion of ethanol improved by 13 % and 4%, respectively using multi-reflux ratio policy.

Prapainainar et al. (2014) studied experimentally the production of methyl acetate via esterification of acetic acid using semi-batch reactive distillation. Their study demonstrated that the maximum conversion of acetic acid reached 79.50% and highest purity of methyl acetate achieved 0.680 mole fraction using Amberlyst-IR 120 H^+ compared to those obtained by using acid-doped raschig ring catalyst.

Using Aspen Batch Distillation model, Akkaravathasinp et al. (2015) investigated the effect of feed location of semi-batch distillation system via esterification reaction of acetic acid and methanol to form methyl acetate. The main objective was to maximise the productivity of methyl acetate with purity of 95 wt%. It was found that the location of feed (acetic acid) significantly affected the yield and the purity of methyl acetate at the top plate of the column. Also, the optimal feed plate of acid was plate four which gives the maximum yield and concentration of methyl acetate as 74.74% by mole and 97.36 wt%, respectively.

More recently, Lee et al. (2016) suggested two-step operations in sequence (SBD and IBD) for two reaction systems: the esterification of acetic acid with ethanol and isopropanol to form ethyl acetate, and isopropyl acetate, respectively. Acetic acid was used as a side feed charge into the column in both reaction schemes. Their systematic method identified the composition of alcohol to minimise both the total operating time and the energy consumption rate.

2.5 Batch Reactive Distillation in Divided-Wall Column

Although the application of divided-wall systems has been widely focused on continuous reactive column by a large number of scholars (Mueller and Kenig, 2007; Hernández et al., 2009; Delgado-Delgado et al., 2012; Cheng et al., 2013; Dai et al., 2015; Suo et al., 2017; and Zheng et al., 2017), only very limited investigations were reported in the literature on the use of dividing -wall batch reactive distillation column by some researchers (Safe et al., 2013; and Lopez-Saucedo et al., 2016).

Recently, Safe et al. (2013) presented a model reduction and optimization of a dividing-wall batch distillation process for the synthesis of ethyl acetate via esterification of acetic acid with ethanol to achieve maximum purity for ethyl acetate and lower operating batch time. The optimal operation of dividing-wall batch mode is evaluated in terms of maximum quantity of ethyl acetate produced by optimizing the liquid and vapour split ratios. Their optimization results showed that the use of dividing-wall batch is a more effective operation in terms of maximum quality of ethyl acetate and lower batch time as compared to the classical batch distillation column.

Lopez-Saucedo et al. (2015) considered the optimization of a dividing-wall batch and semi-batch distillation operations for the production of methyl acetate in terms of lower energy demand. Their study indicated that in terms of energy saving, when the results of two new unconventional configurations are compared to a conventional batch distillation column, no energy minimizations nor maximum purity of methyl acetate at the end of the operation were noticed when a divided-wall is added to the batch distillation column.

More recently, Lopez-Saucedo et al. (2016) developed a mathematical model for dividing-wall batch reactive distillation (DWBD) column for the production of ethyl acetate via esterification of acetic acid with ethanol. For a given separation task, the optimal operation of DWBD mode is evaluated in terms of maximum conversion rate. Their optimization results indicated that the use of DWBD system has no benefits in terms of energy consumption and conversion level as compared to the classical CBD column. This is due to the fact that liquid and vapour split fractions were not optimised which could further improve the process efficiency and the energy reduction.

No work has been investagted yet on the use of diveded-wall distillation operation for esterification reaction of decanoic acid and methanol. Therefore, this thesis will discuss in detail the synthesis of methyl decoante using different types of diveded-wall batch reactive distillation systems.

2.6 Batch Reactive Distillation in Inverted Column

The inverted batch reactive distillation column is more appropriate when the main products being the heaviest boiling points components (Mujtaba and Macchietto, 1994). The research in the inverted processes has received limited attention as compared to conventional columns.

Edreder et al. (2011) studied optimal operation modes of conventional and inverted batch reactive columns for hydrolysis of methyl lactate to lactic acid. For a given separation task, the dynamic optimization problem is formulated in terms of minimum operation time considering piecewise-constant reflux ratio and a single interval reboil ratio as the control variables for both the distillation columns. They found that the IBD outperformed CBD for higher product purity, whereas, for lower product purity the CBD operation performed better than IBD mode in terms of batch time.

Kao and Ward (2014a) improved the batch capacity for inverted batch distillation process with off-cut collection for the synthesis of lactic acid through the hydrolysis reaction of methyl lactate. They concluded that the IBD with off-cut policy can provide a much better performance than IBD without off-cut recycling in terms of maximum batch capacity.

Kao and Ward (2015a) investigated the off-cut recycle of an inverted batch operation for the production of dimethyl-acetal, and lactic acid by maximizing the batch capacity. This policy was used to recycle the off-cut from a single-batch into a batch-to batch a part of the initial feed.

2.7 Batch Reactive Distillation in Middle-Vessel Column

The middle-vessel batch distillation operation is the combination of conventional and inverted batch columns, where the feed is loaded in the middle-vessel and the reaction products are simultaneously withdrawn from the top and the bottom of the column. Edreder et al. (2012) considered the simulation of middle-vessel batch reactive distillation column for the synthesis of lactic acid via the hydrolysis of methyl lactate using the gPROMS modelling software. They concluded that the removal of both reaction products (methanol and lactic acid) in middle-vessel batch improved the conversion of methyl lactate and saved the operating batch time. Edreder et al. (2013) made a comparison of optimum operation between conventional batch and middle-vessel batch reactive columns for the production of lactic acid in terms of lower batch time. They found that the middle-vessel distillation process is effective than conventional batch column in terms of reduction in batch time, which can be as high as of 20 %. For the same reaction system, Edreder et al. (2014) compared the performance of middle-vessel reactive distillation with the conventional batch column in terms of lower energy consumption rate. They showed that for lactic acid purity of 0.80 mole fraction, an energy saving of 23.3 % was attained with the middle-vessel column compared to that obtained by using a conventional column. Kao and Ward (2014b) proposed a middle-vessel batch configuration with off-cut collection for two reaction schemes: hydrolysis of methyl lactate and production of dimethyl-acetal. For the hydrolysis of methyl lactate, the batch capacity for MVD column was increased by 30.7% compared to a conventional batch process. While, the batch capacity of MVD process for the production of dimethyl-acetal was improved by 60.4%

compared to an inverted process. The optimum process of batch-to-batch system with off-cut recycling in terms of maximization of batch capacity using MVD column for the synthesis of dimethyl-acetal was studied by Kao and Ward (2015a). As seen, no investigations so far have been carried out employing the middle-vessel batch system for the optimal production of benzyl acetate. This thesis will focus into the optimal operation of MVD column involving the esterification of acetic acid and benzyl alcohol in terms of minimum batch time.

2.8 Conclusions

This chapter has discussed in detail the previous publications in open literature using different types of conventional and unconventional reactive distillation columns. The conclusions of this chapter can be summarized as follow:

- The purification of impure lactic acid has been carried out previously in reactive distillation (batch or continuous) as a two-step procedure: esterification of impure lactic acid into methyl lactate followed by hydrolysis of methyl lactate into pure lactic acid (Kim et al., 2000; Kumar et al., 2006 a; and Kumar et al., 2006 b). However, all the previous studies focused on the synthesis of lactic acid and not the methyl lactate (see Figure 2.1).
- Some publications in the literature investigated the synthesis of methyl lactate via the esterification reaction of lactic acid and methanol using continuous and semi-continuous operations (Thotla and Mahajani, 2009; Chen et al., 2013; and Zhang et al., 2015; Chen et al., 2016; and Cao et al., 2017). No consideration was given to the optimisation of several types of batch distillation systems (CBD, i-CBD, and i-SBD) for optimal synthesis of methyl lactate.

- Most investigations on the synthesis of methyl decanoate (low concentration achieved) via the esterification reaction of decanoic acid and methanol were considered only in a continuous reactive distillation process (Steinigeweg and Gmehling, 2003; and Machado et al., 2011).
- Most of the work has focused on experiments with different kinds of reactors for the production of ethyl benzoate from the esterification process of benzoic acid and ethanol (Plazl, 1994; Pipus et al., 2000; Lee et al., 2005; and Wu et al., 2013).
- Most of the work has been carried out only in a batch reactor for the esterification of acetic acid and benzyl alcohol to produce benzyl acetate (Roy and Bhatia, 1987; Kirumakki et al., 2004; and Ali and Merchant, 2009).

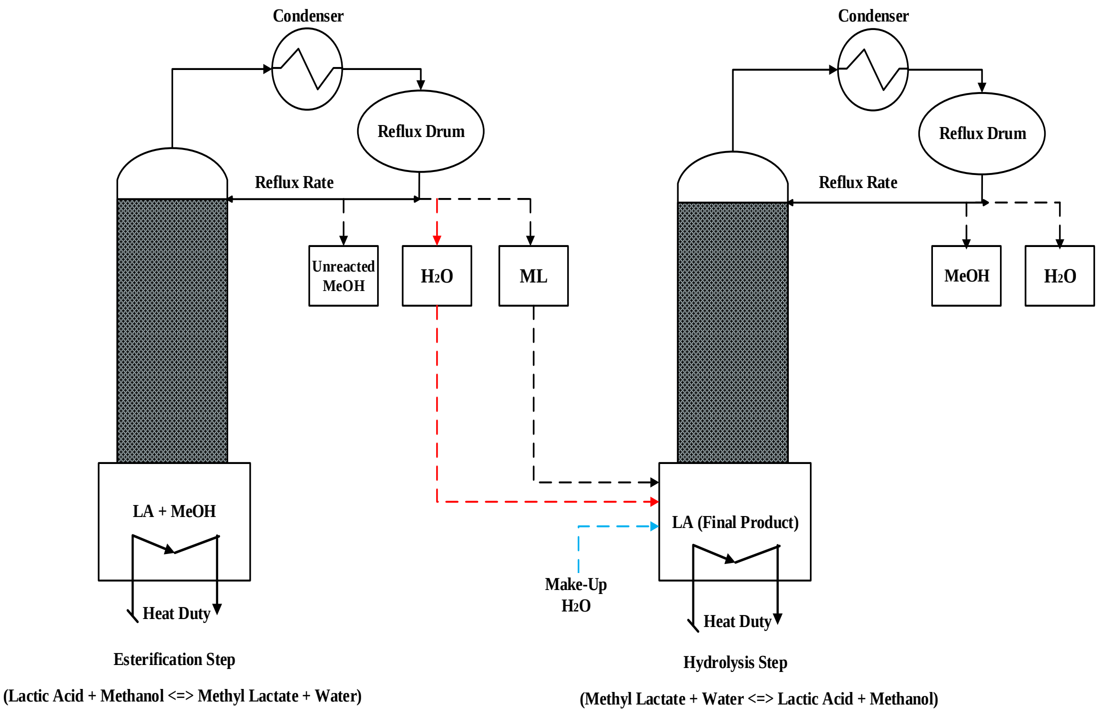

Figure 2.1 Schematic diagram of distillation system of lactic acid production

Chapter Three

New Reactive Distillation Configurations and Their Applications

3.1 Introduction

This chapter proposes and investigates in detail the novel works on conventional and unconventional batch configurations for the synthesis of a number of alkyl esters such as methyl lactate (ML), methyl decanoate (MeDC), and ethyl benzoate (EtBZ) via esterification reactions. These are: (1) integrated conventional batch distillation (i-CBD), (2) integrated semi-batch distillation (i-SBD), (3) split reflux divided-wall (sr-DWBD), and (4) integrated divided-wall batch distillation (i-DWCBD) configurations. Also, the implementations of these batch column configurations for such reaction systems are discussed.

3.2 New Batch Distillation Configurations for Synthesis of Alkyl Esters

3.2.1 Integrated Conventional Batch Distillation Operation

In this column configuration, a part of the recycling distillate (containing a high purity of methanol) is fed back into the still pot in an integrated manner as the process continues (Figure 3.1).

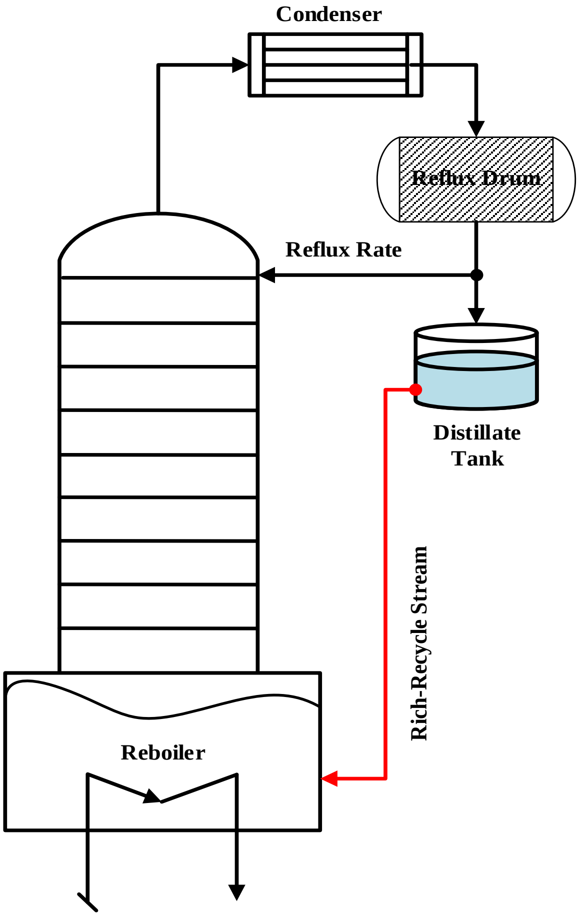

Figure 3.1 Schematic Diagram of Integrated Conventional Batch Distillation System

3.2.2 Integrated Semi-Batch Distillation Operation

In the i-SBD system, all distillate in the accumulator tank of SBD column is transferred into a CBD to separate methanol at a desired composition (0.950 mole fraction) and combined with make-up methanol of the same quality before being fed to the next batch of SBD in the i-SBD process as shown in Figure 3.2. Note, the first two batches of SBD are run with continuous feeding of fresh methanol. Note, the operating batch time for CBD column is assigned to be the same as the operating time of the SBD.

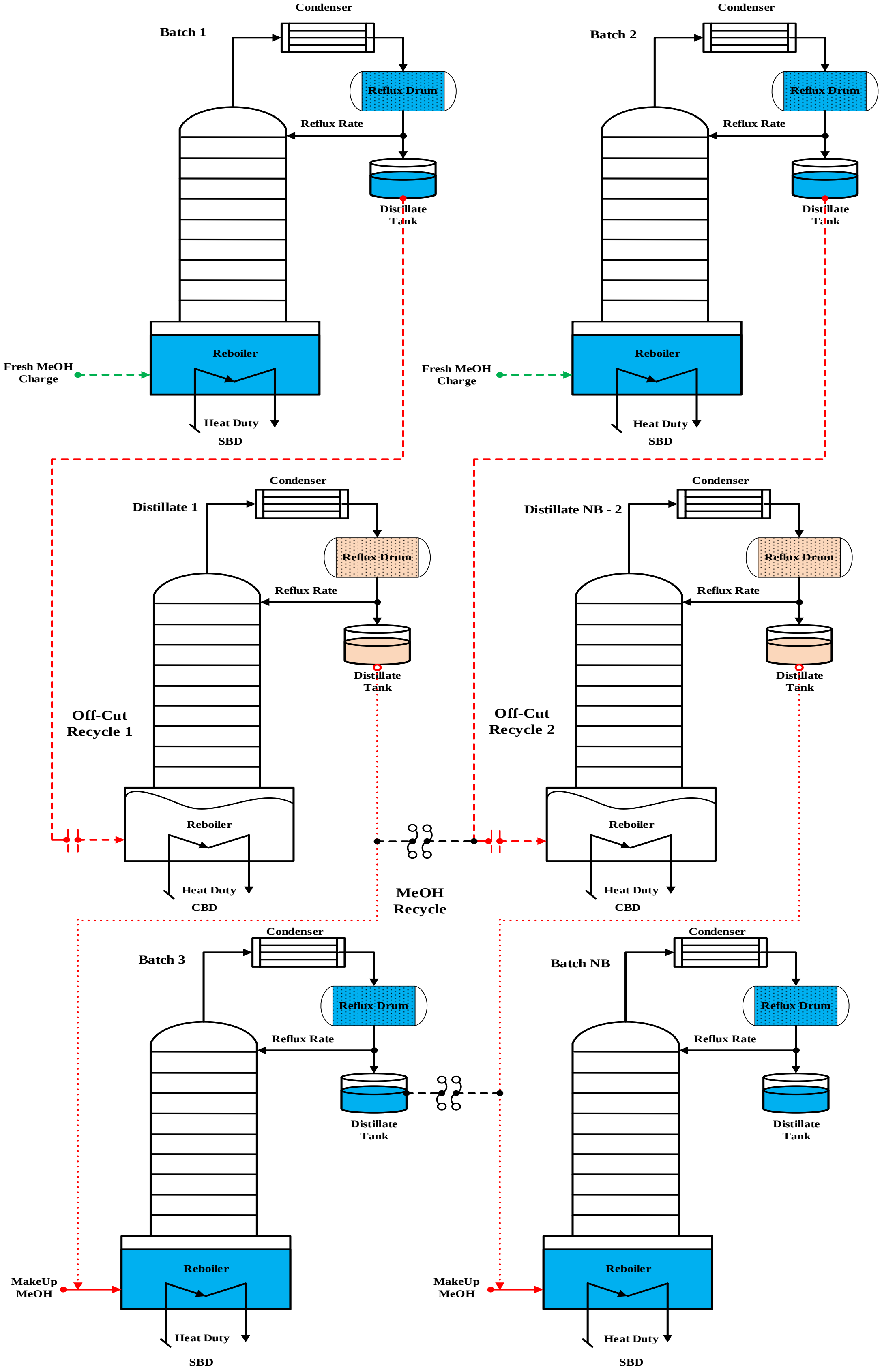

Figure 3.2 Schematic Diagram of Integrated Semi-Batch Distillation System

Therefore, while the CBD mode is in progress for the first batch, SBD for the second batch will be in progress in parallel. The feed for the second batch of CBD will be ready from the second batch of SBD when the CBD is finished with the first batch of methanol recovery task. Note, the first two batch of SBD operation will not have recycled rate of methanol. However, a pseudo-steady state operation will be in place after the second batch of SBD.

3.2.3 Split Reflux Divided-Wall Distillation Operation

The reflux rate from the condenser drum is split into two streams (reflux rate 1 and 2) in this batch configuration, where stream 1 is refluxed back into the top stage of the distillation column (similar to DWBD), and stream 2 goes into the pot drum as as the process proceeds (Figure 3.3a).

3.2.4 Integrated Divided-Wall Distillation Operation

The i-DWCBD scheme is suggested here to improve the process efficiency, the economic performance and the energy saving, as well as the highest achievable conversion. Figure 3.3b shows the i-DWCBD operation with recycled distillate (including a high concentration of unreacted methanol) from the distillate tank into pot drum to have further chemical reaction. Note, the difference between the sr-DWBD and the i-DWCBD batch configurations is that, the recycle stream in the sr-DWBD operation contains lower amount of methanol and more of water, but the recycle stream in the i-DWCBD operation has more methanol than water. Also, the split stream in Figure 3.3a, is taken from the refluxed liquid to the column section while, the recycled stream in Figure 3.3b is from the accumulator tank. Again, the divided stream in Figure 3.3a is the fraction of liquid, which is returned to the rectifying section as reflux.

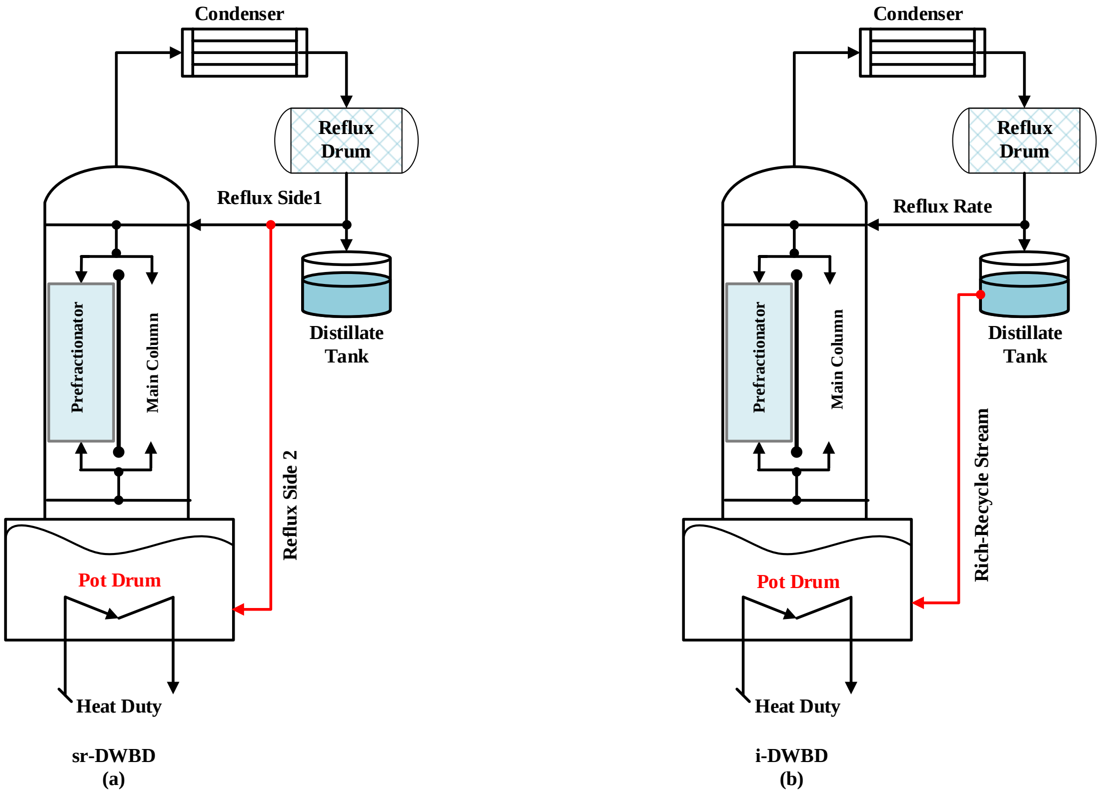

Figure 3.3 Schematic diagram of two column configurations: (a) split reflux-divided wall (sr-DWBD), and (b) integrated divided wall columns (i-DWCBD)

3.3 Applications of New Configurations for Different Reaction Schemes

The production of a number of esters such as methyl lactate (ML), methyl decanoate (MeDC), and ethyl benzoate (EtBZ) by esterification reactions of acids with alcohols in a reactive distillation (batch or continuous) is cost-intensive and operationally challenging operation. It is difficult to keep the reactants together in the reaction region due to wide boiling point differences between the reactants. Note, the normal boiling point temperature of each component for three reaction schemes is shown in Table 3.1.

With regard to the boiling points of the different components of the reaction mixture, alcohol has the lowest boiling point in the mixture followed by water, alkyl esters and acids. With distillation in progress in all reaction schemes (in a reactive distillation column), one of the reactants (in these esterification reactions) being the lowest boiling point compound in the reaction mixture will disengage itself from the other reactants (acid) thus causing operational challenge. Consequently, the conversion of the acid to the desired product (alkyl ester) will be quite limited. Carboxylic acids (lactic, decanoic, and benzoic acids) having the highest boiling point in the mixture will stay at the pot tank most of the time. However, the severity of this operational challenge will depend upon the differences in the boiling point temperature of the alcohol with the rest of the chemical species in the reaction mixture or on the relative volatility of the alcohol (methanol or ethanol) in the mixture.

Table 3.1 Reactions together with the boiling points for all reaction schemes

Methyl Lactate (ML) Scheme				
	LA (490.15) +	MeOH (337.15) <=>	ML (417.15) +	H_2O (373.15)
C.O.*	4	1	3	2
Methyl Decanoate (MeDC) Scheme				
	DeC (543.15) +	MeOH (337.15) <=>	MeDC (505.13) +	H_2O (373.15)
C.O.	4	1	3	2
Ethyl Benzoate (EtBZ) Scheme				
	BeZ (523.0) +	EtOH (351.40) <=>	EtBZ (485.90) +	H_2O (373.15)
C.O.	4	1	3	2

*C.O. = Component order in terms of boiling point temperatures

Note, the relative volatility of methanol in MeDC scheme will be higher than that of the ML scheme if the relative volatility in those systems is based on the heaviest component in the mixture. Therefore, more challenging will be the MeDC system, then EtBZ system and then ML system in terms of differences in boiling points between component 1 and 4. However, since in all these chemical reaction schemes, ester (component 3) is recovered in the bottom product, the separation of water (the second lightest component) from the reaction system as the distillation continues will also be challenging and will also influence on the overall performance of the distillation column.

With respect to the difference in boiling point temperature of compound 2 and 3, MeDC system will offer less challenge compared to EtBZ and ML systems. Hence, the difficulty of separating water is in inverse order of the challenge of retaining the alcohols with the acids. These are all qualitative expectations from the point of view of boiling temperatures of the reaction components. The ultimate behavior of the reaction system will be based on the reaction model and thermodynamic aspect of each system. Therefore, it is expected that the use of i-CBD, i-SBD, sr-DWBD, and i-DWCBD operations will bring alcohol (from the alcohol-rich side stream) and will enhance the reaction between alcohol and acids and thus will increase the conversion of acid.

3.4 Conclusions

This chapter discussed in detail a number of new batch reactive distillation configurations for the production of alkyl esters via the esterification processes. The effectiveness of using traditional batch reactive column for the formation of methyl lactate, methyl decanoate, and ethyl benzoate is a quite limited because of the depletion of methanol/ethanol from the reaction region due to large differences in boiling point temperatures between the chemical species.

Therefore, the backward reaction is being activated as the process progresses due to the removal of MeOH/EtOH (one of the forward reaction reactants in these esterification reactions), deteriorating significantly the conversion ratio of acid using either batch or continuous reactive operation. To overcome this type of challenging problem and to improve the reaction conversion, innovative batch column operations presented in this work such as integrated conventional batch distillation column, integrated semi-batch distillation column, split-reflux dividing wall batch column, and integrated dividing-wall batch column will be investigated later in Chapter 5, 6, and 7.

Chapter Four

Process Modelling and Optimisation using gPROMS Software

4.1 Introduction

The batch distillation operation is described by unsteady state behaviour as opposed to the continuous mode. The dynamic mathematical model of batch process involves non-steady state mass and energy balances, which is consisted of both set of differential and algebraic equations.

This chapter gives an overview of the literature study in case of modelling, simulation and optimisation problem in different types of batch distillation operations. The numerical methods for solving the optimization problem formulations are outlined.

4.2 Modelling of Batch Distillation Operation

Modelling of engineering systems includes the use of mathematical equations to investigate the dynamic behaviour of a real system. It played a vital role over the years in accomplishing better design and in understanding the dynamic behaviour of the process systems. There are many attractions for mathematical models (based case studies of model equations) rather than using the operations itself. Some of these are given as follows:

A. The comprehensive investigations (including simulation and optimization) using a process model can save the processing time compared to that obtained by a real process.

B. It is inexpensive than a real operation.

C. It is more flexible (the model can be testified with various input data), safer, and the results are much less fatal if some mistakes made during the study.

Modelling of different batch distillation configurations was the main interest research of a number of scholars in the past (Corrigan and Ferris, 1969; Holland and Liapis, 1983; Cuille and Reklaitis, 1986; Nad and Spiegel, 1987; Ruiz, 1988; Lang et al., 1994; Diwekar, 1995; Mujtaba, 2004; and Edreder et al., 2011). This thesis will focus in detail on the rigorous model with reaction kinetic for the several reaction schemes using different batch column systems.

4.2.1 Rigorous Model with Chemical Reactions

4.2.1.1 Conventional Batch Distillation Column (CBD)

The model equations developed by Mujtaba and Macchietto (1997) are shown in the following section, with reference to the CBD column configuration presented in Figure 4.1. The model contains column hold-up, reaction taking place in the trays, in the total condenser, and in the pot tank, and rigorous phase equilibrium. The column trays are computed from the top to the bottom. In each tray, the liquid stream leaving the tray is in equilibrium with vapour stream leaving the same tray. The detailed model is based on the following assumptions:

- Negligible vapour hold-up
- Adiabatic trays (no heat loss)
- Perfect mixing on all column stages
- Fast energy dynamics
- Constant molar hold-up on stages and in the total condenser

- Constant operating pressure (atmospheric pressure)
- No azeotrope formation
- Total condensation (no sub-cooling)

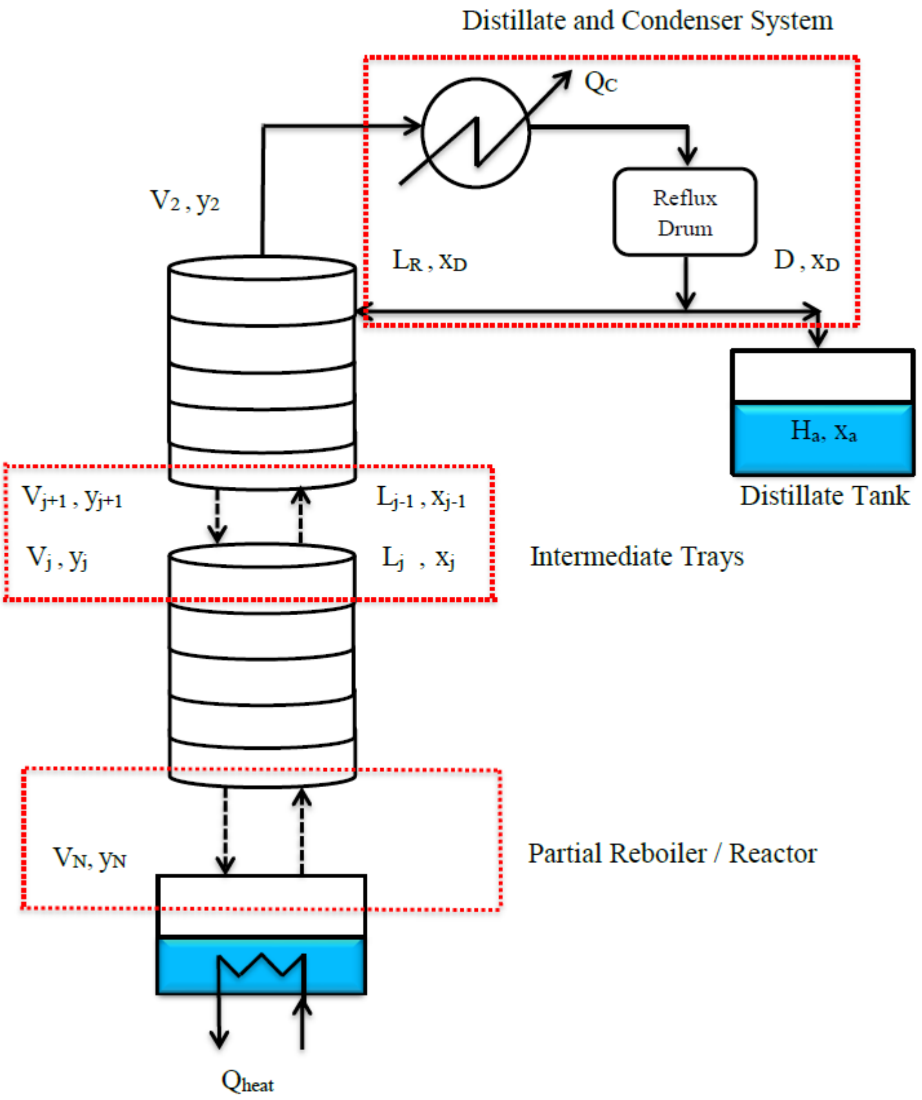

Figure 4.1 Schematic Diagram of Conventional Batch Column (CBD)

The model equations for the condenser and distillate accumulator are presented first and then the equations for the internal stages and the partial reboiler are presented where the trays are calculated from the top to the bottom. j and i denote the number of stages and chemical compounds, respectively. The model equations of a conventional distillation column with chemical reaction, which describe the physical and chemical process are presented below:

Condenser System and Distillate Tank: j=1

- Distillate Accumulator Total Mole Balance:

$$\frac{dH_a}{dt} = D \tag{4.1}$$

- Component Mole Balance:

a) Distillate Accumulator:

$$H_a \frac{dx_{ai}}{dt} = D\,(x_{Di} - x_{ai}) \tag{4.2}$$

b) Condenser Holdup Tank:

$$H_c \frac{dx_{ci}}{dt} = V_2\, y_2 - (V_2 + \Delta n_1 H_c)\, x_{Di} + r_{1i} H_c \tag{4.3}$$

- Energy Balance:

$$0 = V_2 H_2^V - (V_2 + \Delta n_1 H_c)\, H_1^L - Q_c \tag{4.4}$$

- Physical Properties and other equations:

$$H_1^L = H_1^L\,(x_{D1}, T_1, P) \tag{4.5}$$

$$T_1 = T_1(x_{D1}, P) \tag{4.6}$$

$$r_{1j} = r_{1j}\,(k_e, x_{Di}) \tag{4.7}$$

$$\Delta n_1 = \sum r_{1j} \tag{4.8}$$

$$L_1 = R\,(V_2 + \Delta n_1 H_c) \tag{4.9}$$

$$D = (1 - R)\,(V_2 + \Delta n_1 H_c) \tag{4.10}$$

Intermediate plates: j= 2 to N-1

- Total Mole Balance:

$$0 = L_{j-1} + V_{j+1} - L_j - V_j + \Delta n_j H_j \tag{4.11}$$

- Component Balance:

$$H_j \frac{dx_j}{dt} = L_{j-1}\, x_{j-1} + V_{j+1}\, y_{j+1} - L_j\, x_j - V_j\, y_j + H_j r_{ji} \tag{4.12}$$

- Energy Balance:

$$0 = L_{j-1}\, H_{j-1}^L + V_{j+1}\, H_{j+1}^V - L_j\, H_j^L - V_j\, H_j^V \tag{4.13}$$

- Equilibrium:

$$K_{j,i} = \frac{y_{j,i}}{x_{j,i}} \qquad (4.14)$$

- Restrictions:

$$\sum y_{j,i} = 1 \qquad (4.15)$$

- Relations Defining Physical Properties and Chemical Reactions:

$$K_{j,i} = K_{j,i}(y_{j,i}, x_{j,i}, T_j, P) \qquad (4.16)$$

$$H^L_{j,i} = H^L_{j,i}(x_{j,i}, T_j, P) \qquad (4.17)$$

$$H^V_{j,i} = H^V_{j,i}(y_{j,i}, T_j, P) \qquad (4.18)$$

$$r_{j,i} = r_{j,i}(k_e, x_{j,i}) \qquad (4.19)$$

$$\Delta n_j = \sum r_{j,i} \qquad (4.20)$$

Partial Reboiler: j= N

- Total Mole Balance:

$$\frac{dH_n}{dt} = L_{n-1} - V_n + \Delta n_n H_n \qquad (4.21)$$

- Component Mole Balance:

$$H_n \frac{dx_n}{dt} = L_{n-1}(x_{n-1} - x_n) - V_n (y_n - x_n) + H_n r_n \qquad (4.22)$$

- Energy balance:

$$0 = L_{n-1}(H^L_{n-1} - H^L_n) - V_n (H^V_n - H^L_n) + Q_{heat} \qquad (4.23)$$

Note, the other equations for the reboiler drum are similar to the intermediate stages equations (4.16 - 4.20) where j replaced by N.

4.2.1.2 Integrated Conventional Batch Distillation (i-CBD)

Referring to Figure 4.2 for an integrated batch distillation column (i-CBD), the equations for the total condenser, and the intermediate trays shown in section 4.2.1.1 will be the same.

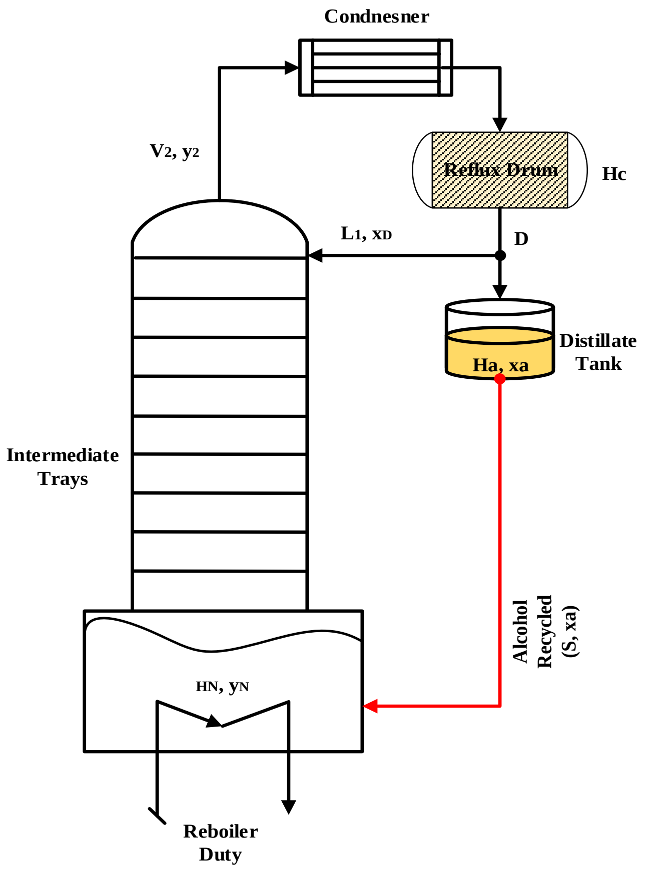

Figure 4.2 Schematic Diagram of Integrated Conventional Mode (i-CBD)

The model equations for the distillate accumulator and reboiler drum can be presented as follows:

Condenser and Distillate Accumulator: j=1

- Accumulator Total Mole Balance:

$$\frac{dH_a}{dt} = D - S_{MeOH} \tag{4.24}$$

- Component Mole Balance:

a) Distillate Accumulator:

$$H_a \frac{dx_{ai}}{dt} = (D - S_{MeOH}) \times (x_{Di} - x_{ai}) \tag{4.25}$$

Partial Reboiler: j= N

- Total Mole Balance:

$$\frac{dH_n}{dt} = L_{n-1} - V_n + S_{MeOH} + \Delta n_n H_n \tag{4.26}$$

- Component Mole Balance:

$$H_n \frac{dx_n}{dt} = L_{n-1}(x_{n-1} - x_n) - V_n\,(y_n - x_n) + S_{MeOH}\,(x_{ai} - x_n) + H_n r_n \qquad (4.27)$$

- Energy balance:

$$0 = L_{n-1}\,(H^L_{n-1} - H^L_n) - V_n\,(H^V_n - H^L_n) + S_{MeOH}\,(H^a - H^L_n) + Q_{heat} \qquad (4.28)$$

4.2.1.3 Semi-Batch Distillation Column (SBD)

The distillate tank, total condenser, and the internal trays equations in the rigorous dynamic model for SBD are similar to those presented in the CBD column.

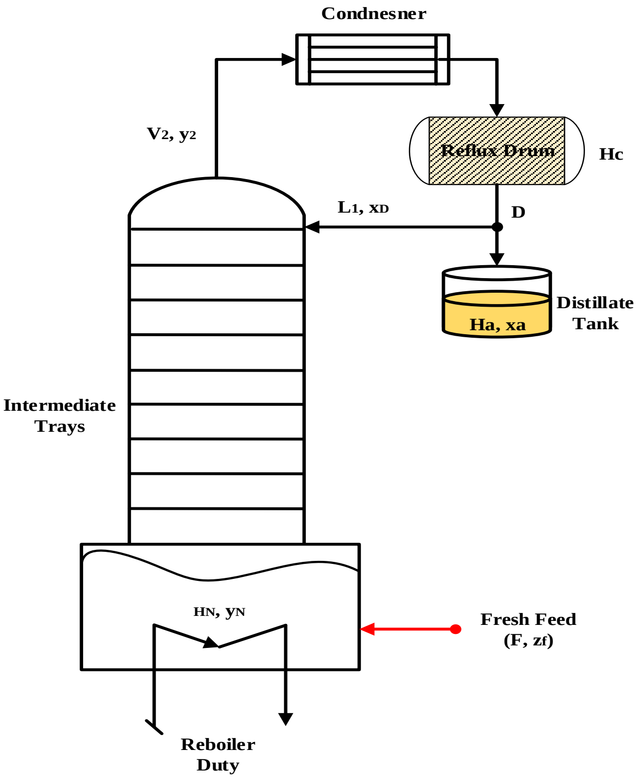

Figure 4.3 Schematic Diagram of Semi-Batch Mode (SBD)

The model equation for the reboiler stage referring to the scheme of a typical SBD process (Figure 4.3) is given below:

Partial Reboiler: j= N

- Total Mole Balance:

$$\frac{dH_n}{dt} = L_{n-1} - V_n + F_{MeOH} + \Delta n_n H_n \qquad (4.29)$$

- Component Mole Balance:

$$H_n \frac{dx_n}{dt} = L_{n-1}(x_{n-1} - x_n) - V_n (y_n - x_n) + F_{MeOH} (z_f - x_n) + H_n r_n \qquad (4.30)$$

- Energy balance:

$$0 = L_{n-1} (H^L_{n-1} - H^L_n) - V_n (H^V_n - H^L_n) + F_{MeOH} (H^f - H^L_n) + Q_{heat} \qquad (4.31)$$

4.2.1.4 Integrated Semi-Batch Distillation (i-SBD)

For the SBD of i-SBD column, the model equations are the same as those presented in section 4.2.1.3. In contrast, the second column is a conventional batch distillation without any chemical reaction, which is used to separate methanol at a desired purity (see section 4.2.1.1).

4.2.1.5 Inverted Batch Distillation Column (IBD)

Referring to Figure 4.4 for inverted batch column configuration, the internal tray equations in model presented in section 4.2.1.1 will remain the same. The model equations for the total condenser and for the still pot for are shown below.

Condenser: j=1; i= n_c

- Total Mole Balance:

$$\frac{dH_c}{dt} = V_2 - L_1 + \Delta n_1 H_c \qquad (4.32)$$

- Component Mole Balance:

$$\frac{d(H_c x_{c,i})}{dt} = V_2 y_{2,i} - L_1 x_{1,i} + H_c r_{c,i} \qquad (4.33)$$

- Energy balance:

$$0 = V_2 H^V_2 - L_1 H^L_2 - Q_c \qquad (4.34)$$

Reboiler Holdup and Product Tanks: j=N; i= n_c

- Total Mole Balance:

a) Product Tank:

$$\frac{dH_B}{dt} = B \qquad (4.35)$$

b) Reboiler Holdup Tank:

$$\frac{dH_n}{dt} = L_{n-1} - B - V_n + \Delta n_n H_n \qquad (4.36)$$

- Component Mole Balance:

a) Product Tank:

$$\frac{d(H_B x_B)}{dt} = B\,(x_{n,i} - x_{B,i}) \qquad (4.37)$$

b) Reboiler Holdup Tank:

$$\frac{d(H_n x_n)}{dt} = L_{n-1}x_{n-1,\,i} - B\,x_{n,\,i} - V_n y_{n,\,i} + H_n r_n \qquad (4.38)$$

- Energy Balance:

$$0 = L_{n-1}H^L_{n-1} - BH^L_n - V_n H^V_n + Q_{heat} \qquad (4.39)$$

- Reboil Ratio:

$$R_b = \frac{V_n}{L_{n-1}} \qquad (4.40)$$

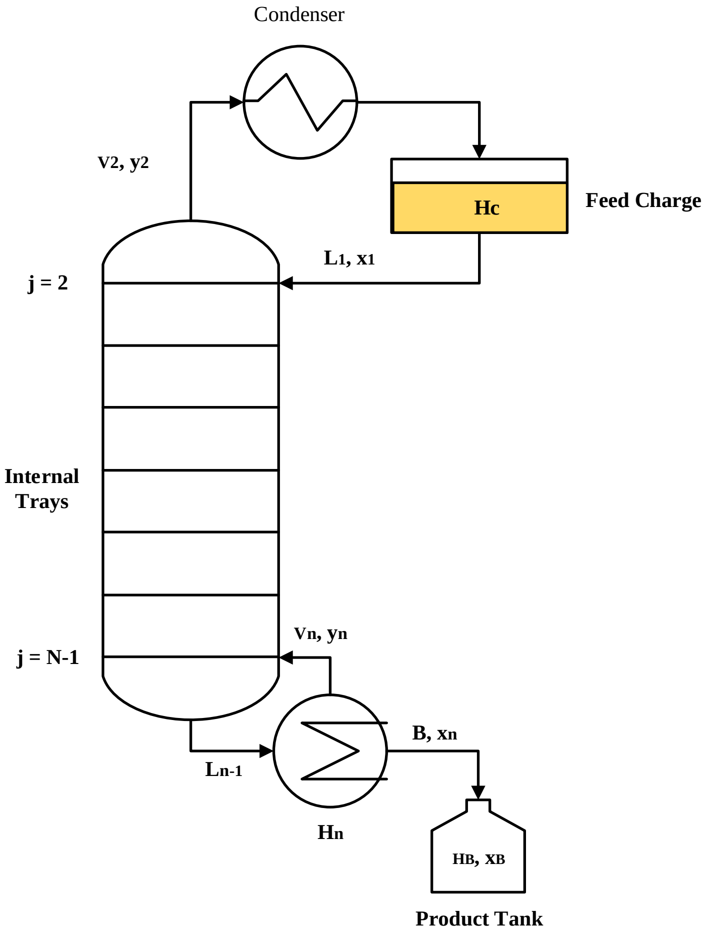

Figure 4.4 Schematic Diagram of Inverted Batch Column (IBD)

4.2.1.6 Middle-Vessel Batch Distillation Column (MVD)

With reference to the MVD column configuration shown in Figure 4.5, the model equations for the rectifying section are the same as those presented for CBD column, whereas, the still pot equations are same as the IBD system (see section 4.2.1.5). Model equations for the feed tank and feed trays are presented below.

Feed Tank and Feed Plate: j=1; i= n_C

- Total Mole Balance:

a) Feed Tank:

$$\frac{dH_f}{dt} = L_f - F + \Delta n_f H_f \tag{4.41}$$

b) Feed Tray:

$$0 = L_{j-1} - L_j + V_{j+1} - V_j - L_f + F + \Delta n_j H_j \tag{4.42}$$

- Component Mole Balance:

a) Feed Tank:

$$\frac{d(H_f x_f)}{dt} = L_f x_j - F x_f + H_f r_f \tag{4.43}$$

b) Feed Tray:

$$H_j \frac{dx_j}{dt} = L_{j-1} x_{j-1} - L_j x_j + V_{j+1} y_{j+1} - V_j y_j - L_f x_j + F x_f + H_j r_j \tag{4.44}$$

- Energy Balance:

$$0 = L_{j-1} H^L_{j-1} - L_j H^L_j + V_{j+1} h_{j+1} - V_j H^V_j - L_f H^L_j + F H^f_L \tag{4.45}$$

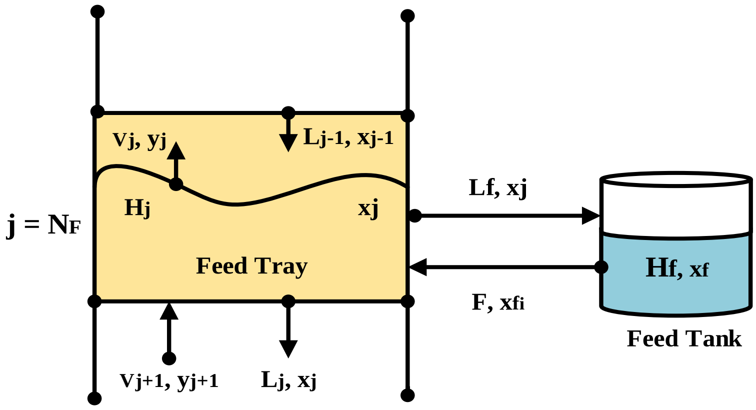

Figure 4.5 Schematic Diagram of the Feed Tray and Feed Tank for MVD

4.2.1.7 Divided-Wall Distillation Process (DWBD)

With reference to Figure 4.6, the DWBD model is given by the set of Equations 4.46 to 4.65, which are derived from Mujtaba (2004), and Safe et al. (2013). The model equations of DWBD are similar to those for batch distillation operation but contain the vapour and liquid split ratios. It comprises of four main sections, namely; total condenser, main column, prefractionator, and still pot.

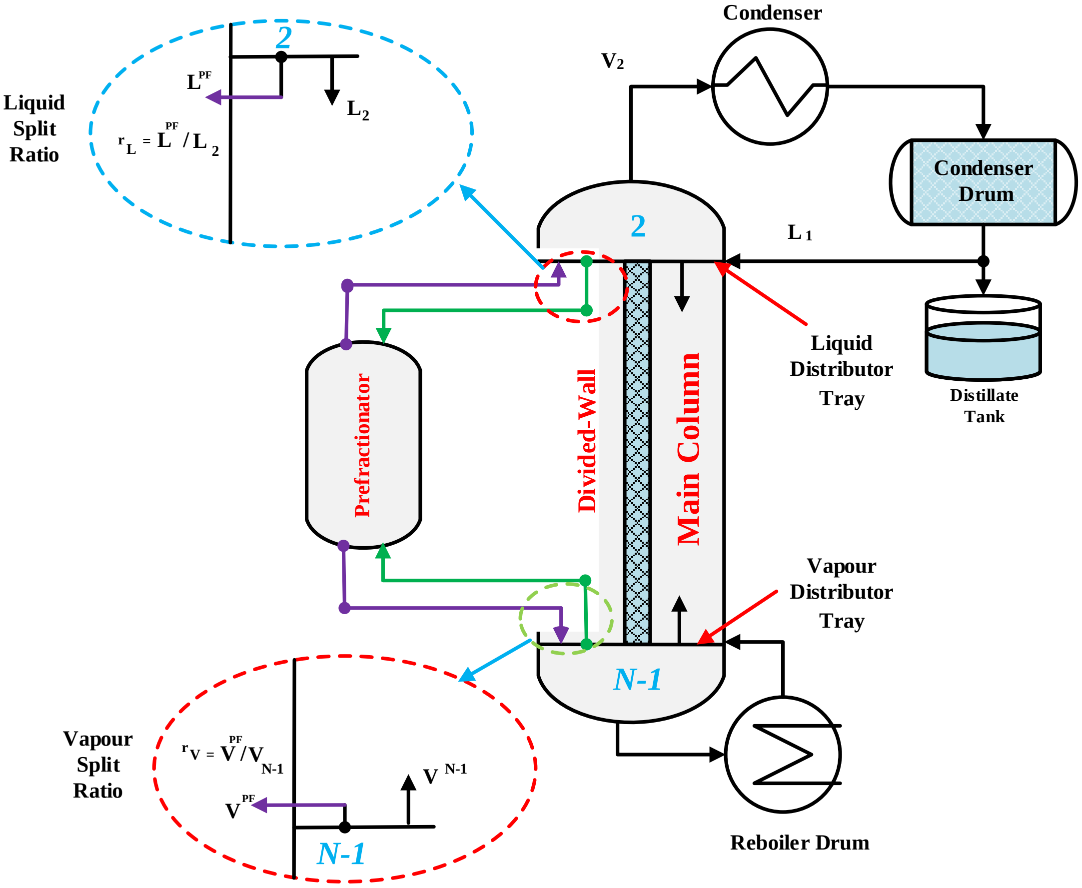

Figure 4.6 Schematic Diagram of Dividing-Wall Batch System (DWBD)

Condenser System and Distillate Tank: j=1

- Distillate Accumulator Total Mass Balance:

$$\frac{dH_a}{dt} = D \tag{4.46}$$

- Component Mole Balance:

a) Distillate Accumulator:

$$H_a \frac{dx_{ai}}{dt} = D\,(x_{Di} - x_{ai}) \tag{4.47}$$

b) Condenser Holdup Tank:

$$H_c \frac{dx_{ci}}{dt} = V_2\, y_2 - (V_2 + \Delta n_1 H_c)\, x_{Di} + r_{1i} H_c \tag{4.48}$$

- Energy Balance:

$$0 = V_2 H_2^V - (V_2 + \Delta n_1 H_c)\, H_1^L - Q_c \tag{4.49}$$

Liquid Distributor tray: j= 2

- Total Mole Balance:

$$0 = L_{j-1} - L_j - L^{PF} + V^{PF} + V_{j+1} - V_j + \Delta n_j H_j \tag{4.50}$$

- Component Mole Balance:

$$H_j \frac{dx_{j,i}}{dt} = L_{j-1} x_{j-1,i} - L_j x_{j,i} - L^{PF} x_{j,i} + V^{PF} y^{PF} + V_{j+1} y_{j+1,i} - V_j y_{j,i} + H_j r_{j,i} \tag{4.51}$$

- Energy Balance:

$$0 = L_{j-1} H_{j-1}^L - L_j H_j^L - L^{PF} H_j^L + V^{PF} h^{PF} + V_{j+1} h_{j+1} - V_j\, h_j^V \tag{4.52}$$

Intermediate plates for the main column: j= 3 to N-2

- Total Mole Balance:

$$0 = L_{j-1} - L_j + V_{j+1} - V_j + \Delta n_j H_j \tag{4.53}$$

- Component Mole Balance:

$$H_j \frac{dx_j}{dt} = L_{j-1} x_{j-1} - L_j\, x_j + V_{j+1} y_{j+1,i} - V_j y_{j,i} + H_j r_{ji} \tag{4.54}$$

- Energy Balance:

$$0 = L_{j-1}\, H_{j-1}^L - L_j H_j^L + V_{j+1} h_{j+1} - V_j H_j^V \tag{4.55}$$

Intermediate plates for the prefractionator: j = 3 to N-2

- Total Mole Balance:

$$0 = L_{j-1}^{PF} - L_j^{PF} + V_{j+1}^{PF} - V_j^{PF} + \Delta n_j^{PF} H_j^{PF} \tag{4.56}$$

- Component Mole Balance:

$$H_j^{PF} \frac{dx_{j,i}^{PF}}{dt} = L_{j-1}^{PF} x_{j-1,i}^{PF} - L_j^{PF} x_{j,i}^{PF} + V_{j+1}^{PF} y_{j+1,i}^{PF} - V_j^{PF} y_{j,i}^{PF} + H_j^{PF} r_{j,i}^{PF} \tag{4.57}$$

- Energy Balance:

$$0 = L_{j-1}^{PF} H_{j-1}^{PF} - L_j^{PF} H_j^{PF} + V_{j+1}^{PF} h_{j+1}^{PF} - V_j^{PF} h_j^{PF} \tag{4.58}$$

Vapour Distributor tray: j= N-1

- Total Mole Balance:

$$0 = L_{j-1} - L_j + L^{PF} - V^{PF} + V_{j+1} - V_j + \Delta n_j H_j \tag{4.59}$$

- Component Mole Balance:

$$H_j \frac{dx_{j,i}}{dt} = L_{j-1}x_{j-1,i} - L_j x_{j,i} + L^{PF}x^{PF} - V^{PF}y_{j,i} + V_{j+1}y_{j+1,i} - V_j y_{j,i} + H_j r_{j,i} \tag{4.60}$$

- Energy Balance:

$$0 = L_{j-1}H^L_{j-1} - L_j H^L_j + L^{PF}H^{PF} - V^{PF}h^V_j + V_{j+1}h_{j+1} - V_j h^V_j \tag{4.61}$$

- Equilibrium Relationship and Summations:

$$K_{j,i} = \frac{y_{j,i}}{x_{j,i}} \quad \text{where} \quad \sum x_{j,i} = 1 \quad \text{and} \quad \sum y_{j,i} = 1 \tag{4.62}$$

- Reflux Ratio:

$$R_{DWBD} = \frac{L_1}{V_2} \tag{4.63}$$

- Liquid Split Ratio:

$$r_L = \frac{L^{PF}}{L_2} \tag{4.64}$$

- Vapour Split Ratio:

$$r_V = \frac{V^{PF}}{V_{N-1}} \tag{4.65}$$

Note, the model equations for the pot drum are similar those presented in the CBD process (see section 4.2.1.1).

4.2.1.8 Split Reflux Divided-Wall Distillation Process (sr-DWBD)

The process model of sr-DWBD mode is most similar to the DWBD process discussed in section (4.2.1.7) except that the additional terms for the reflux side stream (Figure 4.7a) are to be inserted to model equations in the reboiler section as presented below.

- Reflux Ratio:

$$R = \frac{L_1 + L_2}{V_2} \tag{4.66}$$

Reboiler Tank: j= N

- Total Mole Balance:

$$\frac{dH_n}{dt} = L_{n-1} - V_n + L_2 + \Delta n_n H_n \tag{4.67}$$

- Component Mole Balance:

$$H_n \frac{dx_n}{dt} = L_{n-1}(x_{n-1} - x_n) - V_n (y_n - x_n) + L_2 (x_{Di} - x_n) + H_n r_n \quad (4.68)$$

- Energy balance:

$$0 = L_{n-1} (H^L_{n-1} - H^L_n) - V_n (h^V_n - H^L_n) + L_2 (H^L_1 - H^L_n) + Q_{heat} \quad (4.69)$$

4.2.1.9 Integrated Divided-Wall Distillation Process (i-DWCBD)

Note also, the i-DWCBD process model is exactly similar to the DWBD process presented in section (4.2.1.7) except that the additional terms for the recycled methanol-rich stream (Figure 4.7b) to be inserted into the model equations as shown below.

Condenser System and Distillate Tank tray: j =1

$$\frac{dH_a}{dt} = D - S_{MeOH} \quad (4.70)$$

- Component Mass Balance:

a) Distillate Accumulator:

$$H_a \frac{dx_{ai}}{dt} = (D - S_{MeOH}) \times (x_{Di} - x_{ai}) \quad (4.71)$$

Partial Reboiler: j= N

- Total Mass Balance:

$$\frac{dH_n}{dt} = L_{n-1} - V_n + S_{MeOH} + \Delta n_n H_n \quad (4.72)$$

- Component Mass Balance:

$$H_n \frac{dx_n}{dt} = L_{n-1}(x_{n-1} - x_n) - V_n (y_n - x_n) + S_{MeOH} (x_{ai} - x_n) + H_n r_n \quad (4.73)$$

- Energy balance:

$$0 = L_{n-1} (H^L_{n-1} - H^L_n) - V_n (h^V_n - H^L_n) + S_{MeOH} (H^a - H^L_n) + Q_{Heat} \quad (4.74)$$

- Reflux Ratio:

$$R_{i\text{-}DWCBD} = \frac{L_1}{V_2} \quad (4.75)$$

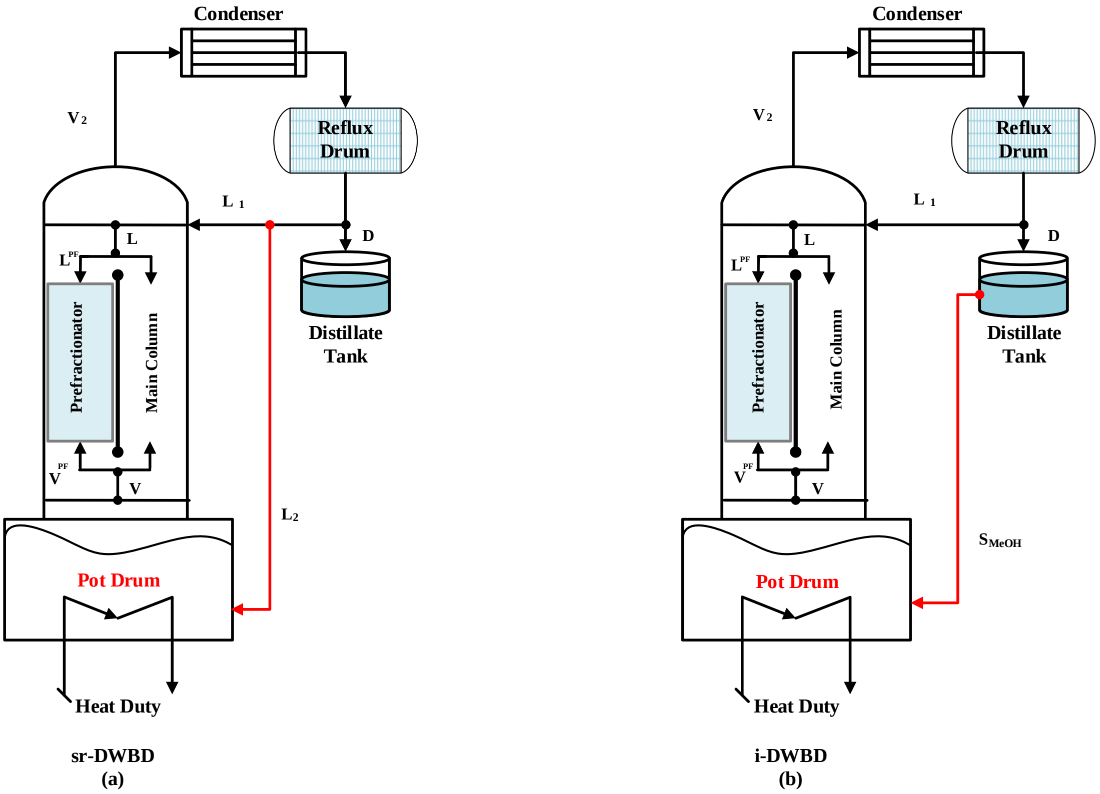

Figure 4.7 Schematic diagram of two column systems: (a) split reflux-divided wall (sr-DWBD), and (b) integrated divided wall columns (i-DWCBD)

4.3 Optimisation

Customarily, the challenges in engineering process design or plant operation can be solved in many possible ways. Using optimisation, a variety of methods of solution are available: from the rudimentary multiple run approach of trial and error to more advanced numerical approaches. This variety comes because optimisation is not straightforward in the real world; it requires a practical approach. The main goal of optimisation is to find the optimal operating parameters of the process, which produces the best operation performance. Some benefits of optimization would involve improved reaction conversion, yield of valuable product, productivity, profitability, production batch time, and thermal energy consumption.

Aris (1960) investigated the first discussion about seeking the optimum operational policy of dynamic optimization problem. A large number of dynamic optimization problems have been suggested in the past due to the increased importance of dynamic systems in chemical industries. Korovessi and Linninger (2005) used a common solution strategy to solve the optimum control issue, which was Non-Linear Programming Algorithm (NLP). The NLP method is one of the numerical tools that can be employed in the process models including highly non-linear algebraic equations. Performing NLP approaches into optimization problems include the discretisation of control profile by applying the control vector parameterisation (CVP) method. The CVP method is used to transform the optimum control problem into a finite nonlinear programming (NLP) problem. It is extensively used due to its straightforwardness in handling stiff and nonlinear systems by isolating the complexities between the process model and the optimization objectives.

4.4 gPROMS Software

The gPROMS (**g**eneral **Pro**cess **M**odelling **S**ystem) package is a powerful general-purpose modelling, simulation and optimisation tool, employed to develop the design and process of continuous and dynamic operations. gPROMS has a wide variety of applications and it can be used in petrochemicals, food, pharmaceuticals, specialty chemicals and robotics industries. gPROMS was established by Process System Enterprise, based at Imperial college of London and has been extensively utilized for industrial processes such as batch distillation system (Winkel *et al*., 1995). Here, the different types of batch reactive distillation systems considered in this thesis, modelled, and optimised using the software package (gPROMS).

gPROMS has a lot of advanced features including the ability to evaluate an infinite number of parameters and to utilize data from multiple steady-state and dynamic experiments. It also offers the user full flexibility in that they can specify different variance models for different variables in different experiments. Furthermore, it has a built-in interface to MS Excel allowing the user to examine automatically the statistical importance of results, produce plots overlaying model data and experimental data, and plot confidence ellipsoids. gPROMS has a number of benefits that make it an attractive tool for solving steady-state and dynamic modelling problems. Some of these advantages for gPROMS are clear and concise language, unparalleled modelling power, and the ability to model process discontinuities and operating conditions among several others (gPROMS Introductory User Guide, 2017).

4.4.1 Defining a Model/Process/Optimisation Entities

The gPROMS model builder is chosen in this work due to some reasons such as less time for constructing the model because the solution technique is required to be specified rather than to be written, several simulation and optimisation activities can be implemented using the same model, and it has rational editors for easy establishment and repairs.

The model entity is general information to be specified in any MODEL is characterized in the following:

- A set of constant parameters that clarify the system, which are declared in the PARAMETER section.

- A set of variables that describe the time-dependent behaviour of the system, which are declared in the VARIABLE section.
- A set of model equations involving the stated variable and parameters, which are declared in the EQUATION section.

The Process entity (contains specification for simulation the batch distillation system). It is portioned into sections that include information necessary to define a dynamic simulation activity. The main process sections employed to perform the simulation studies in this work are Unit, Set, Assign, Initial, Solution parameters, and Schedule.

In the optimization entity, the parameters for dynamic optimization problem formulations are specified in several cases, the values are expressed in the form: [guessed value, lower bound, upper bound]. Some of the specifications for the dynamic optimisation include:

- The time horizon for the process
- The total number of intervals.
- The control values within the time-intervals
- The end point of constraints.
- The objective function to be maximised or minimised.

Note, all the model equation for the batch process presented earlier (section 4.2) are modelled within gPROMS model builder 4.2.0. Figures A.1, A.2, and A.3 in Appendix A show the detailed gPROMS program for the optimal synthesis of benzyl acetate.

4.5 Conclusions

This chapter discussed different types of rigorous models with chemical reaction, which have been used for conventional and unconventional batch distillation process and these models will be utilized in Chapters 5, 6 and 7, and 8. In addition, the solution methods for dynamic optimisation problems, which offer optimal operation strategies for a variety of objective functions including these models are outlined. The dynamic optimization problem cases are transformed to non-linear programming (NLP) problems by Control Vector Parameterization (CVP) algorithm and are solved using efficient SQP method within gPROMS software tool.

This chapter includes brief general overview of the gPROMS modelling tool, some advantages and uses are shown and found to be easy, flexible, and user-friendly software. Further information about the gPROMS software can be found in detail at www.psenterprise.com. In this thesis, gPROMS is used for the modelling, simulation, and optimisation of the different types of batch reactive columns.

The gPROMS Model Builder has been used over the last few years to handle different types of batch reactive distillation columns. However, developing a process model in gPROMS software can be time consuming, particularly when a rigorous model is used. Therefore, different model assumptions are typically made to simplify the process model. For instance, an ideal vapor-liquid equilibrium phase is assumed, and column hydraulics and vapor hold-ups are neglected. Also, the gPROMS model builder has limited physical property libraries.

Chapter Five

Optimization of Lactic Acid Esterification Process

5.1 Introduction

In this chapter, the optimization of different batch column configurations for the synthesis of methyl lactate (ML) via the esterification of lactic acid (LA) with methanol (MeOH) is considered. The following case studies are considered in this chapter:

- Case Study 1: Methyl Lactate Synthesis using Batch Distillation: Operational Challenges and Strategy for Enhanced Performance.
- Case Study 2: Integrated Batch Reactive Distillation Column Configurations for Optimal Synthesis of Methyl Lactate.

5.2 Methyl Lactate Production

The conversion of lactic acid into its alkyl esters is worth studying since lactic acid can be manufactured easily by fermentation or by chemical synthesis from many carbohydrates (Filachione et al., 1945). Methyl lactate is a colourless and clear liquid having a minty odour. It is a useful product as chiral pharmaceuticals and agrochemicals, plasticizer agent, cleaning agent, green solvent, or intermediate and its two functional groups can be used to prepare numerous derivatives. In general, methyl lactate is a powerful component, which has good possibilities of application at industrial levels, food industries, cosmetic and personal care (hair shampoos, makeup, hair colours and dyes, etc.) uses (Ullmann’s Encyclopedia, 1985; Gelbard, 2005; and Acton, 2013).

The global demand for lactate ester products were about 2505.0 kilotons in 2013 and are anticipated to be around 3569.6 kilotons by 2020. Increasing the global demands for lactate esters are anticipated to have a positive impact on the market growth (Grand View Research, 2015). There are a number of chemical reaction systems, which can be used to produce methyl lactate, and some of these are listed in Table 5.1.

Table 5.1 Several Proposed Reaction Systems for Methyl Lactate Formation

Reaction System	Reference
AmL+ MeOH => ML+ AM	(Filachione et al., 1945)
EL + MeOH ⇔ ML+ EtOH	(Özen, 2004)
LA + MeOH ⇔ ML+ H_2O	(Sanz et al., 2004)
AgL + CH_3CL => ML + AgCL	(Özen, 2004)
GLA or DHA => HC => ML	(West et al., 2010)

In this work, it is attempted to take into account again at the esterification step in detail with the objective of enhanced recovery and formation of methyl lactate (ML) rather than focusing on the purification of lactic acid (LA), which has already attracted quite a bit of attention in recent years (Edreder et al., 2011; and Mujtaba et al., 2012). First of all, the restrictions of batch reactive distillation column are explored here for the production of ML. Then the improvement of the conversion rate of lactic acid is investigated by continuously feeding methanol into a semi-batch distillation column and dealing with the operational challenges due to this mode of operation. The ultimate aim was to achieve the best operating policy of the semi-batch system for the synthesis of methyl lactate. Note also, the recovery of water is not suggested or attempted before the recovery of methyl lactate like others. Rather, the proposed strategy will yield methyl lactate and water simultaneously in the pot and distillate tank.

Secondly, the recycling and recovery of methanol in an integrated manner are considered in both new integrated conventional (i-CBD) and integrated semi-batch (i-SBD) distillation operations. The performances of i-CBD and i-SBD configurations are evaluated in terms of maximum profitability via the minimization of batch time.

5.3 Process Model

The model equations are presented in chapter four.

5.3.1 Operation Modes and Energy Consumption

Mujtaba (2004) outlined different modes to operate batch distillation process: (A) Constant vapor boil-up rate, (B) Constant condenser vapor load rate mode and (C) Constant reboiler duty mode. Mujtaba et al. (2012) proposed the following equations to compute the total energy consumption rate in the column for each mode:

Mode A:

$$Q_{tot}= V\int_{0}^{t_f} \lambda_r \, dt \tag{5.1}$$

Mode B:

$$Q_{tot}= \int_{0}^{t_f} Q_{heat} \, dt \tag{5.2}$$

Mode C:

$$Q_{tot}= Q_{heat} \times t_f \tag{5.3}$$

Where λ_r is the enthalpy heat of vaporisation, which changes with time as the mixture concentration in the reboiler changes. In this work, the operation mode (B) is used when the condenser vapor load (V_C) is kept constant. Note also, the reboiler heat duty (Q_{heat}) progressively increases in this operation mode to retain the constant vapour boil-up rate and vapour load to the condenser. This mode of operation has been extensively employed by some authors in the past (Nad and Spigel, 1987; and Wajge and Reklaitis, 1999). The differentiation of Equation (5.2) gives:

$$\frac{dQ_{tot}}{dt} = Q_{heat} \tag{5.4}$$

The above differential equation is inserted into the model equations presented in chapter four. Q_{tot} at the end of operating time (t_f) will give the energy usage rate of the process.

5.3.2 Reaction Kinetics

The production of methyl lactate was considered via the esterification of lactic acid (LA) with methanol (MeOH) over an acid catalyst such as the cation-exchange resin Amberlyst 15. A quasi-homogeneous (QH) activity ($a_i = \gamma_i x_i$) based on kinetic model was taken from Sanz *et al*. (2004) and has the following form:

$$-r_1 = \left\{ 1.16 \times 10^6 exp\left(\frac{-48.52}{RT}\right) a_1 a_2 - 1.65 \times 10^5 exp\left(\frac{-50.91}{RT}\right) a_3 a_4 \right\} \tag{5.5}$$

The QH model is used in this work due to a good description for the kinetic behavior of the global system where one of the reactants is highly-polar.

5.3.3 Vapour-Liquid Equilibrium (VLE)

K-values (VLE constants) are computed from (Eq. 5.6) where γ_i is calculated from the UNIQUAC equation.

$$K_i = \gamma_i \frac{P_i^{sat}}{P} \tag{5.6}$$

The enthalpy of each component in vapour phase can be calculated from the empirical equations is provided by Aspen HYSYS® (HYSYS, 2017):

$$h_{vi} = \left\{ a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4 + a_5 T^5 \right\} \times M_{wti} \tag{5.7}$$

$$H_{vi} = \sum h_{vi} y_{j,i} \tag{5.8}$$

Where, a_0, a_1, a_2, a_3, a_4, and a_5 are the coefficients of vapour enthalpy taken from the data bank of Aspen Plus. The enthalpy of component in liquid phase were computed by subtracting the latent heat from the vapour enthalpies:

$$H_{Li} = \sum x_{j,i} \left(H_{vi} - \delta_i \right) \tag{5.9}$$

The latent heat (the heat of vaporization) can be written as follow:

$$\delta_i = \delta_{bi} \left(\frac{1 - T_{r1}}{1 - T_{r2}} \right)^{0.38} \tag{5.10}$$

The saturation vapour pressure (P^{sat}) for each pure component has been obtained by using Antoine's equation:

$$Log\ P_i^{sat} = A - \frac{B}{T + C} \tag{5.11}$$

Where A, B, C are the coefficients for the Antoine equations and T is the temperature in Kelvin. The thermodynamic phase equilibria (the activity coefficients) was computed using the UNIQUAC model with the binary interaction parameters and all physical and thermodynamic properties of pure components and Antoine constants were taken from Sanz et al. (2003).

5.4 Case Study 1: Methyl Lactate Synthesis Using Batch Distillation: Operational Challenges and Strategy for Enhanced Performance

5.4.1 Formulation for Optimization Problem

In this study, the aim of the optimization problem of the batch/semi-batch column is to minimize the batch time for a given amount of desired product and concentration of product.

The optimization problem can be described as:

Given:	The column configurations, the feed mole fraction, condenser hold-up, distillate rate, a separation task (i.e obtain the product with desired purity requirement for a key product component).
Optimize:	Reflux ratio (R), and feed rate (F_{MeOH}) profiles (for SBD only)
So as to:	Minimize the production batch time
Subject to:	Process constraints, Model equations (Equality and inequality constraints)

Mathematically, the optimization problem (OP1) can be formed as follow:

$$\begin{array}{lll} OP1 & \underset{\substack{R_{CBD}(t) \\ Or \\ R_{SBD}(t),\ F(t)}}{Min} \quad t_F & \begin{array}{l} (For\ CBD\ Column) \\ \\ (For\ SBD\ \ Column) \end{array} \end{array} \tag{5.12}$$

Subject to :

$f\,(t,\, \dot{x}(t),\, x(t),\, u(t),\, v) = 0; \quad [0 \quad t_F]$ *(Process model, equality constraint)*

$B_{ML} \geq B^{*}_{ML}$ *(Inequality Constraints)*

$x_{ML} \geq x^{*}_{ML}$ *(Inequality Constraints)*

Linear bound on $R\,(t),\, F\,(t)$ *(Inequality constraints)*

$f\,(t,\, \dot{x}(t),\, x(t),\, u(t),\, v) = 0$, represents the process model shown in Chapter Four, where t denotes the independent variable (operating batch time), $x(t)$ is the set of all differential and algebraic variables, $\dot{x}(t)$ denotes the derivative of differential variables with respect to batch time, $u(t)$ represents the control variables, and v is the set of the design variables (fixed parameters). The switching time of interest is $[0 \quad t_F]$, and the function f: is assumed to be continuously differentiable with respect to all its arguments (Ekpo and Mujtaba, 2007). B_{ML}, and x_{ML} are the amount of bottom product and quality of ML at end batch time (t_F) in the reboiler, (denotes that the B^*_{ML} and x^*_{ML} are specified). $R(t)$ is the reflux ratio profile and $F_{MeOH}(t)$ is the methanol feed rate profile (in case of semi-batch mode) which are optimized.

5.4.2 The Problem Specifications

The case study is performed in a ten stages column (containing both total condenser and reboiler) with 2.5 kmol/hr of the condenser vapour load (V_C) at the atmospheric pressure. The total column holdup was assumed to be 4% of the total feed. Half of this total holdup is for the total condenser and the other half is for the column plates (equally divided). The same distributions policy of column hold-up was utilized by many researchers in the past as noted in Mujtaba (2004). The capacity of the pot drum is 5 kmol and the feed composition < Lactic acid (1), Methanol (2), Methyl Lactate (3), Water (4) > is: <0.5, 0.5, 0.0, 0.0>.

The concentrations of reflux drum and column plates are initialized to the feed mole fraction at the beginning of operation. In the start-up period, the distillation column operates at total reflux mode (R = 1) for a certain time until the batch column reaches steady state and then concertation profiles of column are consequently established. After that, the production period for all cases begins from this point (designated as t = 0) onward.

5.4.3 Results and Discussions

5.4.3.1 The conversion of lactic acid in a single stage CBD

It has been generally accepted that a reactive distillation system provides better performance than a batch reactor followed by distillation in terms of conversion of limiting reactant, the higher reaction rates, heat integration benefits, improved conversion and selectivity, and the lower operational costs (Tadé and Tian, 2000; and Edreder, 2010). The esterification reaction of LA is performed in a one-stage distillation batch column (acting as a batch reactor) with total reflux for 5 hours as shown in Figure 5.1. Note, the system reached steady state after half an hour with a highest LA conversion of 65.82%. Figure 5.2 presents the dynamics of the reboiler concentration of the single-stage batch distillation process. It is clear from Figure 5.2 that methyl lactate response takes nearly 0.5 hour to reach a steady state with a maximum quality of methyl lactate of 0.342 (mole fraction).

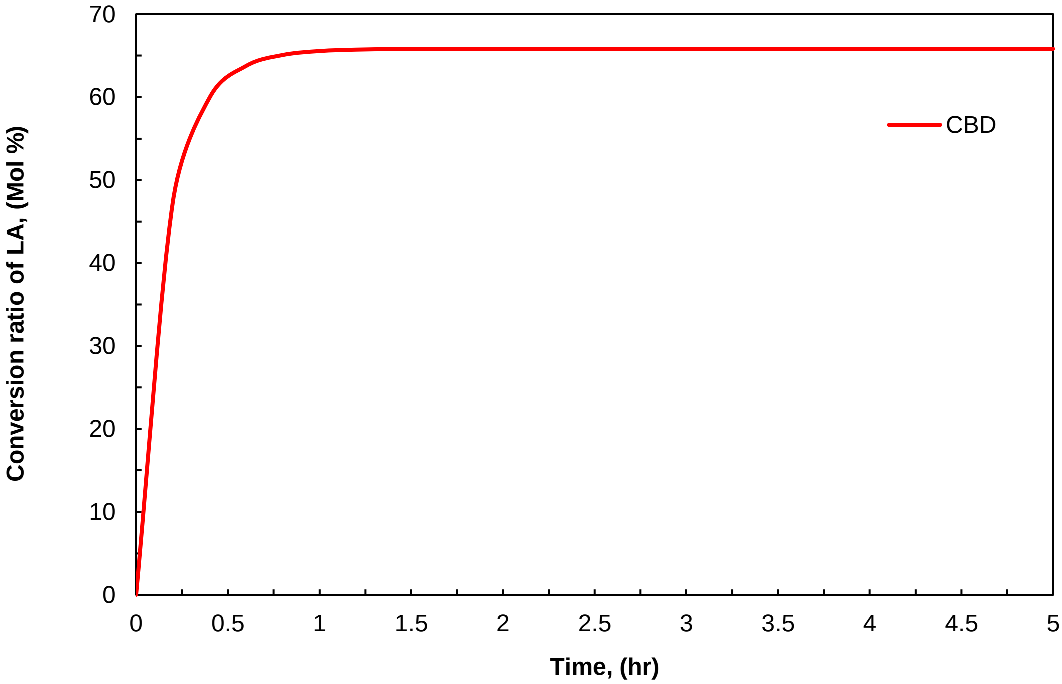

Figure 5.1 Dynamic response of reaction conversion at (V_C = 2.5 & R = 1)

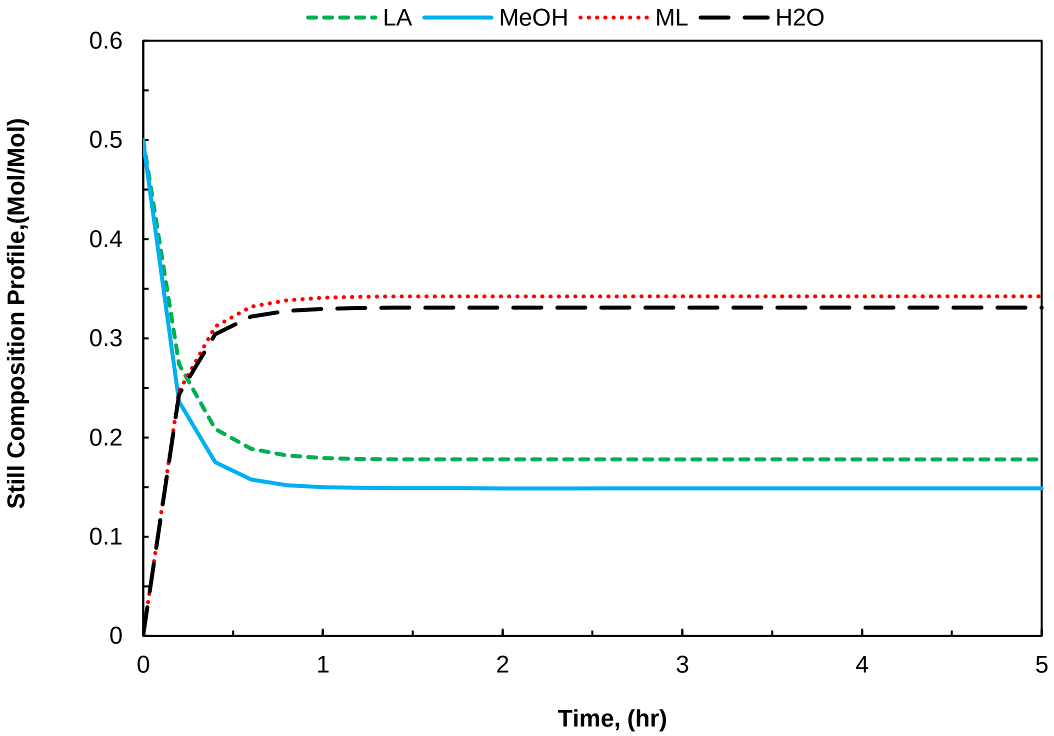

Figure 5.2 The reboiler composition profile at (V_C = 2.5 & R = 1)

5.4.3.2 Restrictions of CBD for methyl lactate production

The restrictions of CBD for the formation of ML are investigated in detail via simulation here. The CBD column is simulated using three different reflux ratios (Table 5.2). The results are analyzed based on a given product amount in the reboiler which is 2.3 kmol. For different reflux ratios, this amount is achieved at different operating time as shown in Table 5.2. Figure 5.3 reveals that for all reflux ratios, the conversion level of acid increases with batch time initially, goes through a maximum and then drops down quite considerably.

It is obvious that due to separation, methanol is removed as a top product (at higher rate at lower reflux values) leaving behind significant quantity of ML and some water in the still pot to activate the backward reaction producing LA and methanol (Figure 5.4). At low reflux ratio, trace quantities of water are also removed with methanol (more ML at the still drum than water) thereby restricting the reversible reaction to some extent leading to more conversion of acid as compared to higher reflux ratio case (Figure 5.3, Table 5.2) and leaving more methyl ester at the pot drum (Figure 5.4). Note, when the one-stage column is operated at total reflux mode (Figure 5.1), methanol is not separated from the reaction system and the system reaches equilibrium with the maximum conversion rate of LA (65.82%) compared to those seen at finite reflux ratio (Figure 5.4).

Table 5.2 The simulation results summary

Reflux Ratio (----)	Distillate rate, L_D (kmol/hr)	Conversion of LA (%)	Operating time, t_f (hr)	Total energy, Q_{tot} (mkJ)
0.95	0.125	21.43	20	1.882
0.80	0.5	38.86	5	0.522
0.60	1	49.76	2.5	0.289

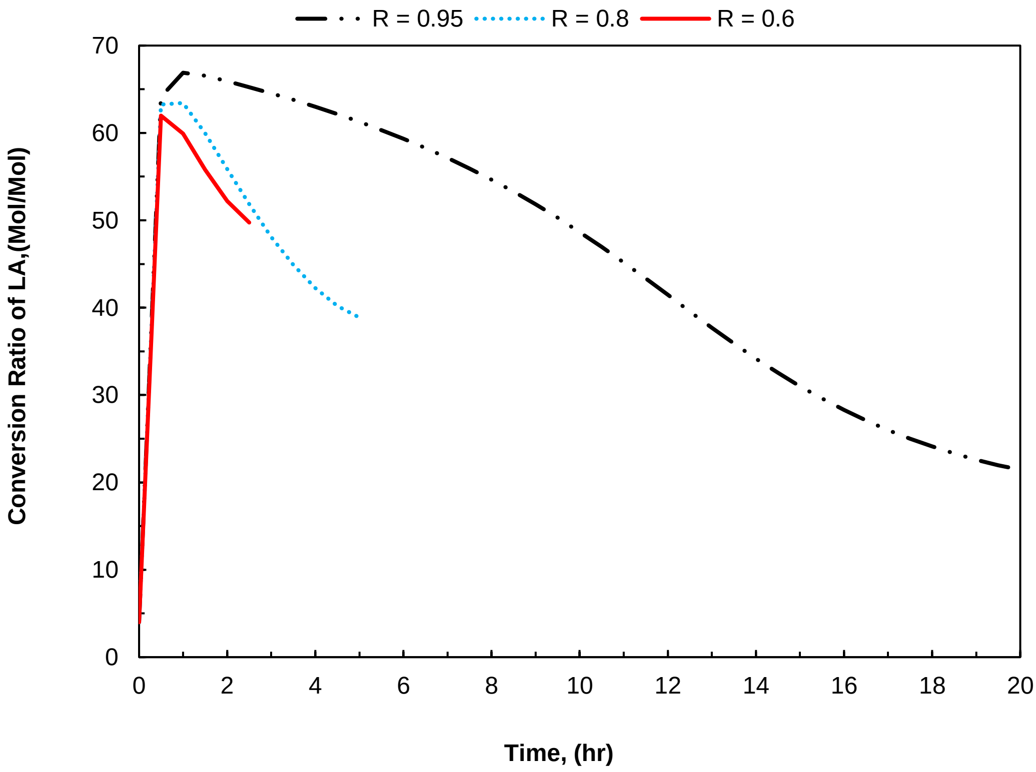

Figure 5.3 Dynamic response of reaction conversion at different reflux ratios

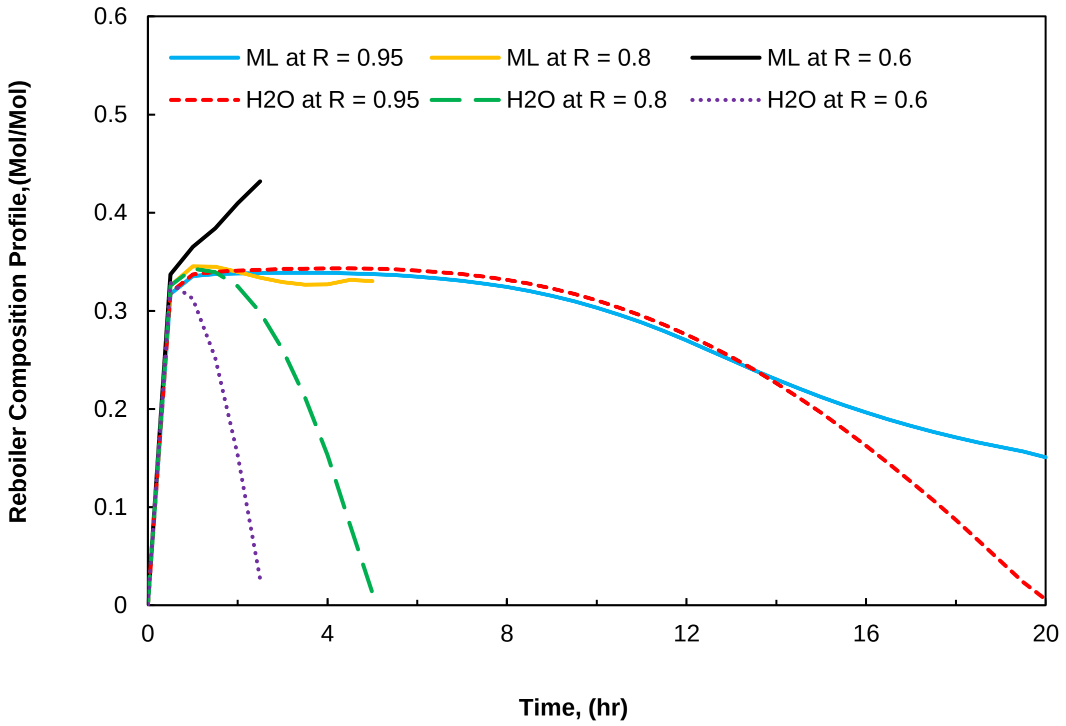

Figure 5.4 The composition profile of H_2O and ML in the pot drum

It will be interesting to study the performance of the same batch reactive column in terms of lower batch time for different quality of ML but for a given amount of reboiler product, which is 2.3 kmol. Table 5.3 shows the optimization results in terms of optimum reflux ratio, conversion of acid, minimum batch time, and the total energy demand for a range of product purity (0.415 to 0.455) at equimolar feed ratio. The results of Table 5.3 illustrated that all reflux ratios, batch time and total energy usage reduce with increasing the desired product purity and the product amount and also it is impossible to achieve a higher conversion of LA using a CBD column. Also, no results were achieved at product concentration of 0.455 mole fraction. This is due to reverse reaction being active and removal of methanol due to distillation. The results shown below so far confirms why CBD is not at all appropriate for the synthesis of ML although considered in the past as a potential manufacturing route.

Table 5.3 Summary of optimization results for CBD column

Product Quality x^{*}_{ML}	Optimum Reflux Ratio, R	Conversion of LA (%)	Minimum batch time, t_f (hr)	Total energy, Q_{tot} (m kJ)
0.415	0.651	47.83	2.86	0.323
0.425	0.622	48.96	2.65	0.303
0.435	0.589	50.14	2.43	0.282
0.445	0.546	51.37	2.20	0.261
0.455**	---**	---**	---**	---**

** Infeasible

5.4.3.3 Semi-Batch Distillation Operation (SBD)

The SBD system is explored here as a feasible and potential candidate for ML synthesis. For different product quality constraints, the optimization results (optimum reflux ratio, optimum feed rate, maximum reflux ratio, conversion of LA, final batch time, and the total energy consumption) are provided in Table 5.4. It can be noted from these results that the batch time, the conversion rate and the energy expense, increase progressively with increasing the product purities (unlike those observed in a CBD mode). This is clear as higher composition of ML dictates more conversion of acid. This can only be obtained by having more methanol feed and higher reflux ratio but at the expense of more operating time and thus more energy requirements. Also note, in all cases R_{max} is calculated for different values of feed rate of MeOH as shown below.

$$R_{Max} = \left(1-\frac{F_{MeOH}}{V_C}\right) \tag{5.13}$$

As illustrated also in Table 5.4, the optimal values of reflux ratios (R_1) are still lower than R_{max} meaning the pot tank never overflows.

It is obvious from Table 5.4 that higher reflux ratio and higher batch time with higher feed rate are needed at 0.85 of ML purity compared to others to fulfil the product specification. A comparison of the results between the conversion of acid using SBD column and the CBD column conversion (Table 5.3) shows that for the same amount of reboiler product (2.3 kmol) SBD system can yield ML at a much higher purity (0.85 compared to 0.445) and can covert more lactic acid (94.55% as opposed to only 51.37%). This is shown in clearly in Figure 5.5.

Table 5.4 Summary of optimization results for SBD column

Product Quality x^*_{ML}	Optimal Feed Rate	Optimal Reflux Ratio	Maximum Reflux Ratio	Conversion of LA (%)	batch time, t_f (hr)	Total energy, Q_{tot} (m kJ)
0.70	0.91	0.285	0.636	79.21	2.85	0.303
0.75	1.33	0.187	0.467	87.72	3.57	0.355
0.80	1.32	0.250	0.471	90.51	4.52	0.436
0.85	1.37	0.300	0.452	94.55	6.58	0.606

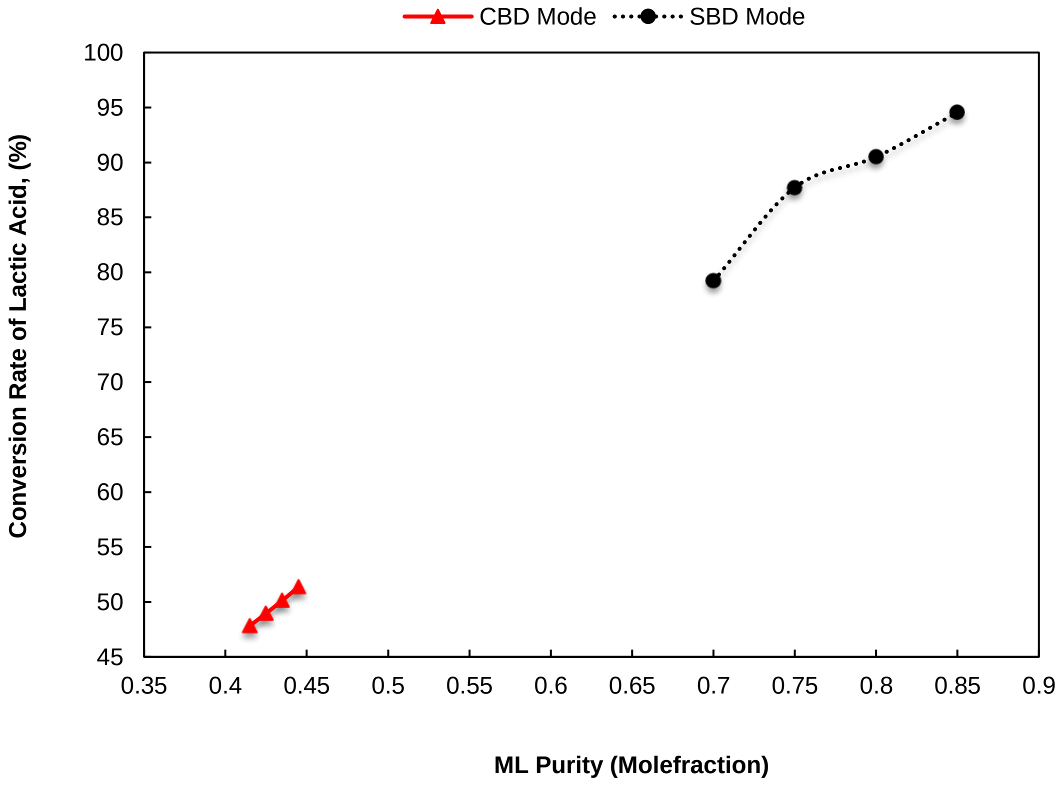

Figure 5. 5 The batch time, energy usage, and LA conversion profiles

5.5 Case Study 2: Integrated batch reactive distillation column configurations for optimal synthesis of methyl lactate

5.5.1 Motivation

Due to the nature of the reaction system, in this work, the recovery and recycling of methanol in an integrated manner are considered in both i-CBD and i-SBD operations.

The performances of those configurations are evaluated in terms of maximum profitability by minimizing the batch time. The piecewise-constant strategy for the optimization constants (reflux ratio, MeOH recycle rate (only for i-CBD), and MeOH feed rate for i-SBD) are utilized in the optimization study.

5.5.2 Economic Analysis

The profit function is commonly employed as an economic indicator for determining the economic feasibility of column configurations. The profit is evaluated based on minimizing the operating batch time. The profit function equations and constants for all i-CBD, SBD, and i-SBD systems can be shown as (Miladi and Mujtaba, 2004):

$$P_{i\text{-}CBD} = (C_{ML}B_{ML} - C_R B_0 - OC) \times N_B - AC \qquad (5.14)$$

$$P_{SBD} = (C_{ML}B_{ML} - C_R B_0 - OC - C_{MeOH\ Charge}) \times N_B - AC \qquad (5.15)$$

$$P_{i\text{-}SBD} = (C_{ML}B_{ML} - C_R B_0 - OC_{i\text{-}SBD} - C_{Makeup_{MeOH}}) \times N_B - AC_{i\text{-}SBD} \qquad (5.16)$$

$$OC\ (\text{The operating cost, \$/Batch}) = \left(\frac{K_3\, V_2}{A_P}\right) \times (t_F + t_s) \qquad (5.17)$$

$$N_B\ (\text{Number of Batches, Batch/ yr}) = \frac{(P_H\ /\ yr)}{(t_F + t_s)} \qquad (5.18)$$

$$AC\ (\text{ Annual Capital Cost, \$/ yr}) = K_1\ (V_2)^{0.5}\ (N)^{0.8} + K_2\ (V_2)^{0.65} \qquad (5.19)$$

$$AC_{i\text{-}SBD} = AC_{SBD} + AC_{CBD} \qquad (5.20)$$

$$OC_{i\text{-}SBD} = OC_{SBD} + OC_{CBD} \tag{5.21}$$

$$TYP\ (Kmol/\,yr) = N_B \times B_{ML} \tag{5.22}$$

Where, OC is the total operating cost ($/batch), N_B (batch/yr) the number of batches produced over year, AC the total annual cost ($/yr), TYP yearly production rate (kmol/yr), factor for total capital costs equation (K_1) =1500; parameter for AC equation (K_2) = 9500; operating costs constants for operating cost equation (K_3) = 180; the operating cost factor (A_P) = 8000; setup time (t_s) = 0.5 hr; Production horizon (P_H) = 8000 hr/yr. Note, the annualised investment cost (AC) is fixed because the total number of stages (N) and the vapor load to condenser (V_2) also kept fixed.

Note, all prices of reactant (LA, and MeOH) are taken from (Alibaba Trade, 2016). From Alibaba Trade (www.alibaba.com/trade), April 2016 the cost of methyl lactate product for 99% quality is found to be 572.61 $/kmol. We apply the exponential trend method to estimate the product prices at other qualities. Based on the trend method used in the past by Mujtaba and Greaves (2006) the price of methyl lactate (ML) at 90% quality is computed to be 269.99 $/kmol. The prices for the reactants (LA, and MeOH) and methyl lactate at various product purities values are tabulated in Table 5.5.

Table 5.5 The costs of reactant and product reaction

The price constants	Cost ($/kmol)
Methanol Reactant Cost at 100% purity	12.83
Methanol Charge Cost at 95% purity	12.19
Lactic Acid Reactant Cost at 100% purity	9.10
Methyl Lactate Cost at 70% purity	74.35
Methyl Lactate Cost at 75% purity	90.89
Methyl Lactate Cost at 80% purity	113.99
Methyl Lactate Cost at 85% purity	169.99
Methyl Lactate Cost at 90% purity	269.99

5.5.3 Optimization Problem Formulation

In this study, the optimum processes of i-CBD, SBD of the i-SBD columns are evaluated based on minimum batch time for a given amount of ML product and desired purity.

As the CBD column has the same processing time as SBD of the i-SBD operation, the optimum operation of CBD is evaluated based on maximization of the quantity of methanol recovery for a given product purity and batch time.

5.5.3.1 Maximum Profitability for i-CBD, and i-SBD Operations

Given: The column configuration, the feed concentration, the vapour load to the condenser, and the desired amount of product and concentration.

Optimize: Reflux ratio (R) and Recycle rate (S_{MeOH}) (for i-CBD)

Or,

Reflux ratio (R) and feed rate (F_{MeOH}) (for SBD of i-SBD)

So as to: Maximize the total annual profit (P)

Subject to: Model equation, Process constraints.

Mathematically the optimization problem (OP1) can be represented as:

$$\begin{aligned} &OP1 \quad \underset{R(t),\ S_{MeOH}}{Max} \quad P \quad \text{(For i-CBD Column)} \\ &\qquad\qquad Or \\ &\qquad\quad R(t),\ F_{MeOH} \quad \text{(For SBD of i-SBD Column)} \end{aligned} \tag{5.23}$$

Subject to :

$$B_{ML} \geq B^{*}_{ML} \quad \text{(Inequality Constraints)}$$

$$x_{ML} \geq x^{*}_{ML} \quad \text{(Inequality Constraints)}$$

$$\text{And} \quad f(t, x', x, u, \wedge) \quad \text{(Model equation, equality constraint)}$$

$$\text{With} \quad f(t_0, x'_0, x_0, u_0, \wedge_0)\ \wedge_0 \quad \text{(Initial condition, equality constraint)}$$

For a given desired product amount and its quality, the minimization of operating batch time will increase the total number of batches produced over production time (N_B) and thus will increase the total yearly revenue.

Therefore, the maximum profit problem of those operations can be transferred into minimum batch time problem as presented below.

5.5.3.1.1 Minimum Operating Time Problem

Mathematically, the optimization problem (OP2) can be represented as follows:

OP2 $\quad Min \quad t_F$

$\quad R(t),\ S_{MeOH}$ $\quad$ *(For i-CBD Column)*

$\quad$ *Or* $\quad$ *(5.24)*

$\quad R(t),\ F_{MeOH}$ $\quad$ *(For SBD of i-SBD Column)*

Subject to :

$\quad B_{ML} \geq B^{*}_{ML}$ $\quad$ *(Inequality Constraints)*

$\quad x_{ML} \geq x^{*}_{ML}$ $\quad$ *(Inequality Constraints)*

And $\quad f\,(t, x', x, u, \wedge)$ $\quad$ *(Model equation, equality constraint)*

With $\quad f\,(t_0, x'_0, x_0, u_0, \wedge_0)\ \wedge_0$ $\quad$ *(Initial condition, equality constraint)*

5.5.3.1.2 Maximum Distillate Amount for CBD Column (of i-SBD process)

Mathematically the optimization problem (OP3) can be represented as:

OP3 $\quad Max \quad D_{MeOH}$

$\quad R_{CBD}(t)$ $\quad$ *(5.25)*

Subject to :

$\quad t_F = t^{*}_{F}$ $\quad$ *(Equality Constraints)*

$\quad x_{MeOH} \geq x^{*}_{MeOH}$ $\quad$ *(Inequality Constraints)*

Where, D_{MeOH} is the distillate amount of methanol, x_{MeOH} is the concentration of recovered methanol at the end batch time (t_F), (t^{*}_{F}, x^{*}_{MeOH}) are the specified batch time and the specified purity of recovered methanol, respectively.

5.5.4 Results and Discussions

5.5.4.1 i-CBD Operation

Note, the problem specifications of i-CBD process and the holdup distribution assumptions are the same as those for CBD column. The column configurations are kept the same as CBD column for easy comparison. Note that, the concentration of ML product requirement is changed from 0.70 to 0.90 mole fraction in each case while the amount of bottom product in the reboiler remains the same at 2.3 kmol. The optimum operating strategy for the i-CBD column are summarised in Table 5.6, including the optimum recycle rate of methanol, optimum reflux ratio profile, conversion of LA, minimum batch time, the total energy usage, and the total amount of methanol recycled over the production time. It can be seen that as the concentration of ML increases from 0.70 to 0.90 mole fraction, the reflux ratio, the operating batch time and the thermal energy consumption increase with the total amount of methanol recycled. Increasing operating batch time clearly helped increasing the conversion rate of lactic acid. It can be seen that the i-CBD system produced a higher purity of ML (0.90 mole fraction), converted more lactic acid (93.33%) compared to those obtained by CBD column (Table 5.3). Note that there is a sharp increase in processing-batch time and thus total energy demand, as well as total quantity of methanol recycle to increase the ML composition from 0.85 to 0.90 (molefraction). For this case, the i-CBD column is required to operate at even a higher reflux ratio to suppress the movement of ML up the column, resulting in lower distillate rate to distillate tank, lower methanol recycle rate from the accumulator tank but longer operating time to satisfy the product specification.

Table 5.6 Optimal operation results for i-CBD column

Product Quality x^*_{ML}	Optimal Recycle Rate	Optimal Reflux Ratio	Conversion of LA (%)	batch time, t_F (hr)	Total energy, Q_{tot} (mkJ)	Amount of Recycled MeOH
0.70	1.06	0.471	78.58	9.48	0.942	10.04
0.75	0.90	0.577	81.60	15.39	1.484	13.79
0.80	0.84	0.622	85.60	23.81	2.248	20.01
0.85	0.75	0.672	89.50	37.22	3.452	28.07
0.90	0.63	0.734	93.33	66.88	6.137	42.00

Using the optimal results of Table 5.6, the overall profit of the operation is calculated. The total number of batches produced over the year, total annual production, total utility cost, annual capital investment cost, and the profit are presented in Table 5.7. As the ML purity and production batch time increase, the number of batches and total yearly product decrease progressively. It is also clear form Table 5.7 that using the i-CBD column is more profitable at product quality case (x^*_{ML} = 0.90) as compared to others ML qualities. This is because a higher annual profit (30511 \$/yr) with the highest composition specification makes a higher priced product (269.99 \$/kmol) than a lower priced product (see Table 5.5). Note, for all product purity considerations, which the annualized capital cost and the utility cost remained the same.

Table 5.7 Profit results of optimal operation for i-CBD column

Purity of ML	Number of Batches, N_B batch/yr	Yearly Product, kmol/yr	Annualized Capital Cost, \$/yr	Total Operating Cost, \$/yr	Total Annual Profit, \$/yr
0.70	802	1843	29752	450	18983
0.75	503	1158	29752	450	19839
0.80	329	757	29752	450	19990
0.85	212	488	29752	450	29466
0.90	119	273	29752	450	30511

The mixture composition profiles in the reboiler and in the accumulator at product purity (x^{*}_{ML} = 0.90) are given in Figures 5.5 and 5.6. It can be seen from Figure 5.5 that the concentration of water (2nd boiling component) rises from zero and reaches the maximum value and then falls down to almost zero (due to removal in the distillate tank, Figure 5.6). More methyl lactate is formed as the batch progresses and stays in the still pot (as the second heavier boiling product). The mole fraction of methanol reactant is reduced with increasing batch time because of its lowest boiling point temperature and gathered in the distillate receiver (Figure 5.6). Further lactic acid is consumed progressively with increasing the operating batch time due consumption by reaction with methanol. A higher reflux ratio with longer operation time is required to keep the reactants (LA and methanol) in the reaction region.

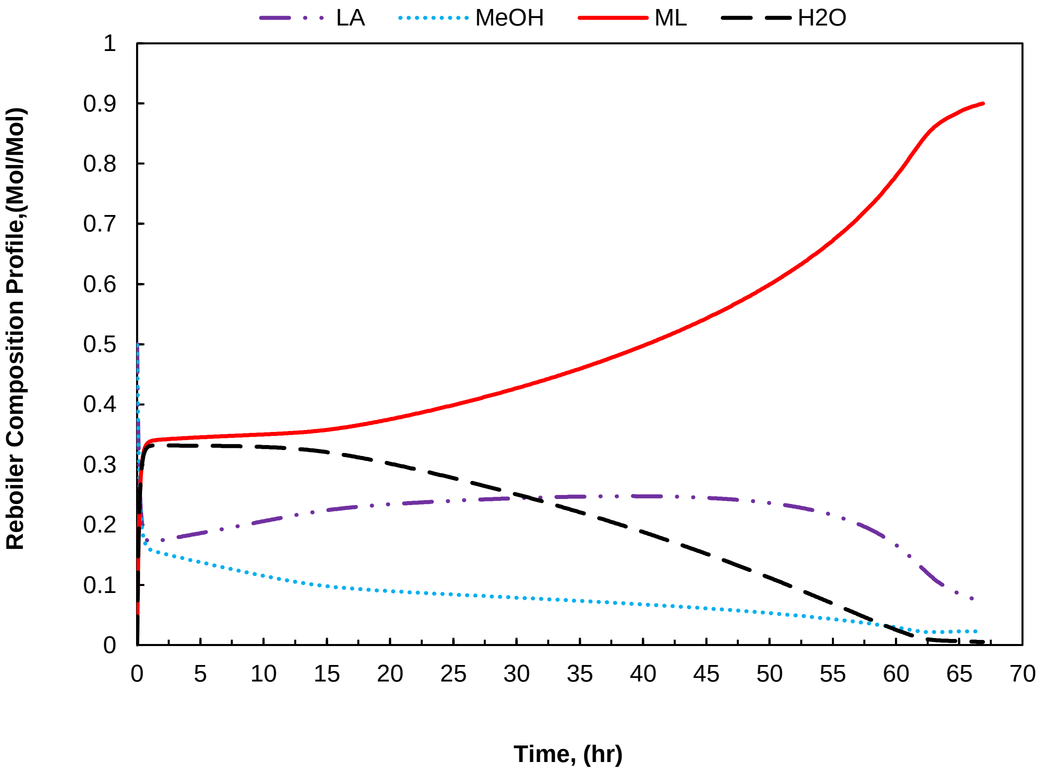

Figure 5.5 The reboiler composition profile of i-CBD column

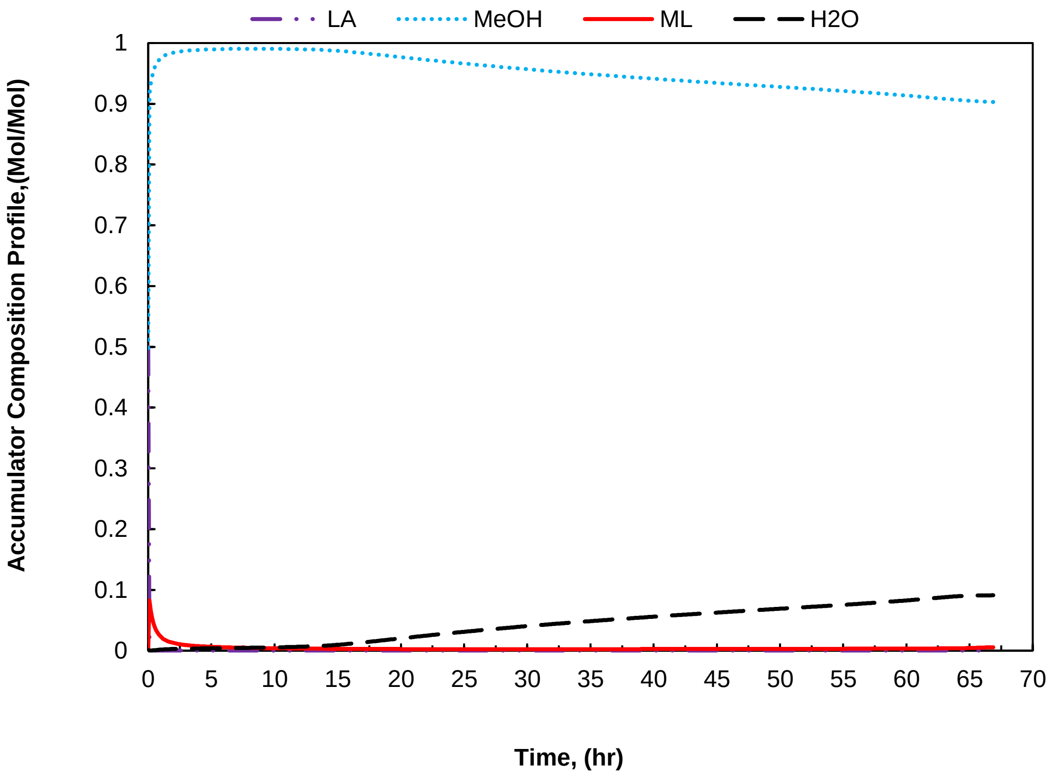

Figure 5.6 The accumulator composition profile of i-CBD column

5.5.4.2 SBD Operation

The main purpose of investigating SBD process again in this case study is to make a direct comparison of the performance by SBD system with i-SBD column (presented in the later section) where the maximum quality of ML is set to 0.90 mole fraction. Note, the problem specifications of SBD operation and the holdup distribution strategy are the same as those for CBD column (see section 5.4.2) and the composition of methanol fed stream is 0.95 mole fraction. Note, the difference in process specifications in this work and in SBD in the earlier section 5.4.3.3 (case study 1). A pure external methanol feed was considered while this work considered external methanol feed is 95% pure (the remainder is water) which is the composition of the recovered methanol from the CBD of i-SBD system. Also, the bottom product amount in the pot drum is set as 2.3 kmol. Table 5.8 shows the optimum feed rate and reflux ratio profiles, maximum allowable reflux ratio, maximum conversion of LA, and minimum batch time, as well as the total energy consuming for different product qualities of ML. It can be noticed that as the concentration of ML increases from 0.70 to 0.90 mole fraction, final batch time, energy consumption and the MeOH feed rate increase together with the conversion of acid except the case with 0.90 mole fraction. For the last case, there is a sharp rise in reflux ratio and production batch time leading to higher thermal energy usage (although methanol fed rate reduced for this case). For all cases, the values of R_{Max} are bigger than actual reflux ratio ensuring no overloading of the still tank.

Table 5.8 Optimal operation results for SBD column

Product Quality x^*_{ML}	Optimal Feed Rate	Optimal Reflux Ratio	Maximum Reflux Ratio	Conversion of LA (%)	batch time, t_f (hr)	Total energy, Q_{tot} (mkJ)
0.70	0.79	0.413	0.684	77.46	3.69	0.383
0.75	1.19	0.267	0.523	85.29	3.90	0.39
0.80	1.03	0.426	0.589	87.07	6.12	0.588
0.85	1.12	0.449	0.551	92.00	9.84	0.901
0.90	0.97	0.579	0.611	95.45	31.63	2.769

For each bottom product purity constraints, the results in terms of number of batches (N_B), total production rate (TYP), and yearly capital cost (AC), and total operating cost (OC) for SBD column, as well as the profit (Profit) are shown in Table 5.9. As the number of batches (N_B) decreases with increasing operating batch time (t_F), total yearly product (TYP) reduces. The maximum yearly revenue ($/yr) profile for both i-CBD and SBD processes is shown in Figure 5.8. It is clear from Table 5.9 and Figure 5.8 that as the product composition requirement increases from 0.70 to 0.85 mole fractions together with price of ML product, the total yearly revenue increases gradually and are better than i-CBD in most cases. However, note, for 0.90 of ML product quality, there is a sharp reduction in the annual profit due to significant increase in the batch time and the prices of total amount of charged methanol (see Table 5.8). This makes SBD operation uncompetitive (compared to even the revenue obtained by i-CBD operation) at higher product concentration and hence the proposed i-SBD operation.

Table 5.9 Profit results of optimal operation for SBD column

Purity of ML	Number of Batches, N_B batch/yr	Yearly Product, kmol/yr	Annualized Capital Cost, $/yr	Total Operating Cost, $/yr	Total Annual Profit, $/yr
0.70	1907	4387	29752	450	19007
0.75	1818	4182	29752	450	47587
0.80	1208	2777	29752	450	61367
0.85	774	1780	29752	450	83299
0.90	249	573	29752	450	3736

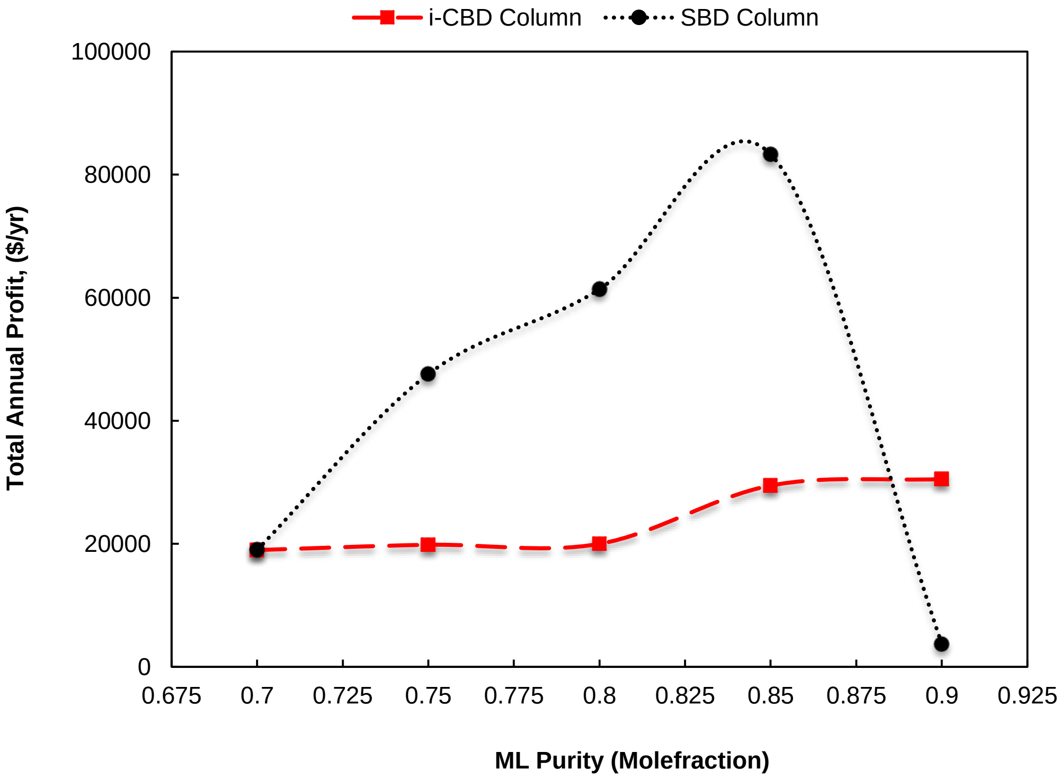

Figure 5. 7 The total annual profit profiles for both i-CBD and SBD systems

The composition profiles of the reboiler and the accumulator tank of SBD column at product purity constraint (x^*_{ML} = 0.90) are given in Figures 5.9 and 5.10 respectively. It can be noticed from Figure 5.9 that the mole fraction of water (as the second light boiler) increases from zero and reaches to the higher value and then falls down to almost zero (due to removal in the distillate tank, Figure 5.10). Lactic acid as the heaviest boiling component is nearly consumed through the chemical reaction with methanol (in the bottom receiver) and resulting higher conversion rate of acid at the end of reaction (Figure 5.9, Table 5.10). In the pot drum, the concentration of both the reactant elements, namely lactic acid and methanol, gradually reduces as long as the reaction continues. In the same operation time, methyl lactate starts moving up and finally, the reboiler drum is enriched with methyl lactate having a maximum achievable quality of 0.90.

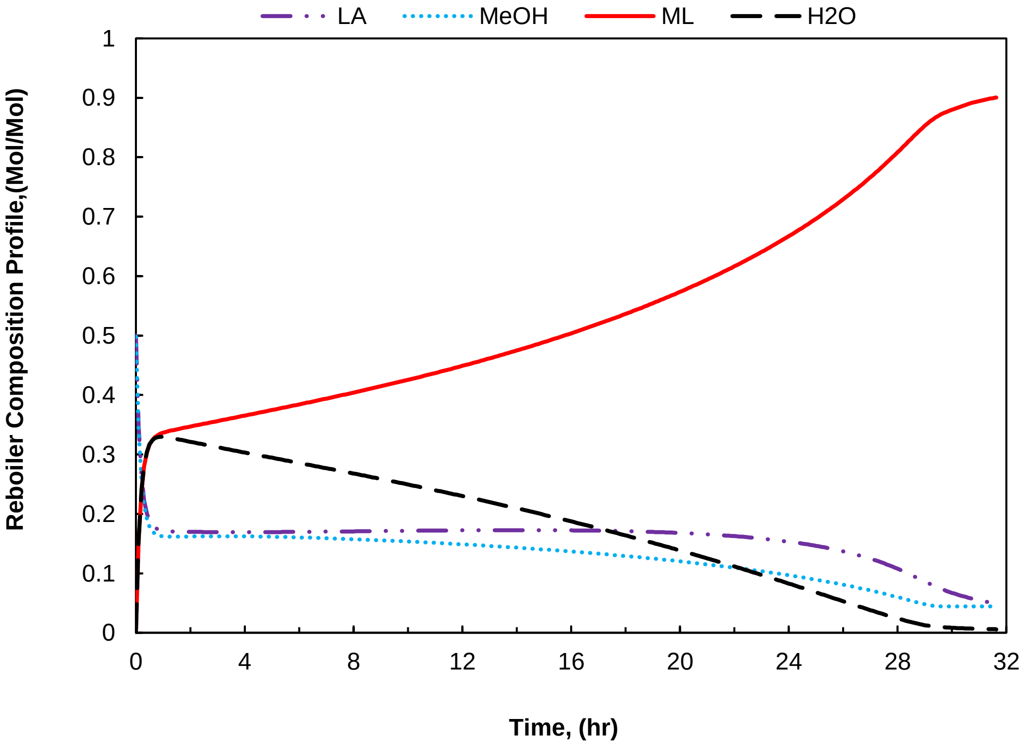

Figure 5.9 The reboiler composition profile of SBD column

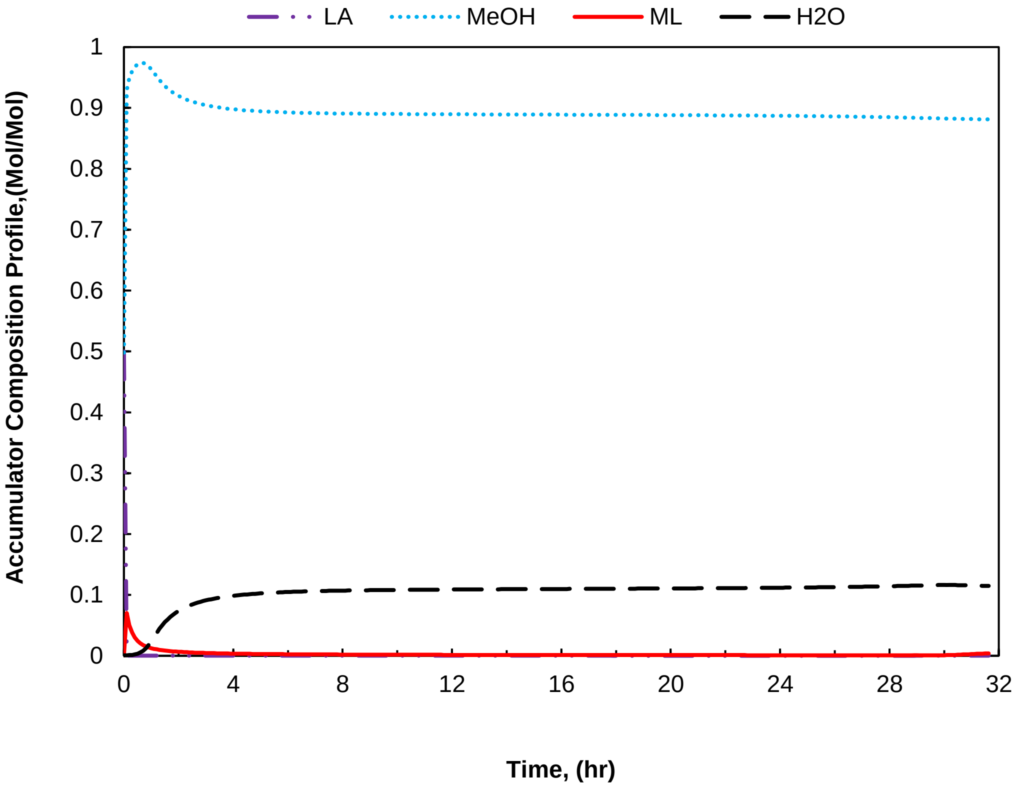

Figure 5.8 The accumulator composition profile of SBD column

5.5.4.3 The Performance of i-SBD Column

The feasibility of the i-SBD configuration is discussed here in detail, where the ML synthesis reaction takes place in SBD only. The CBD recovers methanol from the distillate tank of SBD at 0.950 mole fraction composition and which is fed back into the SBD mode together with make-up methanol (same composition). Note, the column specifications and operating variables for both columns of i-SBD configuration are the same as those in section 5.5.4.2 except that the total number of stages (including condenser and partial reboiler) and vapour load to condenser in the CBD column are 6-plates and 1.0 kmol/hr respectively. Two scenarios are considered here, scenario one is with single-reflux control interval, and scenario two is with mulita-reflux intervals. As before, the ML product purity is changed from 0.70 to 0.90 mole fraction in each scenario with the still pot product amount being kept fixed at 2.3 kmol so that comparison of performances of i-SBD can be made with i-CBD and SBD in terms of maximum yearly profit.

5.5.4.3.1 Scenario 1: Optimal operation using one-reflux interval

The results of SBD process are the same as those shown in Table 5.8. However, parts of these results are presented in Table 5.10 together with those obtained for CBD column for convenience. As can be noticed from Table 5.10, increasing ML concentration increases the total amount of methanol fed with higher composition of methanol and thus increases the quantity of methanol recovered from the CBD column. As the methanol feed concentration of the CBD increases, it decreases the reflux ratio (as the separation process becomes easier). Since the total quantity of methanol fed to SBD increases, the quantity of make-up methanol also increases for the SBD system (see Eq. 5.26). Note, the amount of make-up methanol is computed using the following form:

$$Makeup_{MeOH} = F_{MeOH} - D_{MeOH} \qquad (5.26)$$

Table 5.10 Optimal operation results for i-SBD unit using one control interval

SBD (1st)				CBD (2nd)			i-SBD
Purity of ML,	Optimal Feed Rate	Optimal Reflux Ratio	Total Fed Sum	Optimal Reflux Ratio	MeOH Distillate Sum	Make-Up MeOH	Batch Time, t_F, hr
0.70	0.79	0.413	2.92	0.414	2.16	0.75	3.69
0.75	1.19	0.267	4.65	0.351	2.53	2.12	3.90
0.80	1.03	0.426	6.29	0.342	4.03	2.27	6.12
0.85	1.12	0.449	11.05	0.284	7.05	4.00	9.84
0.90	0.97	0.579	30.77	0.182	25.86	4.91	31.63

Table 5.11 illustrates the profitability of one-reflux i-SBD system. The results in Table 5.11 visibly indicate that the employ of i-SBD operation is significantly

more profitable than both i-CBD and SBD columns in terms of using single-reflux control interval. As an example, for the scenario with 0.9 mole fraction of ML the i-SBD configuration gave 55.13% and 94.51% higher yearly profits compared to that of the i-CBD and SBD columns, respectively.

Table 5.11 Profitability for i-SBD system using one control interval

Purity of ML, x^*_{ML}	Total Annualized Capital Cost, $/yr	Total Operating Cost, $/yr	Total Annual Profit, $/yr
0.70	43799	630	55119
0.75	43799	630	89446
0.80	43799	630	106438
0.85	43799	630	135490
0.90	43799	630	68004

5.5.4.3.2 Scenario 2: Optimal operation using two-reflux intervals

Similar to Table 5.10, Table 5.12 presents the optimal results for two-reflux process. The trend of the results of each operation is qualitatively similar to those summarised in Table 5.10. Table 5.13 displays the summary of profitability of i-SBD configuration for multi-reflux operation.

The annual revenue of i-SBD system with two-reflux control intervals is about 84.65% more compared to the one-reflux i-SBD operation due to lower batch time and amount of MeOH make-up charge which are needed to meet the product specification (0.90 molefraction).

For all product concentrations, the total capital and the operating costs of the i-SBD operation kept the same for both scenarios.

Table 5.12 Optimal Operation results for i-SBD using two control intervals

SBD (1^{st})				CBD (2^{nd})			i-SBD
Purity of ML,	Feed Rates F_1, F_2	Reflux Ratios R_1, R_2	Total Fed Sum	Optimal Reflux Ratio	MeOH Distillate Sum	Make-Up MeOH	Batch Time, t_F, hr
0.70	0.76, 0.87	0.164, 0.513	2.00	0.447	1.39	0.61	2.52
0.75	1.10, 0.00	0.249, 0.988	3.50	0.380	2.05	1.44	3.31
0.80	1.07, 0.97	0.182, 0.542	3.90	0.398	2.28	1.62	3.79
0.85	0.05, 1.06	0.164, 0.559	3.83	0.451	2.58	1.25	4.70
0.90	0.58, 0.87	0.297, 0.647	6.00	0.410	4.48	1.52	7.59

Table 5.13 Profitability for i-SBD using two control intervals

Purity of ML, x^*_{ML}	Total Annualized Capital Cost, \$/yr	Total Operating Cost, \$/yr	Total Annual Profit, \$/yr
0.70	43799	630	98430
0.75	43799	630	127236
0.80	43799	630	203467
0.85	43799	630	364929
0.90	43799	630	443051

5.6 Conclusions

In this chapter, the synthesis of methyl lactate via the esterification of LA is considered in batch and semi-batch reactive distillation operations. It is found that the efficiency of using the CBD process is a quite limited due to the separation of methanol from lactic acid in the reactive region because of the large variation in boiling points between the reactants. With the loss of methanol reactants (one of the forward reaction reactants), the reverse reaction is activated along the process reducing the conversion rate of acid drastically. Therefore, the use of SBD process is suggested where methanol is continuously fed into the still pot to overcome interaction between the reactants and to enhance the conversion level of LA to ML.

Operating constraints are put in place to prevent overflowing of the pot drum due to the continuous methanol feed. Instead of separating methyl lactate in a sequential way (unreacted methanol, water, ML) in the top tank, ML is gathered as the bottom product together with any unreacted acid. The performances of those columns are determined in terms of minimum operating time using model-based techniques where a detailed model of the process is developed using gPROMS Model Builder 4.2.0 and is embedded within the optimization framework. Obviously, the SBD process outperforms the CBD mode significantly in terms of product purity and conversion ratio of lactic acid.

This chapter also presented two novel batch reactive column configurations: i-CBD column and i-SBD columns to overcome the limitations of CBD process. The performances of these column configurations are determined in terms of profitability for a defined separation task.

Piecewise-constant reflux ratio, methanol recycled rate policy (for i-CBD only), and methanol feed rate policy (for i-SBD) are considered. Visibly, the integrated batch distillation systems are found to outperform the traditional batch operations (CBD or SBD modes) to achieve higher ML purity specifications with lower batch time and energy consumption, and maximum yearly profit.

Also, the optimization results for a given separation task indicate that using two-control intervals is more attractive strategy compared to a one-control interval in terms of batch time and energy savings, and highest achievable profit in the i-SBD column. Also, i-SBD operation outperforms i-CBD system in several respects.

Chapter Six

Optimization of Decanoic Acid Esterification Process

6.1 Introduction

In this chapter, the optimization of using different types of conventional and unconventional batch column configurations for the synthesis of methyl decanoate via the esterification of decanoic acid with methanol is considered. The following case studies are considered in this chapter:

- Case Study 1: Synthesis of Methyl Decanoate using Different Types of Batch Reactive Distillation Systems.
- Case Study 2: Feasibility of Novel Integrated Dividing-Wall Batch Reactive Distillation Processes for the Synthesis of Methyl Decanoate.

6.2 Methyl Decanoate Production

Methyl decanoate, also known as methyl caprate, is a fatty acid methyl ester (FAME; biodiesel) produced from decanoic acid and methanol. FAME is an alternative source of fossil fuels, an organic, non-toxic and biodegradable fuel sources with properties similar to those of petroleum-diesel that is manufactured mostly from renewable energy sources (such as animal fats, vegetable oils, or even waste oils from the food industry).

Esters are fatty acids, which are key products of the chemical process industry and one of the renewable biomass sources for production of biodiesel. Biodiesel production has received considerable research over the past 15 years due to its potential for decreasing energy usage and greenhouse gas emissions, thus reducing global warming (Singh et al., 2004; and Wang and

Oehlschlaeger, 2012). It is very extensively utilized in numerous industrial applications such as important chemical intermediates, plasticizers in polymer processing, cosmetics and personal-care products, emulsifiers, flavorings, stabilizers, green solvents, resins, surfactants, lubricants, pharmaceutical and food industries, and detergents (Zaidi et al., 2002; Omota et al., 2003; Noirot, 2004; Brahmkhatri and Patel, 2012; and Barros et al., 2013). The worldwide demands for FAME biodiesel products were 22.5 million-tons in 2011 and are around 31 million-ton in 2016 (Unnithan, 2016). In general, biodiesels consisting of fatty acid methyl esters (FAME) are usually synthesized by two main routes: the esterification of Free Fatty Acids (FFA) with methanol to produce fatty acid alkyl ester (biodiesel) and water (by-product), or the trans-esterification of Tri-alkyl Glycerides (TAG) with an alcohol (usually methanol) resulting in a long-chain mono-alkyl ester and glycerol (by-product) using homogeneous or heterogeneous reaction systems as summarized in Table 6.1.

Table 6.1 Several proposed reaction systems for biodiesel synthesis

Reaction System	Reference
FFA + MeOH ⇔ FAME+ H_2O	(Ozcanli et al., 2013; Kiss, 2013; and Banchero et al., 2015)
TAG + 3 MeOH ⇔ 3 FAME+ Glycerol	(Banerjee and Chakraborty, 2009; Kiss and Bildea, 2012; Barros et al., 2013; Mazubert et al., 2013; and Banchero et al., 2014)

The use of batch reactive distillation system for the synthesis of Methyl decanoate is non-existent. In this work, batch reactive distillation column is considered to see whether it can improve the conversion rate of acid and the purity of methyl decanoate. The conventional batch distillation (CBD) operation together with the novel configurations such as i-CBD and SBD systems are used in this work. The performances of i-CBD and SBD columns are evaluated in terms of the minimum energy demand. In this chapter, it will also be considered if excess methanol in the feed is actually essential when operating in batch reactive distillation mode. Also, in this chapter, the two-novel integrated divided-wall batch distillation (i-DWCBD) with recycling from the distillate tank and reflux split divided-wall batch distillation (sr-DWBD) with refluxing from the reflux drum are proposed for the optimal synthesis of methyl decanoate. The performances of those columns are evaluated in terms of minimum energy requirement.

6.3 Process Model

The model equations and assumptions can be seen in Chapter 4.

6.3.1 Kinetics modelling and phase equilibria (VLE)

Steinigeweg and Gmehling (2003) explored the kinetic behaviour of DeC esterification and methanol to produce methyl decanoate by examining two kinetic models: the pseudo-homogeneous (PH), and the modified Langmuir-Hinshelwood-Hougen-Watson (LHHW) models. Both models PH and LHHW activity ($a_i = \gamma_i \, x_i$) depended on kinetic equation are employed and have the following form, respectively:

$$- r_1 = M_{cat} \left\{ 9.1164 \times 10^5 exp\left(\frac{-68.71}{RT}\right) a_1 \, a_2 - 1.4998 \times 10^4 \, exp\left(\frac{-64.60}{RT}\right) a_3 \, a_4 \right\} \qquad (6.1)$$

$$- r_1 = M_{cat} \left\{ \frac{3.1819 \times 10^6 \, exp\left(\frac{-72.23}{RT}\right) a_1 \, a_2}{(2.766 \, a_4)^2} - \frac{3.5505 \times 10^5 \, exp\left(\frac{-71.90}{RT}\right) a_3}{(2.766 \, a_4)} \right\} \qquad (6.2)$$

The PH model is not complex, has smaller parameter constants; therefore, this kinetic model is employed in this work for case study 1. Note also, Machado et al. (2011) also used the PH model for their simulation studies of a continuous reactive distillation operation.

While, the modified Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic model is employed in case study 2. This kinetic model is considered here due to the good description for the kinetic behaviour of the system by adsorption of water content by Amberlyst-15.

Note, all the phase equilibria equations (vapour-liquid equilibrium) for the production of methyl decanoate are same as those given in the previous section (5.3.3). The saturation vapour pressure (P^{sat}) of the pure components is obtained by using Antoine's form:

$$Log\ P_i^{sat} = A_1 - \frac{A_2}{T + A_3} \tag{6.3}$$

Where A_1, A_2, A_3 are the regression constants (with appropriate units) for the Antoine equation and T the temperature in Kelvin. The Antoine equation constants employed in this work were taken from Steinigeweg and Gmehling (2003). The liquid-activity coefficients (VLE) were calculated using the NRTL method with the binary interaction parameters taken from the Aspen Plus data bank.

6.4 Case Study 1: Synthesis of Methyl Decanoate Using Different Types of Batch Reactive Distillation Systems

6.4.1 Dynamic Optimization Problem

The optimization problems can be described as follows:

Given:	The column configurations, the feed concentration, vapour load to the condenser and desired product amount and its quality.	
Optimize:	Reflux ratio (R)	(for CBD Column)
	Reflux ratio (R), and Recycle rate (S_{MeOH})	(for i-CBD Column)
	Reflux ratio (R_{SBD}), and feed rate (F_{MeOH})	(for SBD Column)
So as to:	Minimize the total energy usage	
Subject to:	Model equations, Operation constraints	

Mathematically, the optimization problem (OP1) can be represented as follows:

$$\begin{array}{lll} OP1 \quad \underset{\substack{R_{CBD}(t) \\ Or \\ R_{i\text{-}CBD}(t),\ S_{MeOH}(t) \\ Or \\ R_{SBD}(t),\ F_{MeOH}(t)}}{Min} \ Q_{tot} & \begin{array}{l} (For\ CBD\ Column) \\ \\ (For\ i\text{-}CBD\ Column) \\ \\ (For\ SBD\ Column) \end{array} & (6.4) \\ Subject\ to: & & \\ B_{MeDC} \geq B^{*}_{MeDC} & (Inequality\ Constraints) & \\ x_{MeDC} \geq x^{*}_{MeDC} & (Inequality\ Constraints) & \end{array}$$

Where Q_{tot} is the total energy consumption, B_{MeDC} and x_{MeDC} are the product quantity (MeDC) in the pot tank and its purity at final batch time, (B^{*}_{MeDC} and x^{*}_{MeDC} are the specified amount of product and its purity). $R(t)$ is the time dependent reflux ratio, $S_{MeOH}(t)$ is the recycle rate of methanol (in the case of i-CBD mode), and $F_{MeOH}(t)$ is the feed rate of methanol (for SBD mode), which are optimized.

6.4.2 Results and Discussions

6.4.2.1 The Performance of CBD Column

The formation of methyl decanoate has been simulated in a 20-plate batch distillation system (including a condenser and a reboiler) with (754 W) of reboiler heat duty and 5 kmol of total feed charged to the reboiler with the following concentration in mole fraction: 0.341 decanoic acid, 0.659 methanol, 0.0 methyl decanoate, and 0.0 water. The total column holdup is four percent of the initial feed charge (of which fifty percent of this total holdup is placed in the reflux drum and the rest is distributed on the trays (equally divided). Note, the feed specifications and the operating variables (including reboiler heat duty and weight of catalyst) remain the same as those available in the literature (Steinigeweg and Gmehling, 2003; and Machado et al., 2011) for comparison purposes. The concentrations of all stages and condenser are initialized to the fresh feed compositions at the beginning of the process. Then, the mole fraction profiles of the distillation column are established after the column gets to the steady-state under the total reflux procedure for a certain time. Then (designated as t = 0) the production procedure for all case studies begins. It will be interesting to study the performance of the CBD operation in terms of minimum energy consumption for different purity of MeDC but for a given amount of reboiler product (mainly MeDC) which is fixed at 2.2 kmol. The results in terms of optimal reflux ratio, minimum batch time, total energy consumption, and conversion rate of acid for a range of desired product purity considerations (0.350 to 0.420) are summarized in Table 6.2. The optimization results of Table 6.2 showed that all values of the reflux ratio, batch-processing time, energy demand, and conversion rate of DeC increase gradually with increasing the quality of the product. Also, it can be noted that it is difficult to accomplish a high conversion ratio of fatty acid using a CBD process. Note, at a concentration of 0.410, the CBD column was running at a higher reflux ratio compared to others and it was not possible to obtain methyl decanoate at a purity > 0.420 using the CBD process. This is due to the reverse reaction being active with fast removal of methanol reactant from acid in the still drum because of the wide difference in boiling points between the chemical reactants.

In this work, the reflux ratio is defined as the internal reflux ratio ($R = \frac{L}{V_C}$) bounded between 0 (= zero reflux ratio) and 1 (= total reflux ratio) as opposed to the external reflux ratio ($r = \frac{L}{D}$) bounded between 0 (= zero reflux) and ∞ (= total reflux). Note, however, for the same feed concentration (i.e., with excess methanol) in a continuous reactive distillation column Steinigeweg and Gmehling (2003) attained an even lower conversion and product composition (42.99% and 0.314 molefraction). There is no doubt that CBD column provides slightly better conversion rate and quality.

Table 6.2 Optimal operation results for the MeDC production for CBD column

Purity of MeDC	Optimal Reflux Ratio	Batch time, t_F, hr	Energy Usage, Q_{tot}, GJ	Conversion of DeC (%)
0.350	0.421	79.5	0.216	43.07
0.370	0.571	100.4	0.273	45.53
0.390	0.674	126.3	0.343	48.03
0.410	0.834	232.7	0.632	50.49
0.420	---[a]	---[a]	---[a]	---[a]

[a] Infeasible

6.4.2.2 The Performance of i-CBD and SBD Columns

The influence of feed molar ratio on the overall performance of i-CBD and SBD operations is examined in detail in this work. The excess methanol in the feed stream as used by Steinigeweg and Gmehling (2003) in a continuous reactive distillation system is considered here.

6.4.2.2.1 Case A: i-CBD process (Excess Methanol)

The optimum results for the i-CBD column are listed in Table 6.3, including the optimum recycle rate, optimum reflux ratio, operating batch time, total energy consumption, and the maximum conversion, as well as the total amount of recycled MeOH for four product qualities of MeDC. It can be realized from Table 6.3 that the optimum recycled rate of methanol, the production batch time and the total energy consumption with total methanol recycled amount, gradually increase with increasing MeDC purities. Increasing the operating time visibly assisted increasing the conversion of decanoic acid. A comparison of the results between the conversion of DeC using the i-CBD process and the CBD process conversion (Table 6.2) reveals that for the same amount of still pot product (2.2 kmol) the i-CBD operation can produce MeDC at a much higher composition (0.750 compared to 0.410) and can convert more acid (91.83% as opposed to only 50.49%).

It is noticed also form Table 6.3 that no results were achieved at a product purity of 0.800 mole fractions due to the small amount of reaction reactants (decanoic acid and methanol) in the still tank and the remaining reactants (especially methanol) are trapped in the intermediate stages and the reflux drum.

Table 6.3 Optimal Operation results for the production of MeDC for i-CBD

Purity of MeDC	Optimal Recycle Rate	Optimal Reflux Ratio	Batch time, t_F, hr	Energy Usage, Q_{tot}, GJ	Conversion of DeC (%)	MeOH Recycle Amount
0.65	0.05	0.089	198	0.537	79.51	9.87
0.70	0.05	0.109	253	0.686	85.58	13.39
0.73	0.05	0.089	305	0.827	89.35	17.35
0.75	0.06	0.087	359	0.975	91.83	21.21
0.80	---[a]	---[a]	---[a]	---[a]	---[a]	---[a]

[a] Infeasible

6.4.2.2.2 Case B: SBD process (Excess Methanol)

Note, the problem specifications and operating conditions for SBD column are similar to those utilized in the CBD column (see section 6.4.2.1). As before, the concentration of MeDC in the still drum is varied from 0.650 to 0.800 mole fraction in each case while the quantity of bottom product is kept constant at 2.2 kmol so that comparison of performances of the SBD process can be carried out with i-CBD column in terms of the minimum energy demand at an excess of methanol reactant. Table 6.4 summarizes the optimizations results in terms of minimum energy consumption rate, optimum methanol feed rates, reflux ratio profiles, maximum allowable reflux ratio, final batch time, total energy usage rate, maximum conversion, and total methanol amount for a different bottom product quality. As before, the optimal operation results in Table 6.4 clearly indicate that the batch time, the thermal energy consumption, and the conversion rate increase progressively with increasing the MeDC mole fractions.

Note, although the reflux ratio increased for this case, there is a sharp increase in the total amount of charged methanol leading to higher production time and total energy usage for 0.750 of product purity. As shown also in Table 6.4, the optimum values of all reflux ratios are lower than R_{Max} ensuring no overflowing of the reboiler for all the MeDC composition conditions. However, higher quantity of methanol fed, and higher batch-processing time are needed to strip off all the DeC from the bottom tank. Note also, it was found from Tables 6.3 and 6.4 that the performance of the i-CBD column outperformed the performance of the SBD to fulfil the specified product specifications with lower operation time and total energy demand. For instance, the reductions in the batch time and total energy usage rate are 27.18% at MeDC quality of 0.75 mole fraction compared to that obtained by employing the SBD operation. However, the SBD process is better than the i-CBD mode in terms of highest achievable conversion. It is noticed that 3.25% of conversion ratio of acid can be improved at 0.75 of product quality as compared to that obtained by using the i-CBD column. It was not possible to achieve a higher product concentration at 0.800 of MeDC mole fraction.

Note, the SBD case (Table 6.4) needed higher batch time compared to the i-CBD case (Table 6.3). A lower quantity of total methanol recycling was needed for i-CBD compared to that for SBD. Since the desired product amount in the reboiler is kept constant in both operations, the removal of a larger amount from the still pot in the case of SBD required a longer processing time.

Table 6.4 Optimal Operation results for the production of MeDC for SBD

Purity of MeDC	Optimal Feed Rate	Optimal Reflux Ratio	R_{Max}	Batch time, t_F, hr	Energy Usage, Q_{tot}	Conversion of DeC (%)	MeOH Charge Amount
0.65	0.06	0.046	0.232	231	0.627	83.49	12.92
0.70	0.06	0.099	0.244	295	0.799	88.61	16.48
0.73	0.06	0.043	0.147	410	1.112	93.63	26.11
0.75	0.06	0.149	0.234	493	1.339	94.91	28.37
0.80	---[a]	---[a]	---[a]	---[a]	---[a]	---[a]	---[a]

[a] Infeasible

6.4.2.3 The selection of kinetic model

Although Steinigeweg and Gmehling (2003) Machado et al. (2011) and this work employed the PH kinetic model, Steinigeweg and Gmehling (2003) showed that the sorption impact of water is ignored in the kinetic model, and with rising water content in the bulk liquid, the reaction rate can slow down and thus increase the operating batch time as noticed in this work.

6.4.2.4 Processing-batch time

All cases presented earlier in this section needed a large time. This is due to fact that the use of low reboiler duty (754 W) and the small quantity of catalyst (3.792 kg) utilized by the original investigators (Steinigeweg and Gmehling, 2003, and Machado et al., 2011) as mentioned earlier. For this purpose, we employed a catalyst amount of 430 kg and a heat duty of 86 kW.

6.4.2.4.1 The performance of i-CBD column

Here, two case studies are examined. Case 1 uses a single-reflux control interval, whereas, Case 2 uses two-reflux intervals strategy. Within each control interval, the reflux ratio and the methanol recycled rate together with the length of intervals will be optimized. As before, the concentration of MeDC product is changed from 0.700 to 0.900 in each case while the amount of bottom product to be achieved is set at 2.2 kmol for both cases.

6.4.2.4.1.1 One Control Interval (NCI=1)

Table 6.5 shows the optimum methanol recycle rate and reflux ratio profiles, final batch time, total energy usage, and maximum conversion rate of DeC, as well as the total amount of methanol recycled for different product compositions of MeDC. It can be noted that, as the quality of MeDC increases from 0.700 to 0.900 mole fraction, the reflux ratio, processing-batch time, and energy consuming increase together with the conversion level of acid and the total amount of methanol recycled. Comparing the results with those shown in Table 6.3 (i-CBD with excess methanol case), the processing batch time is significantly reduced by about 98.86 % for MeDC concentration of 0.750. The operation batch time was greatly reduced due to the higher reboiler heat duty and large catalyst amount, which increased the forward reaction. This visibly established that, with the batch distillation operation, the employ of excess methanol in the feed is not necessary as suggested by earlier researchers (Steinigeweg and Gmehling, 2003, and Machado et al., 2011), who used continuous reactive distillation process for the production of MeDC. However, the i-CBD system with less reboiler heat duty and small catalyst amount offered a better performance than the i-CBD mode with higher reboiler duty and larger catalyst amount in terms of maximum achievable conversion of fatty acid.

Table 6.5 Optimization results for the production of MeDC for i-CBD column at equimolar ratio using one control interval

Purity of MeDC	Optimal Recycle Rate	Optimal Reflux Ratio	Batch time, t_F, hr	Energy Usage, Q_{tot}, GJ	Conversion of DeC (%)	MeOH Recycle Amount
0.70	1.64	0.682	2.33	0.718	74.16	3.82
0.75	1.31	0.771	4.10	1.266	78.40	5.37
0.80	1.12	0.815	6.01	1.855	82.72	6.73
0.85	1.11	0.824	7.05	2.173	87.10	7.79
0.90	1.04	0.841	8.85	2.731	91.45	9.17

6.4.2.4.1.2 Two Control Intervals (NCI= 2)

The optimum operating policy for the i-CBD column is presented in Table 6.6, including the optimal recycle rate and reflux ratio profiles, optimal length period for each interval, maximum DeC conversion, minimum batch time, and total energy consumption for different product purity conditions. It is observed from Table 6.6 that there are reductions in the processing-batch time and total energy expense (by about 23.19%) using two-reflux control intervals as compared to a single reflux control interval i-CBD operation.

Multi-control strategy for the i-CBD column is found to provide much better operational flexibility and shorter the production time and thus energy consumption to achieve higher MeDC quality constraints.

As seen from Table 6.6, at lower MeDC composition requirement, the batch distillation column operates at a higher possible reflux ratio in the first-time interval to push water up to the distillate tank and operates at a low reflux ratio in the second interval to retain both chemical reactants (DeC and MeOH) in the reaction zone to have further reaction to reach the specified purity consideration.

By contrast, the i-CBD process operates at the lower reflux ratio in the first interval and then at the higher reflux ratio in the second interval at the higher MeDC concentration constraint.

Table 6.6 Optimization results for the production of MeDC for i-CBD column at equimolar ratio using two control intervals

Purity of MeDC	Recycle Rates S_1, S_2	Reflux Ratios R_1, R_2	Switching Time t_1, t_2	Conversion of DeC (%)	batch time, t_F (hr)	Energy Usage, Q_{tot}, GJ
0.70	1.07, 1.99	0.757, 0.615	1.34, 0.86	74.38	2.20	0.678
0.75	5.61, 1.43	0.239, 0.724	1.50, 1.10	78.45	2.60	0.801
0.80	0.91, 2.38	0.818, 0.583	1.50, 1.23	83.37	2.73	0.842
0.85	0.06, 2.57	0.880, 0.627	2.26, 1.17	87.86	3.43	1.058
0.90	0.00, 0.91	0.853, 0.873	1.77, 5.03	91.41	6.80	2.097

The composition profiles in the still pot and the distillate tank at the product composition specification (x^*_{MeDC}= 0.90) are given in Figures 6.1 and 6.2 for the single-control interval operation and in Figures 6.3 and 6.4 for the multi-control intervals operation.

It can be seen from Figures 6.1 and 6.3 that the concentration of water in the reboiler rises from zero reaches the higher value, and then gradually falls to almost zero due to its removal in the distillate drum (Figures 6.2 and 6.4). The concentration of methanol reactant is decreased rapidly with increasing the operating batch time due to its highest relative volatility and the efficient removal of water, which collected in the distillate tank (see Figures 6.2 and 6.4).

At the end of the operation, there is still a small percent of acid reactant at the bottom of the distillation column because of consumption by reaction with methanol. As quality of product increases, higher reflux ratio and higher operating time are required to keep both reactants together (DeC and MeOH) in the reaction zone.

The methyl decanoate in the reboiler reached the maximum achievable concentration of 0.90 quicker for the two-reflux control policy than the single-control one.

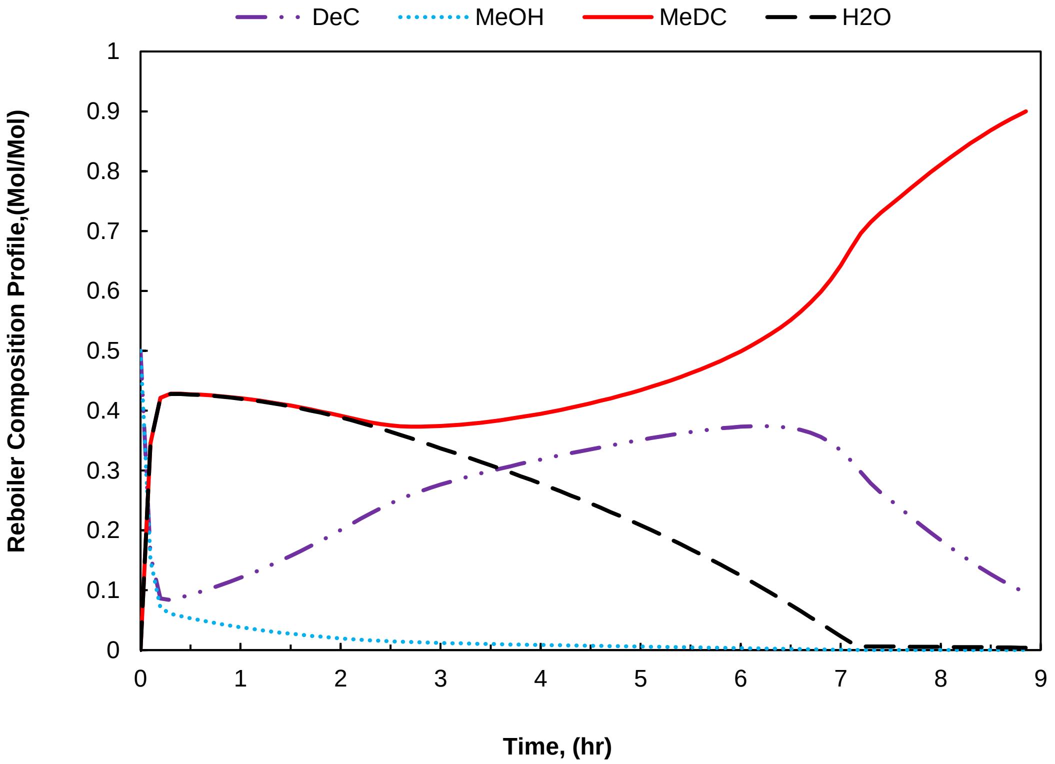

Figure 6.1 The Reboiler Composition profile for One Reflux Interval

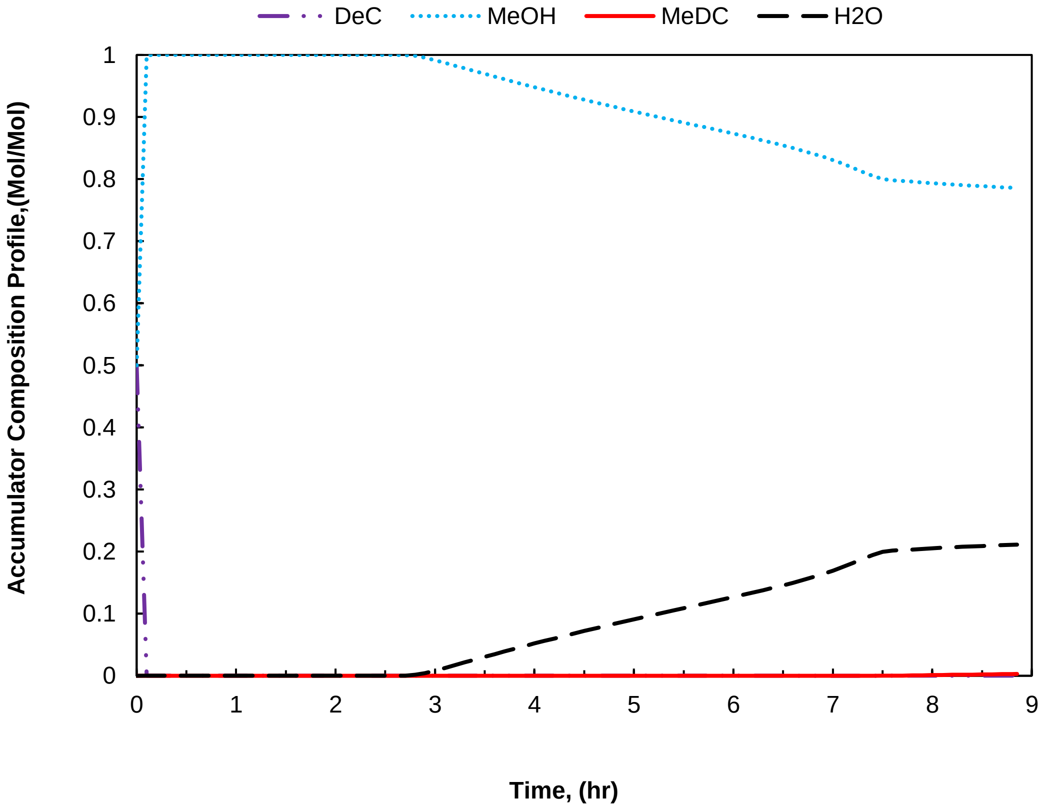

Figure 6.2 The Accumulator Composition profile for One Reflux Interval

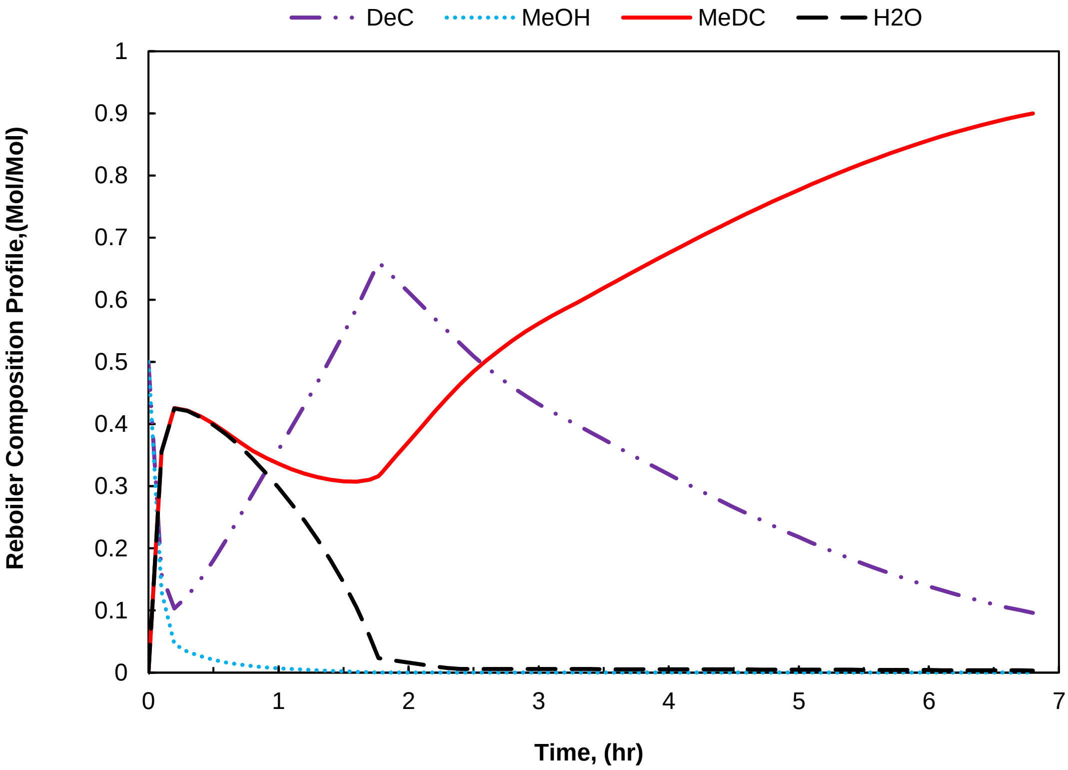

Figure 6.3 The Reboiler Composition profile for Two Reflux Intervals

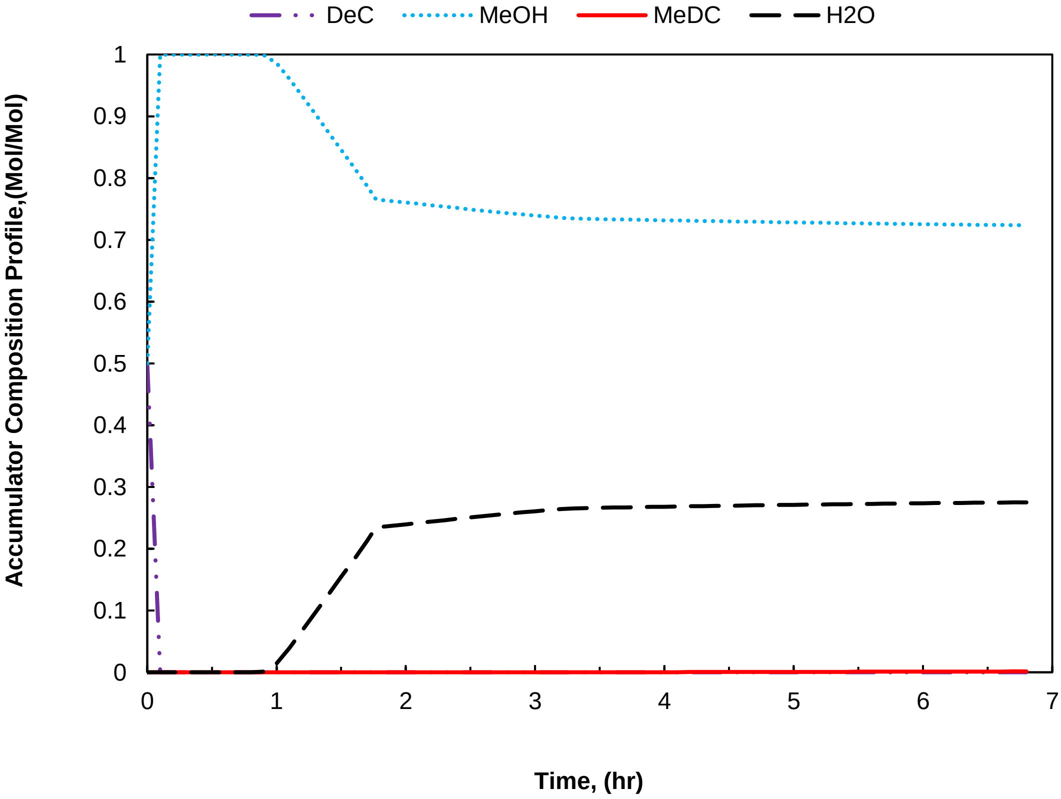

Figure 6.4 The Accumulator Composition profile for Two Reflux Intervals

6.4.2.4.2 SBD column

The influence of equimolar feed ratio on the SBD operation efficiency is studied in terms of minimum energy demand for each product purity. Two scenarios are investigated here. Single and two-control policies are used.

6.4.2.4.2.1 One Control Interval (NCI= 1)

For different bottom product qualities of MeDC, the optimization results (optimal feed rates, optimal reflux ratios, maximum reflux ratios, minimum production time, total energy consumption, maximum conversion (%) of DeC to MeDC, and methanol charge amount) are displayed in Table 6.7.

It can be seen from these results that, as the concentration of MeDC increases from 0.70 to 0.90 mole fraction, the operation batch time, total energy consumption, and conversion ratio increase together with total methanol feed quantity. The results in Table 6.7 clearly show that the SBD process outperforms the i-CBD process in terms of batch time and energy usage savings to accomplish higher MeDC quality specifications at an equimolar ratio except for the conversion of acid (only a slight improvement by i-CBD).

As an example, the processing-batch time and thermal energy expense using the SBD operation (in the case of product concentration 0.90 mole fraction) are saved by an average 18.57% compared to that obtained by the i-CBD operation (Table 6.5). For all cases, R_{Max} is obtained from different values of the feed rate of methanol. Also note, in all cases the maximum reflux ratio (R_{Max}) is found to be greater than the current reflux ratio, preventing the reboiler overloading condition.

Table 6.7 Optimization results for the production of MeDC for SBD column at equimolar ratio using one control interval

Purity of MeDC	Optimal Feed Rate	Optimal Reflux Ratio	R_{Max}	Batch time, t_F, hr	Energy Usage, Q_{tot}	Conversion of DeC (%)	MeOH Charge Amount
0.70	1.33	0.680	0.771	1.70	0.524	73.92	2.26
0.75	1.04	0.800	0.835	3.95	1.219	78.24	4.11
0.80	1.03	0.815	0.842	4.86	1.500	82.64	5.00
0.85	0.93	0.844	0.862	6.82	2.103	86.99	6.32
0.90	0.98	0.840	0.856	7.21	2.223	91.39	7.10

6.4.2.4.2.2 Two Control Intervals (NCI= 2)

For the five MeDC purities considered, the optimal methanol feed rate and reflux ratio profiles, optimal length period, maximum conversion of DeC, final batch processing time, and energy usage rate using two-reflux intervals strategy are reported in Table 6.8. Compared with single-reflux interval SBD operation, the batch time and the total energy consumption are reduced by about 44.69% for MeDC purity of 0.900.

It is obvious from Table 6.8 that the two-reflux strategy gives a huge saving in the processing batch time and the energy demand compared to the single-reflux policy. This clearly shows the advantage of using multi-control intervals policy. It can be seen from Table 6.8 that the SBD system operates at a lower reflux ratio for the first interval for each product purity specification to drive water up to the top of column.

Higher reflux ratio and higher batch time are required to keep both reactants (DeC and MeOH) in the reactive section to have further reaction and to achieve the specified product quality in the second-time interval. Note, the optimal values of R_1 and R_2 are still lower than the maximum reflux ratio (R_{Max}) values, meaning the still drum is never overloaded.

The composition profiles of the still tank and the distillate drum of the SBD operation at the product purity requirement ($x^*_{MeDC} = 0.90$) are displayed in Figures 6.5 and 6.6 for the single-control interval policy, and in Figures 6.7 and 6.8 for the two-control intervals policy.

It can be seen from Figures 6.5 and 6.7 that the concentration of water (2nd boiling component) increases from zero, reaches a maximum value and then falls down to almost zero (due to removal in the distillate tank, Figures 6.6 and 6.8).

The composition of methanol reactant is reduced gradually with increasing time because of its lowest boiling point temperature and gathers in the accumulator tank (Figures 6.6 and 6.8). More methyl decanoate is formed as the batch progresses and remains in the pot drum (as the second heavier boiling product).

Methyl decanoate reached the desired purity faster for the two-control strategy than the single control strategy.

Table 6.8 Optimization results for the production of MeDC for SBD column at equimolar ratio using two control intervals

Purity of MeDC	Feed Rates F_1, F_2	Reflux Ratios R_1, R_2	Switching Time t_1, t_2	Conversion of DeC (%)	batch time, t_F (hr)	Energy Usage, Q_{tot}, GJ
0.70	1.49, 1.09	0.277, 0.735	0.26, 0.87	73.82	1.12	0.347
0.75	0.00, 1.30	0.406, 0.729	0.18, 1.50	78.32	1.68	0.518
0.80	1.17, 1.64	0.708, 0.740	1.73, 0.42	82.94	2.15	0.663
0.85	0.46, 1.64	0.830, 0.694	0.49, 2.05	87.26	2.54	0.784
0.90	0.50, 0.91	0.268, 0.853	0.21, 3.78	91.37	3.99	1.230

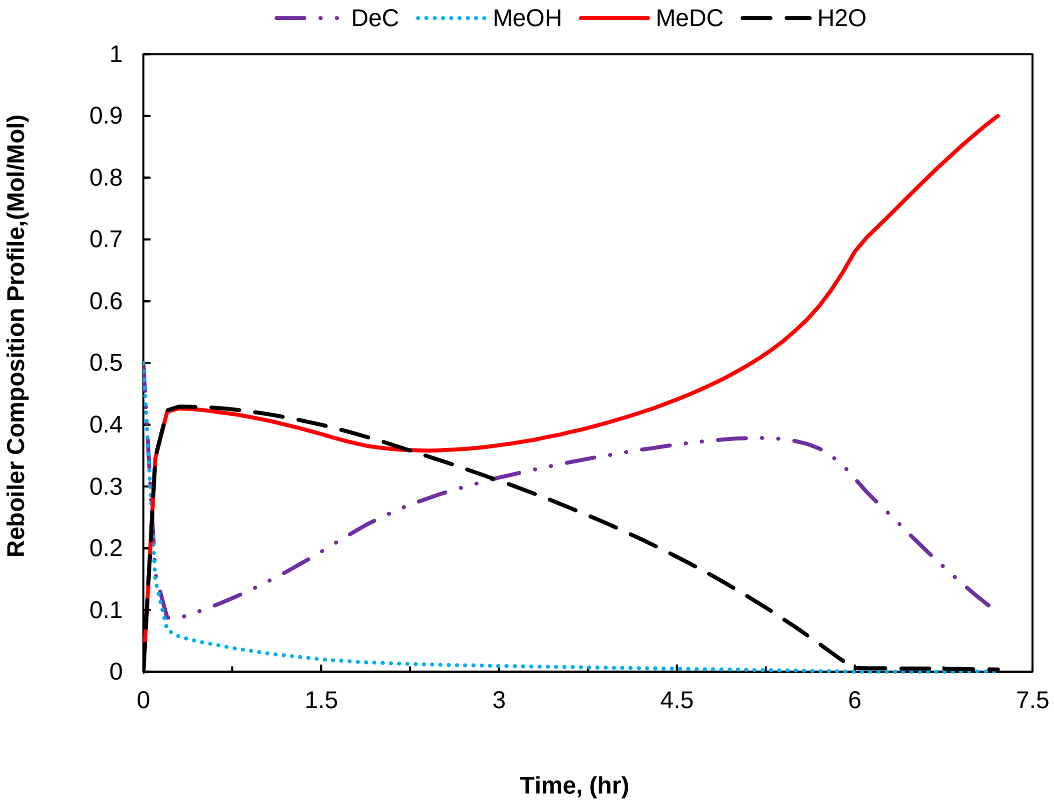

Figure 6.5 The Reboiler Composition profile for One Reflux Interval

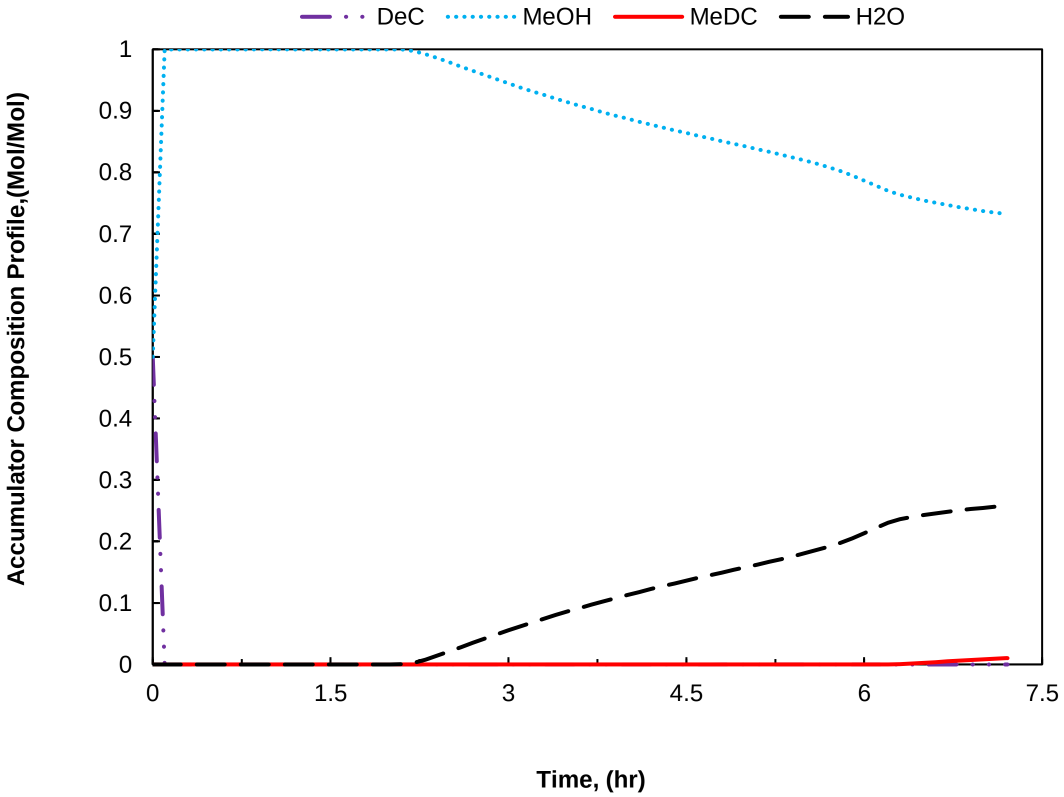

Figure 6.6 The Accumulator Composition profile for One Reflux Interval

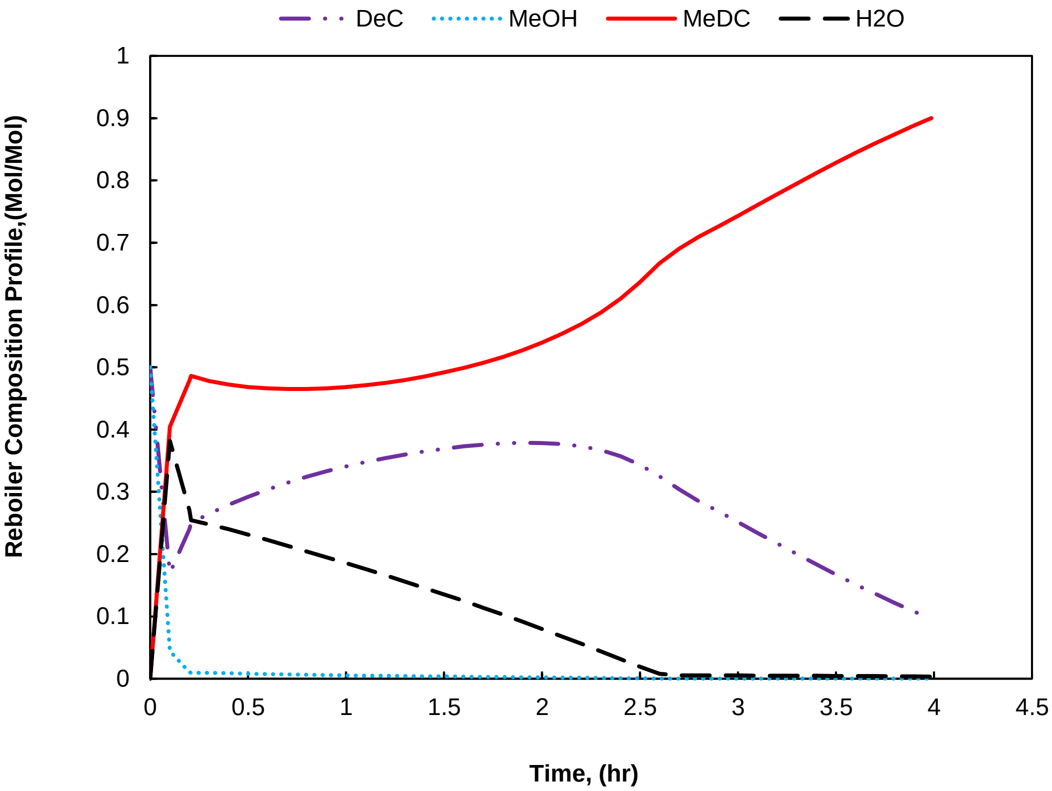

Figure 6.7 The Reboiler Composition profile for Two Reflux Intervals

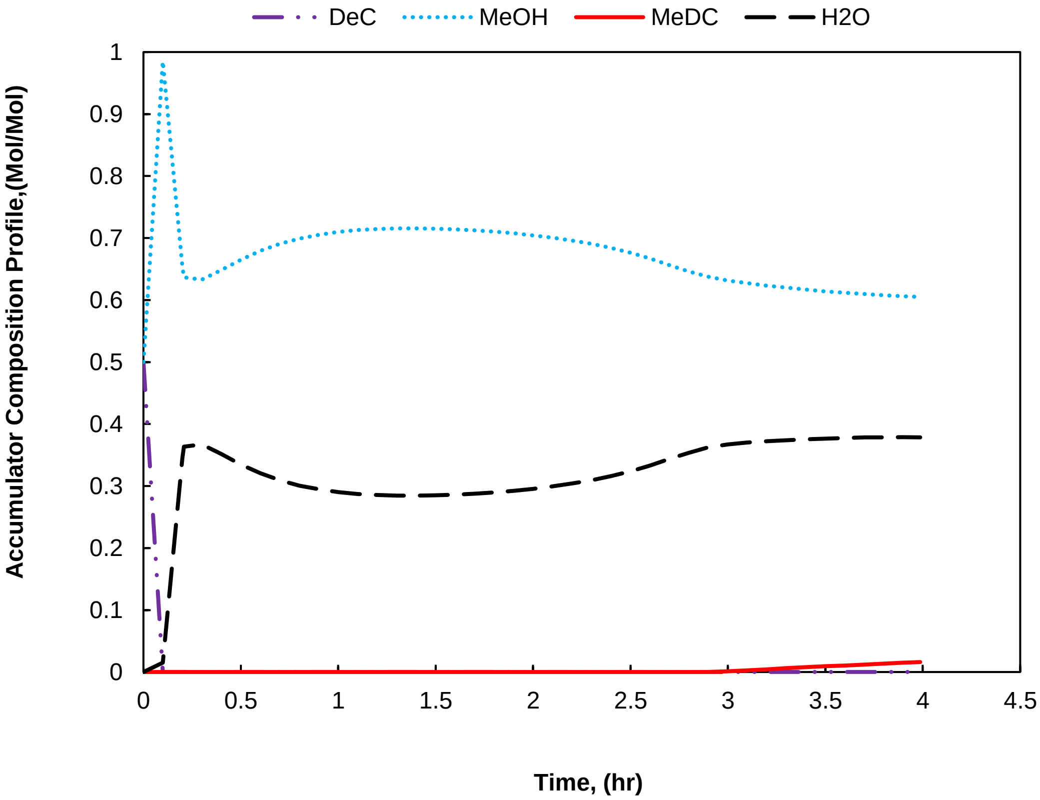

Figure 6.8 The Accumulator Composition profile for Two Reflux Intervals

6.5 Case Study 2: Feasibility of Novel Integrated Dividing-Wall Batch Reactive Distillation Processes for the Synthesis of Methyl Decanoate

6.5.1 Optimization Problem Formulation

The optimization problems can be represented as:

Given:	The column configurations, the feed composition, vapour load to condenser, the product purity and its amount in reboiler.	
Optimize:	R_{CBD}	(CBD Column)
	Or,	
	R_{DWBD}, r_L and r_V	(DWBD Column)
	Or,	
	$R_{sr\text{-}DWBD}$, L_2, r_L and r_V	(sr-DWBD Column)
	Or,	
	$R_{i\text{-}DWCBD}$, S_{MeOH}, r_L and r_V	(i-DWCBD Column)
So as to:	Minimize the total energy demand	
Subject to:	Model equations, Process constraints.	

The optimization problem (OP2) for the column configurations is stated mathematically as:

$$
\begin{array}{llll}
OP2 & Min & Q_{tot} & \\
 & R_{CBD}(t) & & (For\ CBD\ Column) \\
 & Or & & \\
 & R_{DWBD}(t),\ r_L(t),\ r_V(t) & & (For\ DWBD\ \ Column \\
 & Or & & \\
 & R_{sr\text{-}DWBD}(t),\ L_2(t),\ \ r_L(t),\ \ r_V(t) & & (For\ sr\text{-}DWBD\ \ Column) \\
 & Or & & \\
 & R_{i\text{-}DWCBD}(t),\ S_{MeOH}(t),\ \ r_L(t),\ \ r_V(t) & & (For\ i\text{-}DWCBD\ \ Column)
\end{array} \tag{6.5}
$$

Subject to :

$$f\,(t,\ \grave{x}(t),\ x(t),\ u(t),\ v) = 0; \quad [t_0 \quad t_F] \qquad (Process\ model,\ equality\ constraint)$$

$$B_{MeDC} \geq B^{*}_{MeDC} \qquad (Inequality\ Constraints)$$

$$x_{MeDC} \geq x^{*}_{MeDC} \qquad (Inequality\ Constraints)$$

P_{MeDC} and x_{MeDC} are the quantity of product and purity of MeDC at final batch time (t_F) in the reboiler (* denotes that the P_{MeDC} and x_{MeDC} are specified). R (t) the reflux ratio, L_2 (t) the reflux side stream profile (for the sr-DWBD mode), S_{MeOH} (t) is the methanol recycle rate profile (for i-DWCBD mode), and r_L(t) and r_V(t) the ratios of liquid and vapour split into the prefractionator,respectively (for the DWBD, sr-DWBD and i-DWCBD modes), which are optimized into the optimization study as key parameters.

6.5.2 Results and Discussions

6.5.2.1 The performance of traditional CBD operation

The synthesis of methyl decanoate is considered in a CBD with a total of ten plates (including both condenser and reboiler) with constant vapour condenser load of 2.5 kmol/hr. The total fresh amount charged to the still drum is 5 kmol with the following feed concentration <Decanoic Acid, Methanol, Methyl Decanoate, Water> is <0.5, 0.5, 0.0, 0.0>. 4% of the initial feed charge is considered as the total column hold-up (50% of this hold-up is placed in the reflux drum and the rest is equally distributed on the trays). The performance of the CBD column is measured in terms of minimum energy consumption for different MeDC qualities for a given quantity of bottom product, which is 2.5 kmol. The optimal operating strategy for CBD system is displayed in Table 6.9, including the optimum reflux ratio, batch time, minimum energy required, and conversion level of acid for a range of product requirements (0.535 to 0.573) at equimolar ratio in the feed stream. The results of Table 6.9 indicated that all reflux ratio, operating batch time, and energy demand, as well as the maximum achievable conversion increase gradually with increasing the concentration of the product.

As seen, the batch column operates at higher reflux mode and more production time to achieve the maximum MeDC quality of 0.572 mole fraction as compared to others (Table 6.9). It can be noted from Table 6.9 that it is difficult to accomplish a higher conversion rate of DeC and MeDC at a concentration > 0.572 mole fraction using a CBD operation. This is because methanol as reactant reaction is removed from DeC in the bottom tank rapidly (due to large gap in boiling points of reactants) and the reversible reaction being active.

Table 6.9 Optimization results for the MeDC production for CBD column at equimolar ratio

Purity of MeDC	Optimum Reflux Ratio, R	Batch time, t_F, hr	Conversion of DeC (%)	Energy Usage, Q_{tot}, GJ
0.535	0.839	5.71	57.53	0.545
0.545	0.866	6.85	58.52	0.654
0.555	0.891	8.48	59.50	0.809
0.572	0.942	15.87	61.20	1.522
0.573	---[a]	---[a]	---[a]	---[a]

[a] Infeasible

6.5.2.2 Dividing-wall batch distillation process

Having examined the traditional CBD system in section 6.5.2.1, the efficiency of dividing-wall reactive distillation will be explored for the reaction system concerned in terms of minimum energy consuming. Note, the column specifications and operating conditions of the DWBD operation and the hold-up distribution strategy are similar to those used in the CBD process (see section 6.5.2.1) with a difference that a metal-wall divided the column into two vertical sections through trays 3 to 8 (see Figure 6.9).

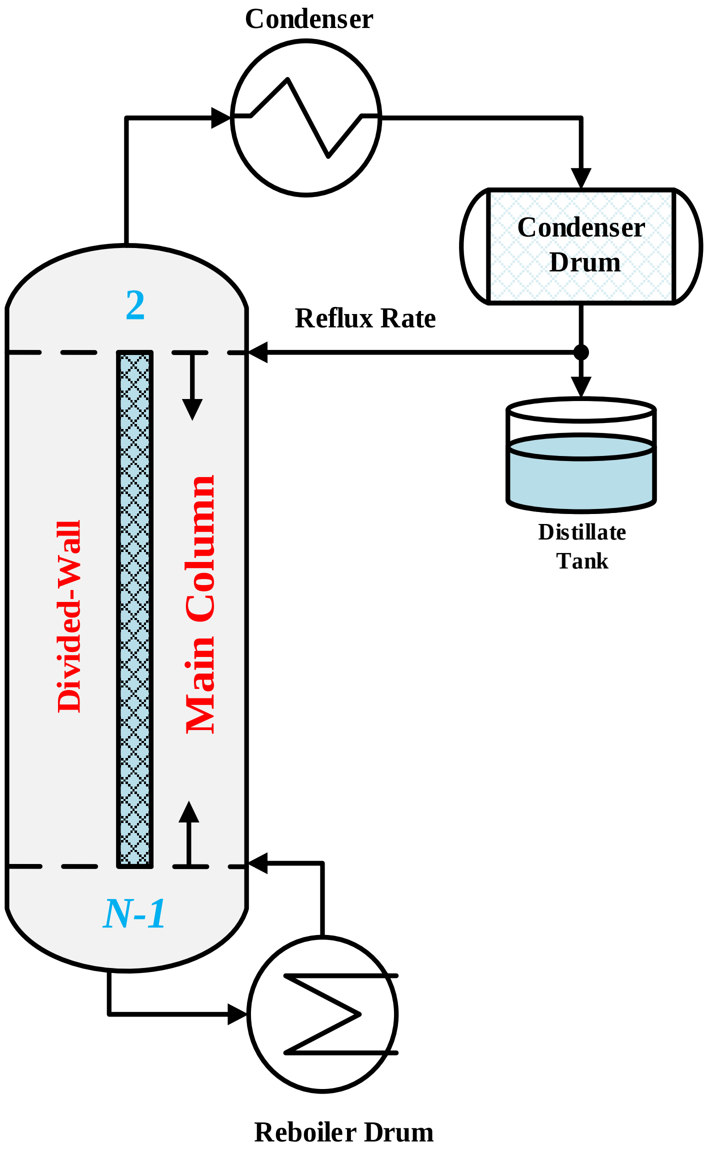

Figure 6.9 The dividing-wall Batch Reactive Distillation System

Table 6.10 presents optimum reflux ratio, vapour split ratio, and liquid split ratio profiles, maximum conversion rate of DeC (%), and minimum operating time, as well as total energy usage for different bottom product purities. For all case studies, the quantity of MeDC in the pot drum is kept constant as 2.5 kmol (same as CBD system). It can be observed that as the purity of MeDC increases, values of reflux ratio, operation batch time, and energy consumption increase together with the conversion ratio of acid. It can be seen form Table 6.10 that the DWBD system provides more economic perspectives and operational flexibilities and significant savings in energy usage than its traditional CBD column.

A comparative analysis of DWBD mode and its CBD counterpart is studied in terms of two performance indicators, namely batch time, and thermal energy demand savings. It is noted that the DWBD configuration results in 38.80% and 38.89% reductions in batch time and energy required, respectively at MeDC quality of 0.572 mole fraction compared to those obtained by utilizing the CBD process (Table 6.9).

Moreover, it can be observed that clearly the DWBD system yielded a higher purity of MeDC (0.605 mole fraction), converted more DeC (64.50%) compared to those obtained by CBD system (Table 6.9). It was found also that the optimum ratios of vapour (r_V) and liquid (r_L) splitting at the bottom and top for the left section of the portion-wall, respectively, have significant impact on the overall performance to achieve the product requirements in terms of higher product purity and a maximum conversion rate of acid compared to the classical CBD column.

However, it was difficult to accomplish higher product purity beyond 0.606 mole fraction of MeDC and conversion of acid due to a fast removal of methanol from the still tank to the distillate tank.

Table 6.10 Optimization results for the MeDC production for DWBD column at equimolar ratio

Purity of MeDC	Optimal Reflux Ratio, R	Vapor Split Ratio, r_V	Liquid Split Ratio, r_L	Conversion of DeC (%)	Batch time, t_F, hr	Energy Usage, Q_{tot}, GJ
0.572	0.905	30.05	0.84	61.21	9.71	0.930
0.585	0.914	41.22	0.22	62.51	10.71	1.029
0.595	0.939	85.92	0.30	63.52	15.00	1.444
0.605	0.966	51.96	0.18	64.50	27.28	2.642
0.606	---[a]	---[a]	---[a]	---[a]	---[a]	---[a]

[a] Infeasible

The profiles of molar concentration of CBD and DWBD operations at the product purity of 0.572 (mole fraction) are displayed in Figures 6.10 and 6.11, respectively.

It can be seen that there is a remixing effect in the intermediate components H_2O with MeOH (the lightest boiling point component), which occurs on top of CBD column at a processing-batch time of 15.87 hours.

This can make the separation more challenging and needs much more energy consumption of about 1.522 GJ. However, the remixing degree in the concentration of H_2O with MeOH can be still noticed at the top of DWBD operation but required a shorter batch time of 9.71 hours in the contrast of CBD configuration. Therefore, the total energy usage for DWBD operation is cut down to 0.930 GJ, which saves 38.89% at MeDC purity of 0.572 mole fraction.

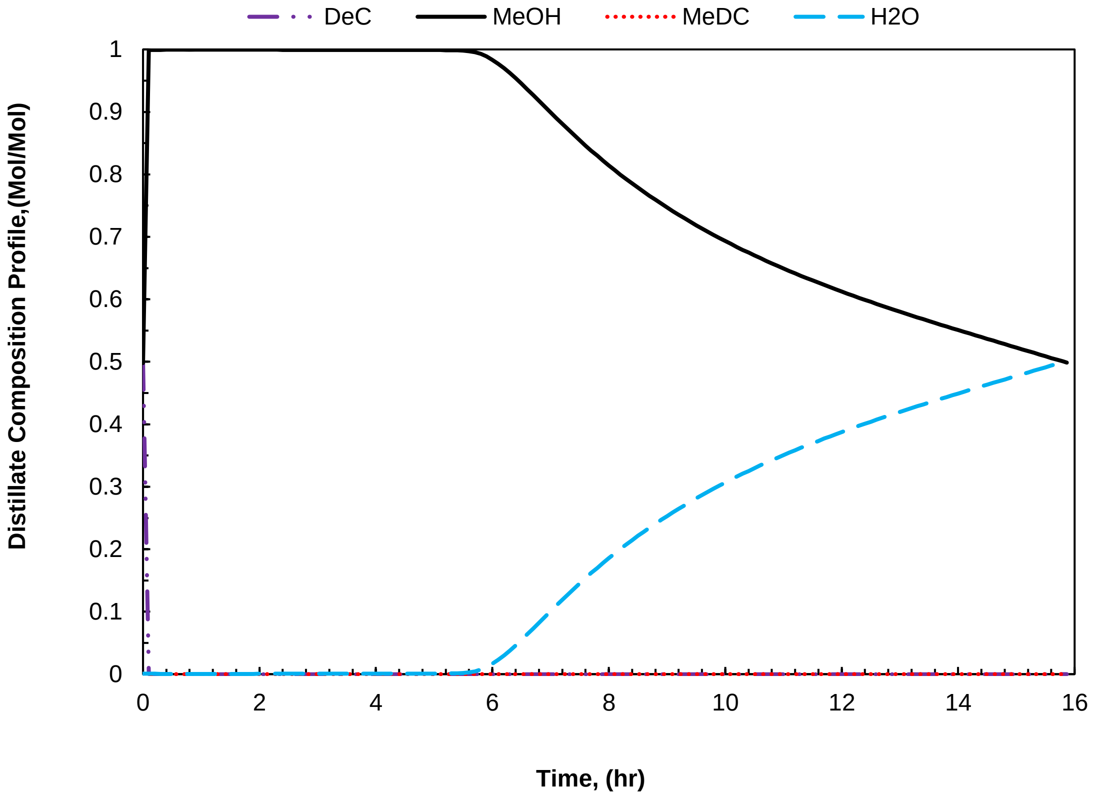

Figure 6.10 Distillate composition profiles of CBD column

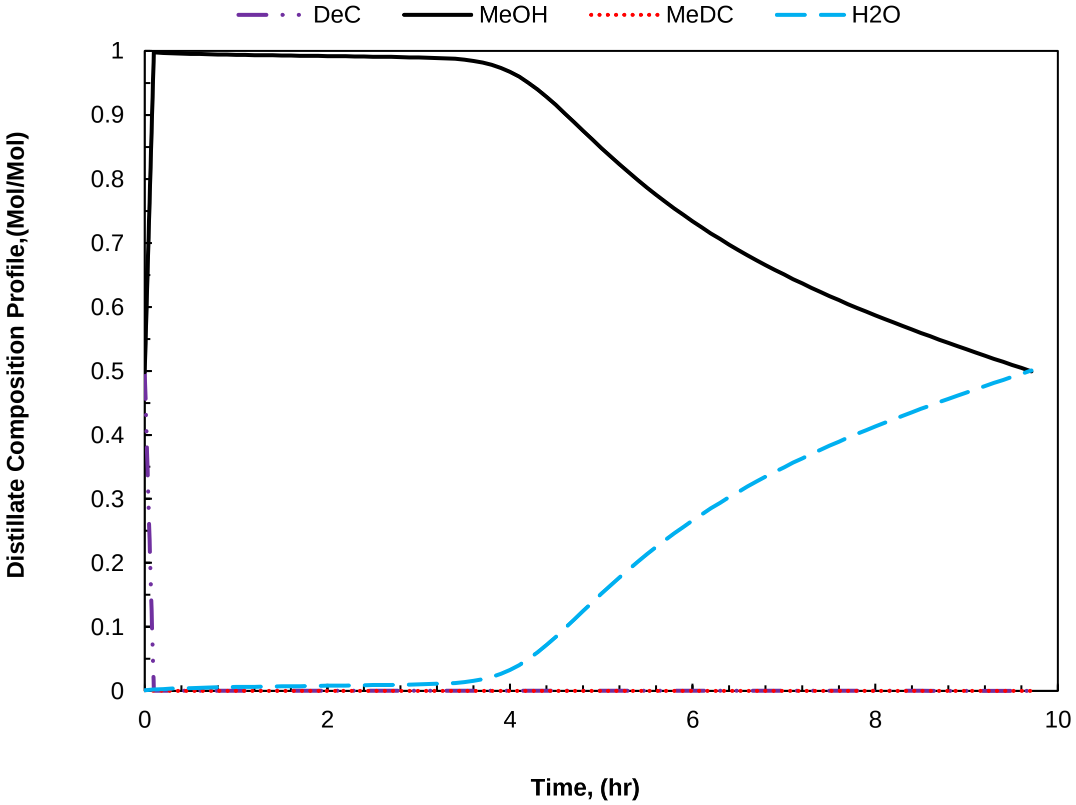

Figure 6.11 Distillate composition profiles of DWBD column

6.5.2.3 The performance of sr-DWBD process

The main aim of employing sr-DWBD column in this study is to compare the performance of sr-DWBD system with the DWBD process (Table 6.10) to see if it can increase the overall conversion of acid and the product concentration, where the maximum purity of MeDC is set to 0.750 mole fraction (Figure 3.3a). Note, the sr-DWBD configurations are similar to those in the DWBD mode for fair comparison (see Section 6.5.2.2). The purity of MeDC requirement is changed from 0.685 to 0.750 in each case study while the quantity of product in the reboiler remains the same as 2.5 kmol. For four product concentrations considered, the operation results (optimal reflux ratio, optimal reflux rate, liquid and vapour split ratios, conversion rate of DeC, and minimum batch time, as well as total energy expense are listed in Table 6.11.

It can be demonstrated from Table 6.11 that the optimum reflux ratio, and the maximum conversion level of DeC, and the batch time with minimum energy consuming, increase progressively with increasing the product qualities. It is clear also from Table 6.11 that more batch time and energy consumption are required at 0.750 of MeDC concentration as compared to the others to reach the product specification (though the reflux side stream decreases for this case).

A comparison of the results between the conversion level of acid utilizing the sr-DWBD column and the DWBD process conversion (Table 6.10) reveals that for the same product amount in the reboiler (2.5 kmol) the sr-DWBD column yielded a higher purity of MeDC (0.750 compared to 0.605) and converted more acid (80.26% as opposed to only 64.50%).

The compositions of the reboiler, reflux drum, and the accumulator tank of the sr-DWBD system at the product quality constraint (x^*_{MeDC}= 0.750) are presented in Figures 6.12, 6.13 and 6.14, respectively.

However, no results were achieved at a product concentration of 0.775 mole fraction as displayed in Figure 6.12 because more water is produced by the chemical reaction in the reflux drum and distillate drum (Figures 6.13 and 6.14), which is refluxed back into pot tank making the reverse reaction is probable. Note, the remixing phenomena of MeOH with H_2O in the sr-DWBD column was decreased and thus upgrade the operation proficiency (Figure 6.14).

Table 6.11 Optimization results for the MeDC production for sr-DWBD column at equimolar ratio

Purity of MeDC	Optimal Reflux Ratio, R	Optimal Reflux Rate, L_2	Liquid, Vapour Split Ratios r_L, r_V	Maximum Conversion of DeC (%)	Final Batch time, t_F, hr	Total Energy Usage, Q_{tot}, GJ
0.685	0.938	2.01	0.52, 26.68	73.72	14.91	1.488
0.700	0.952	1.99	0.62, 10.86	75.13	19.21	1.917
0.725	0.973	2.05	4.90, 189.24	77.84	33.67	3.383
0.750	0.989	2.04	0.51, 38.29	80.26	81.66	8.246
0.775	---[a]	---[a]	---[a]	---[a]	---[a]	---[a]

[a] Infeasible

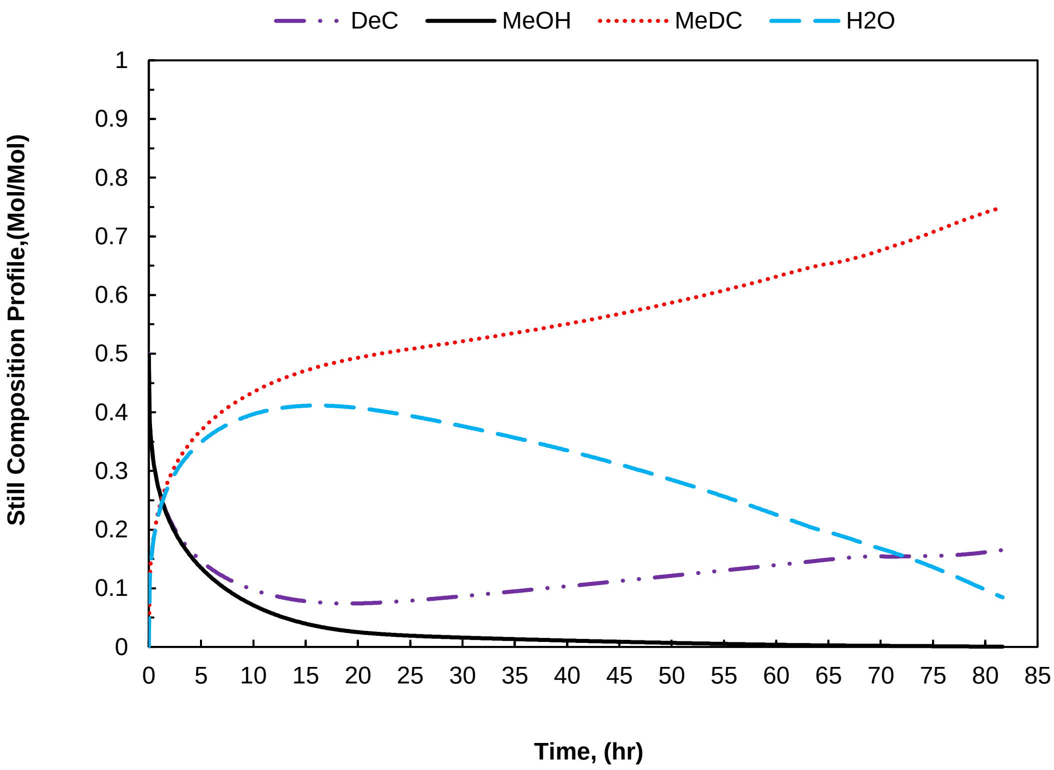

Figure 6.12 Evolution of the still composition of sr-DWBD

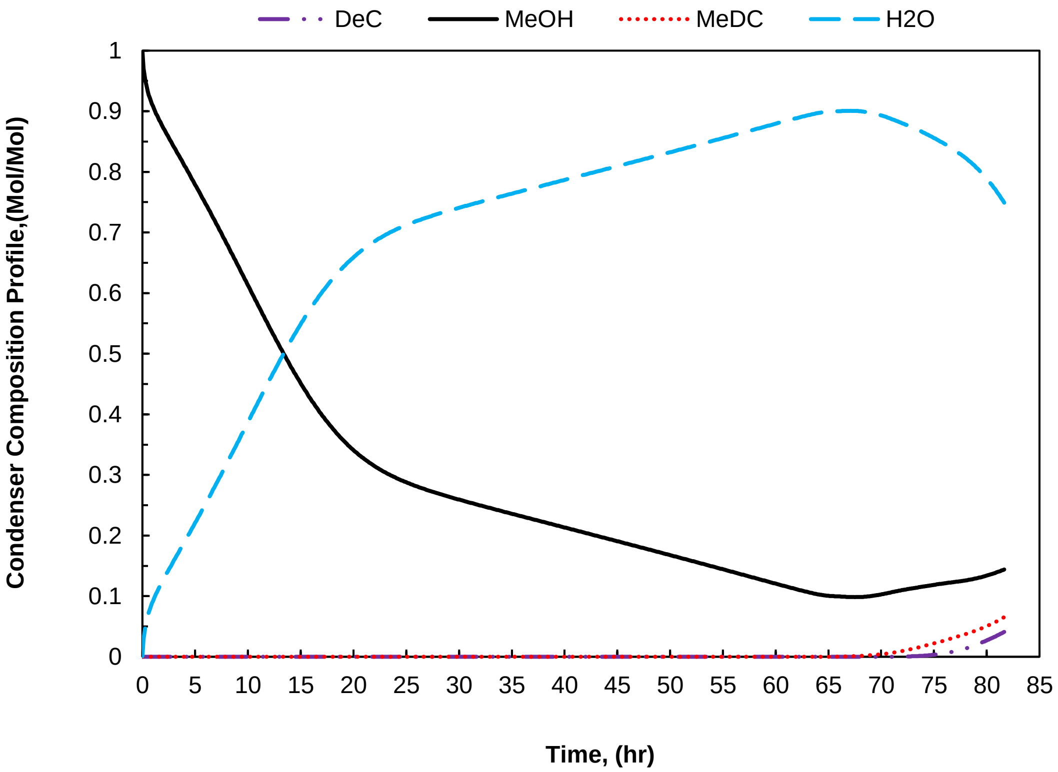

Figure 6.13 Evolution of the reflux drum composition of sr-DWBD

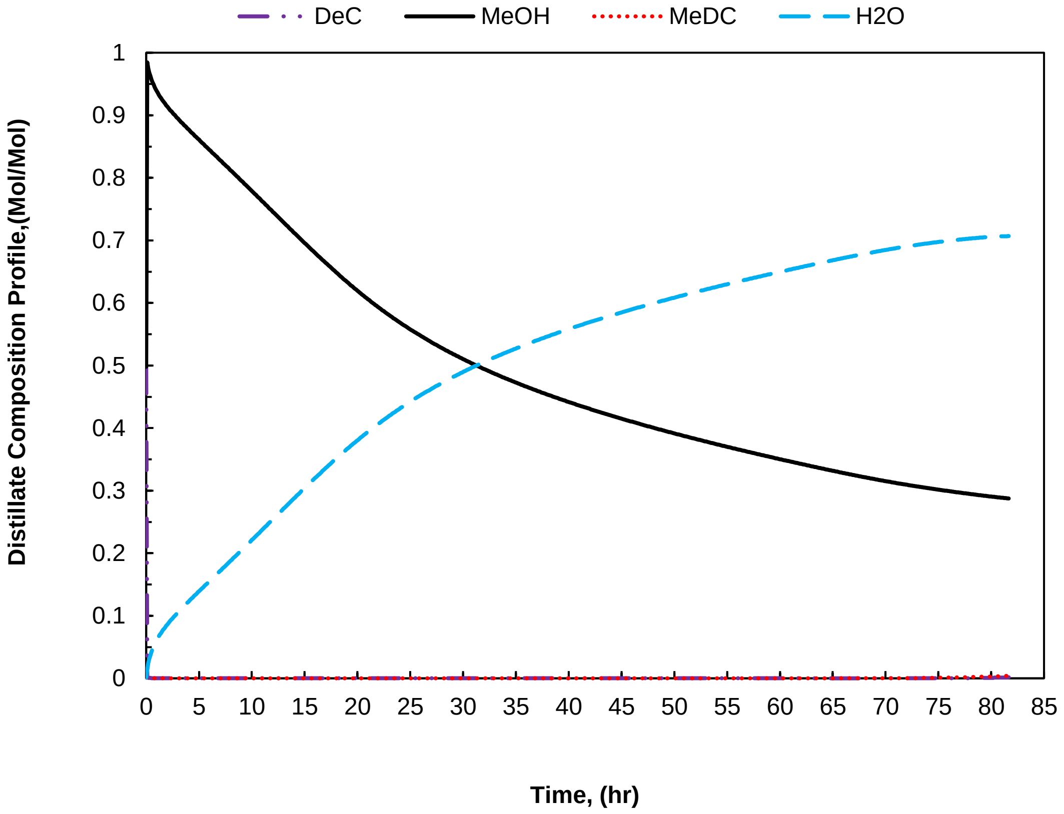

Figure 6.14 Evolution of the distillate composition of sr-DWBD

6.5.2.4 The performance of i-DWCBD process

Note, the operating conditions and problem specifications for the i-DWCBD column presented previously in Figure 3.3b, are the same as those used in CBD system (see Section 6.5.2.1). Two cases are studied here, Case 1 employs single-control interval (NCI = 1), whereas, Case 2 employs two-control intervals policy (NCI = 2).

As before, the MeDC product purity is varied from 0.945 to 0.960 mole fraction in each case while the still product amount remains the same at 2.5 kmol so that the performance comparison of i-DWCBD operation can be made with sr-DWBD operation in terms of higher conversion of acid, and maximum quality of MeDC.

6.5.2.4.1 Case 1: Optimal Operation Using Single-Control Interval

Table 6.12 summarizes the optimum reflux ratio and methanol recycle rate profiles, optimum vapour and liquid split ratios, the maximum conversion (%) of DeC, and minimum batch time, as well as total energy consumption for different bottom product purities of MeDC. It can be noted from Table 6.12 that as the quality of MeDC increases from 0.945 to 0.960 mole fraction, the reflux ratio, the operation time, and energy usage rise together with the maximum conversion of DeC (%). Note, there is a sharp increase in batch time and thus energy demand (Table 6.12) to increase the concentration of MeDC from 0.955 to 0.960 (mole fraction). The i-DWCBD needs to operate at high reflux ratio and high recycle rate of methanol to prevent the move of MeDC up to the distillate drum, and thus requires a longer batch time to fulfil the product condition. As anticipated, an increase in the operating batch time can lead to considerable increase the maximum conversion of acid. A comparison of the results between the conversion of DeC using i-DWCBD mode and the sr-DWBD system conversion illustrates that for the same quantity of bottom product (2.5 kmol) i-DWCBD column can produce more MeDC at a much higher concentration (0.960 compared to 0.750), can convert more acid (99.95% as opposed to only 80.26%). Note also, the results in Table 6.12 clearly indicates that the new i-DWCBD operation is superior to the sr-DWBD column (Table 6.11) in terms of maximum conversion level of DeC, and quality of the MeDC accomplished. This is due to the higher composition of recycled methanol in the i-DWCBD process (having a significant effect on the MeDC synthesis) as given in Figures 6.15 and 6.16 as compared to that in the sr-DWBD column (Figures 6.12 and 6.14).

Table 6.12 Optimization results for the MeDC production for i-DWCBD column at equimolar ratio using one control interval

Purity of MeDC	Optimal Reflux Ratio, R	Optimal MeOH Recycle S_{MeOH}	Liquid, Vapour Split Ratios r_L, r_V	Maximum Conversion of DeC (%)	Final Batch time, t_F, hr	Total Energy Usage, Q_{tot}, GJ
0.945	0.342	1.22	3.51, 3.98	99.28	5.40	0.509
0.950	0.380	1.15	9.96, 8.34	99.52	5.69	0.535
0.955	0.440	1.05	62.28, 161.45	99.79	6.52	0.612
0.960	0.506	1.21	5.03, 48.99	99.95	80.04	7.197

6.5.2.4.2 Case 2: Optimal Operation Using Two-Control Intervals

For different product qualities considered, the optimal operation results (including recycle rate of methanol, reflux ratio profiles, liquid and vapour split ratios, switching period, minimum batch time and total energy expense using multi-reflux intervals operation) are provided in Table 6.13.

Compared with one-reflux i-DWCBD mode (Case 1), the batch time is cut down by about 75.86%, and the energy demand is reduced by 75.37% for MeDC purity of 0.960. It is found from Table 6.13 that the two-control strategy offered great reductions in operation batch time and energy consumption as compared to the one-interval i-DWCBD system. This evidently presents the advantage of using two-control intervals operation in i-DWCBD mode.

It can be noticed form Table 6.13 that for all MeDC purity cases except the last case, the column operates at lower reflux ratio in the first-time interval and then at higher reflux ratio in the second-time interval.

While, the distillation column runs at a higher reflux ratio in the first interval and then operating at a lower reflux ratio in the second interval. More amount of methanol is separated from the batch column at high composition in the first interval but is not recycled leading to higher concertation of acid in the reboiler and possibly having reverse reaction (see Figure 6.17). Whilst, in the second interval methanol is recycled back into still pot converting most of acid and producing more ester.

The mixture concentration profiles in the reboiler and the accumulator drum at the bottom product quality specification ($x^*_{MeDC} = 0.960$) are presented in Figures 6.15 and 6.16 for the one-control interval policy and in Figures 6.17 and 6.18 for the two-control intervals strategy.

It can be observed form Figures 6.16 and 6.18 that the remixing degree was removed completely in the i-DWCBD column. The methyl decanoate in the pot drum reached the maximum achievable concentration of 0.960 in a shorter batch time for the multi-control operation than the one-control case (Figure 6.15).

A higher composition of MeOH is obtained the top of the column, and higher concentration of MeDC is achieved on the pot tank. The quality improvements achieved by the i-DWCBD scheme also reflects the reduction of this remixing phenomenon.

Table 6.13 Optimization results for the MeDC production for i-DWCBD column at equimolar ratio using two control intervals

Purity of MeDC	Recycle Rates S_1, S_2	Reflux Ratios R_1, R_2	Liquid Split Ratios r_{L1}, r_{L2}	Vapour Split Ratios r_{V1}, r_{V2}	Batch time, t_P, hr	Energy Usage, Q_{tot}, GJ
0.945	0.00, 1.29	0.219, 0.416	6.45, 3.98	2.70, 1.68	2.84	0.294
0.950	0.00, 1.36	0.286, 0.358	15.24, 8.61	1.14, 48.61	3.01	0.307
0.955	0.00, 1.28	0.248, 0.412	10.51, 7.19	5.40, 176.9	3.03	0.311
0.960	0.88, 1.51	0.649, 0.345	8.85, 7.96	21.3, 236.7	19.33	1.772

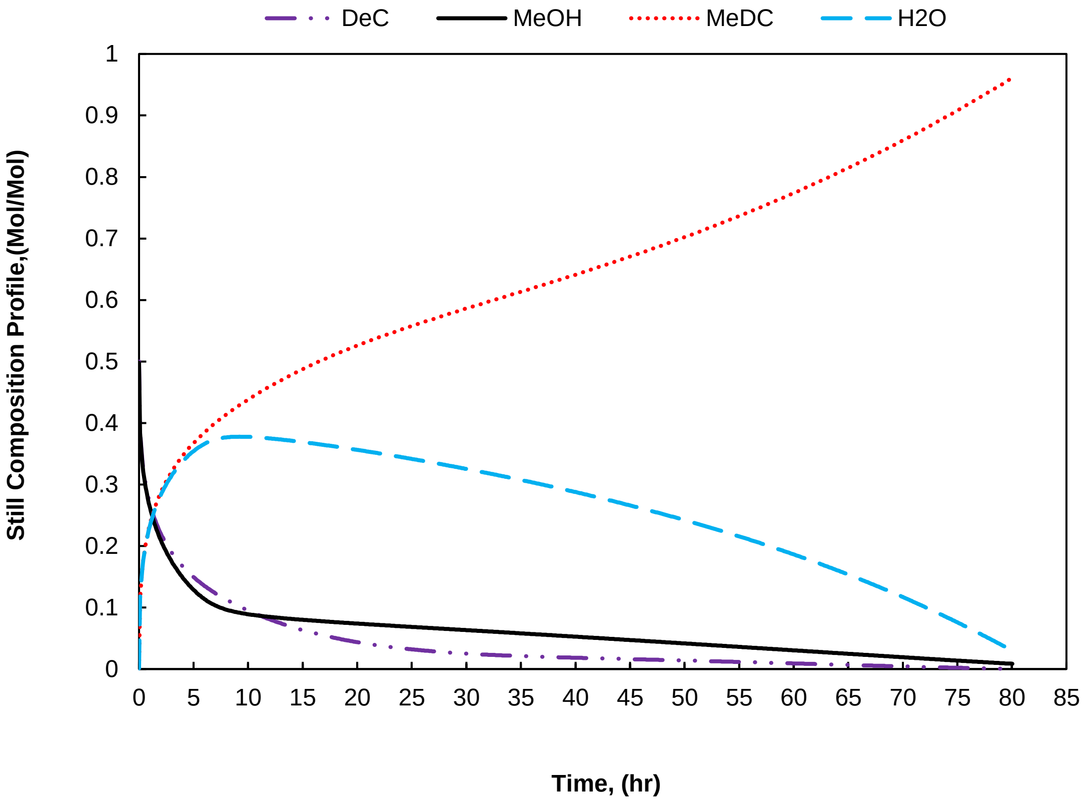

Figure 6.15 Still composition profiles of i-DWCBD for one-control interval

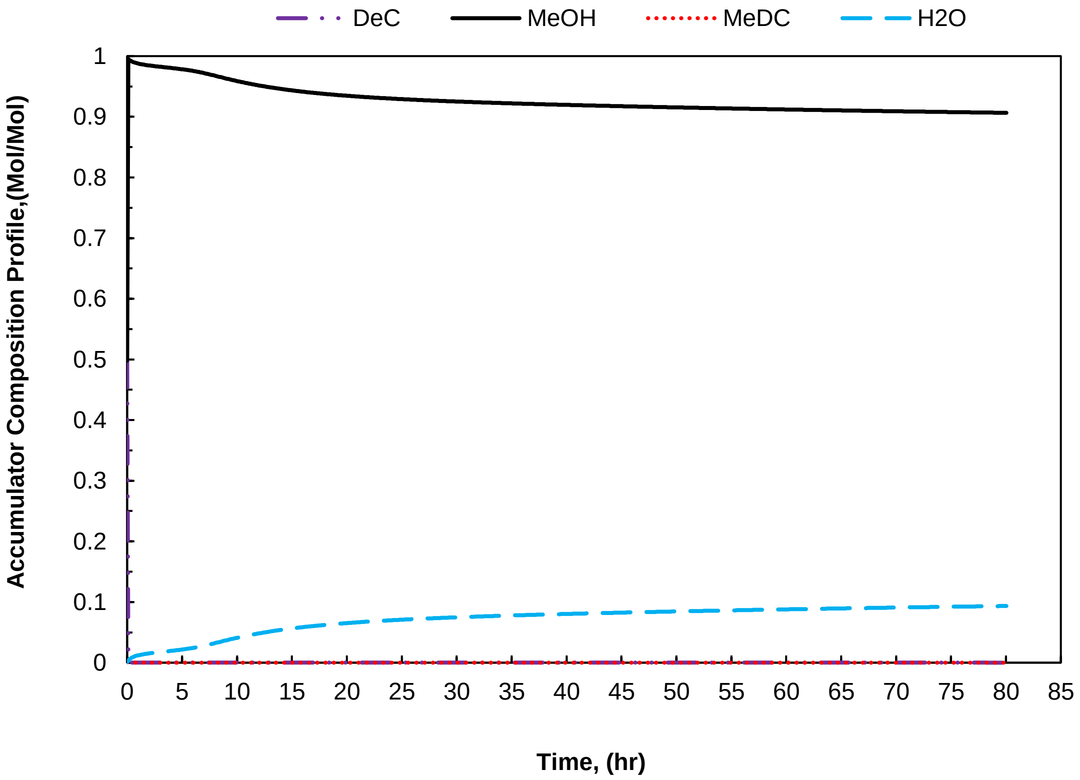

Figure 6.16 Accumulator composition profiles of i-DWCBD for one-control interval

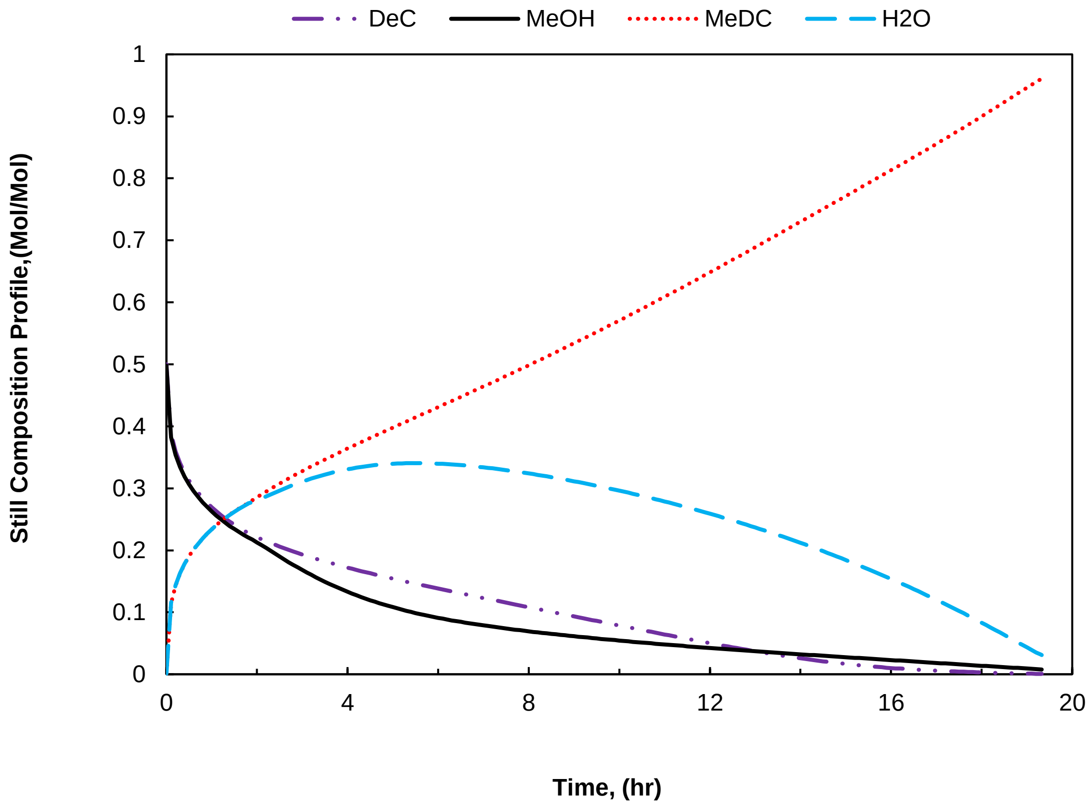

Figure 6.17 Still composition profiles of i-DCWBD for two-control interval

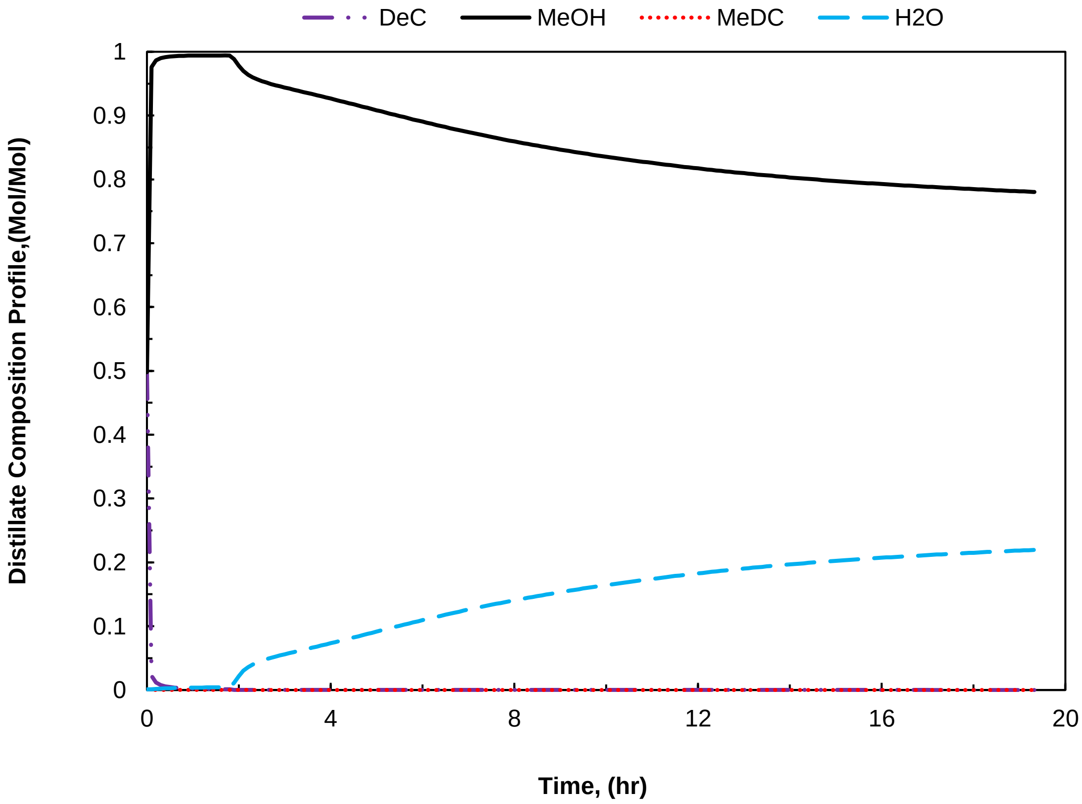

Figure 6.18 Distillate composition profiles of i-DWCBD for two-control interval

6.5.2.5 The performance of sr-DWBD and i-DWCBD with Excess MeOH

The effect of excess methanol in the feed on the overall performance of sr-DWBD and i-DWCBD systems to accomplish maximum possible product quality and conversion level is examined here. Two case studies are investigated. A quantity of 5 kmol is loaded initially into the reboiler with the following compositions in mole fraction: <0.45 DeC, 0.55 MeOH, 0.0 MeDC and 0.0 H_2O> and the amount of product in the pot drum is kept constant at 2.5 kmol (same as utilized in Sections 6.5.2.3 and 6.5.2.4) for making useful comparison.

6.5.2.5.1 Case 1: sr-DWBD column (Excess Methanol)

The optimal results for the sr-DWBD column are shown in Table 6.14, including the optimal reflux ratio, optimal reflux side stream, liquid and vapour split ratios, the conversion level of DeC, and total operating time, as well as minimum energy consuming for three product concentrations of MeDC. It can be seen from the results that the optimum reflux ratio, and the operation time with minimum energy usage and the highest conversion of acid, rise gradually with increasing the MeDC product purities. The results in Table 6.14 show that the sr-DWBD column with the equimolar amount outperforms the sr-DWBD mode with the excess methanol in terms of batch time and energy consumption minimizations to accomplish maximum MeDC concentration requirements except for the conversion ratio of DeC (only an enhancement by the sr-DWBD system with the excess methanol). For instance, the batch time and the energy demand using the sr-DWBD process with the equimolar feed ratio (in the case of product purity 0.725 mole fraction) are reduced by an average 49.66% as compared to that obtained by the sr-DWBD process with the excess methanol

% (Table 6.14). However, the sr-DWBD scheme with the excess feed offered only a better performance than the sr-DWBD mode with the equimolar feed in terms of maximum conversion ratio of acid. For the same amount of pot product (2.5 kmol), it converted more acid (85.09% as opposed to 80.26%).

Table 6.14 Optimization results for the MeDC production for sr-DWBD column at excess methanol

Purity of MeDC	Optimal Reflux Ratio, R	Optimal Reflux Rate, L_2	Liquid, Vapour Split Ratios r_L, r_V	Maximum Conversion of DeC (%)	Final Batch time, t_F, hr	Total Energy Usage, Q_{tot}, GJ
0.700	0.961	1.85	94.20, 536.96	82.30	23.64	2.292
0.715	0.977	1.84	4.17, 92.27	83.89	39.62	3.856
0.725	0.987	1.92	101, 670.00	85.09	68.80	6.722
0.750	---[a]	---[a]	---[a]	---[a]	---[a]	---[a]

[a] Infeasible

6.5.2.5.2 Case 2: i-DWCBD column (Excess Methanol)

Table 6.15 displays the results in terms of minimum energy expense, including the optimum methanol recycled and reflux ratio profiles, optimum liquid and vapour split ratios, final production time, minimum energy usage rate, and the maximum conversion of acid for different product purities of MeDC. It can be seen from these results that no data was obtained at a product quality of 0.875 mole fraction due to the consumption of DeC by chemical reaction with methanol reactant. Obviously, the i-DWCBD mode at the equimolar amount produced a higher quality of MeDC (0.960 mole fraction), converted more DeC (99.95%) compared to those achieved by employing excess methanol in the feed (Table 6.15). This evidently indicates that, with different sorts of dividing-wall batch configurations, the use of excess methanol in the feed mixture is not required to improve the process proficiency and the product purity.

For MeDC purity of 0.860, there is a sharp rise in reflux ratio and batch time resulting in higher energy consuming (however, the recycled rate of methanol decreased in this case). It can be noticed from both Tables 6.14 and 6.15 that the use of excess methanol can only enhance the reaction conversion, which decreases the desired product quality massively.

Table 6.15 Optimization results for the MeDC production for i-DWCBD column at excess methanol

Purity of MeDC	Optimal MeOH Recycle, S_{MeOH}	Optimal Reflux Ratio, R	Liquid, Vapour Split Ratios r_L, r_V	Final Batch time, t_F, hr	Total Energy Usage, Q_{tot}, GJ	Maximum Conversion of DeC (%)
0.845	1.91	0.113	30.05, 51.80	7.41	0.693	98.64
0.855	1.71	0.217	5.98, 20.58	9.39	0.869	99.14
0.860	1.60	0.336	30.95, 25.90	39.52	3.563	99.54
0.875	---[a]	---[a]	---[a]	---[a]	---[a]	---[a]

[a] Infeasible

6.6 Conclusions

For the first time, the performances of different types of conventional and unconventional batch distillation configurations are determined in terms of minimum energy usage under single and multi-reflux intervals strategies for the synthesis of methyl decanoate. It is found that the efficacy of using the traditional conventional (CBD) and dividing-wall batch (DWBD) reactive columns are restricted due to the removal of methanol from DeC in the reactive region because of wide difference in boiling points between the chemical reactants.

Therefore, the reversible reaction is being activated as the process progresses due to the separation of methanol (one of the forward reaction elements), resulting a severe reduction in the reaction conversion.

To overcome these limitations and to improve the conversion ratio of acid, two alternatives of batch configurations are investigated here (1) i-CBD column and (2) SBD column. A detailed model for the process is constructed employing gPROMS Model Builder 4.2.0 and is embedded within the optimization framework. The optimization problem is solved for differing values of MeDC mole fraction ranging from 0.70 to 0.90 mole fraction.

The influence of piecewise constants reflux ratio, methanol recycle rate (for i-CBD column), and methanol feed rate (for SBD column) on the thermal energy consumption are estimated. The results demonstrate that the i-CBD is found to outperform the SBD when excess methanol is used, whereas, at an equimolar ratio case, the SBD outperforms the i-CBD to meet the specified product constrains with the lower batch time and energy demand. Note, for both i-CBD and SBD processes massive savings in the batch time can be accomplished with the higher reboiler duty and larger amount of catalyst.

Note also, the optimization results for a defined separation task indicate that the use of two-reflux operation can considerably upgrade the process efficiency and achieve higher batch time and thermal heat savings compared to the use of a single-reflux interval in both i-CBD and SBD columns for an equimolar ratio. Here also, a new integrated divided-wall batch operation is proposed/used to overcome these restrictions and to improve the conversion level of acid.

The results show that the integrated dividing-wall batch process (i-DWCBD) is found to outperform all CBD, DWBD and sr-DWBD operations by accomplishing the maximum product purity of MeDC and highest conversion rate of DeC.

With equimolar feed case, the performance of i-DWCBD was superior to the i-DWCBD with excess feed case in terms of conversion of fatty acid, and product concentration.

Note also, the optimization results for a given separation task reveal that use of multi-control operation is more beneficial as compared to the single-control operation in terms of batch time and energy savings in the i-DWCBD scheme. Finally note, excess methanol in the feed mixture is required in dividing-wall batch reactive configurations to only improve the conversion of DeC acid.

Chapter Seven

Optimization of Benzoic Acid Esterification Process

7.1 Introduction

This chapter addresses the optimal operations of conventional and integrated batch distillation configurations in terms of minimum batch time for the synthesis of ethyl benzoate via the esterification of benzoic acid and ethanol. A rigorous dynamic model for each of these configurations is incorporated within the optimization framework.

Product amount and quality are employed as constraints. Reflux ratio for conventional column and the recycled rate of ethanol for integrated batch column are utilized as control variables.

7.2 Ethyl Benzoate Production

The global markets for benzoic acid and its derivatives is receiving increasing attention (Gaifutdinova and Beresnev, 2002). Ethyl benzoate is a type of organic ester and a colorless transparent liquid, having a pleasant odour (described as wintergreen, cherry, fruity, medicinal, and grape) that is almost insoluble in water, but miscible with organic solvents.

Ethyl benzoate is a widely employed as solvents of cellulose, plasticizers for synthetic resins, heat resistant lubricants, flavoring agent in various substances including API drug, rubbers, paper, laboratory reagent, food, and cosmetics and personal-cares (sprays foot and powders) (Li et al., 2008; and Wu et al., 2013). It can also be used in perfumery, and for the preparation of tobacco, and artificial flavors due to its low toxicity (Paul and Newman, 1978;

Lewis, 2007; and Lin and Pang, 2016). There are usually two main ways, which can be used to produce ethyl benzoate as shown in Table 7.1.

Table 7.1 Two proposed reaction approaches for ethyl benzoate synthesis

Reaction Way	Reference
The ozonolysis of styrene in the presence of ethanol, and then followed by heating decomposition of the intermediate ozonolysis products.	(Gaifutdinova and Beresnev, 2002)
The acidic esterification of benzoic acid with ethanol to produce ethyl benzoate (main product) and water (by-product) using a heterogeneous reaction system.	(Plazl, 1994; Pipus et al., 2000; and Lee et al., 2005)

As discussed previously in Chapter Three, ethanol has the lowest boiling temperature in the mixture followed by water, ethyl benzoate and benzoic acid (Table 3.1). The ethanol reactant will separate itself from benzoic acid with the CBD in progress, and thus conversion of the acid to the desired product (benzoate) will be restricted.

Benzoic acid having the highest boiling temperature in the reaction mixture will stay at the reboiler drum most of the time. Hence, it is anticipated that recycling of the ethanol (in i-CBD column) will increase the contact of ethanol and benzoic acid and thus will enhance the conversion rate of benzoic acid. However, it looks clear that CBD column is unable to yield a higher product concentration at the equimolar feed ratio. First, the traditional batch reactor-batch distillation approach is used to establish the maximum amount and quality of ethyl benzoate that can be achieved via batch distillation operation. Then, batch reactive distillation is considered to see whether an improved conversion rate of benzoic acid, and yield of product and maximum achievable concentration are possible.

Aiming to increase the reaction conversion and thus product amount, the application of conventional batch and integrated conventional batch distillation processes are utilized in this work. The optimal processes of batch and integrated batch configurations are evaluated in terms of minimum batch time.

7.3 Process Model

The model equations and assumptions can be found in Chapter 4.

7.3.1 Kinetic Modelling and Thermodynamic Aspects

Lee et al. (2005) considered experimentally kinetic study of esterification of benzoic acid (BeZ) and ethanol (EtOH) to form ethyl benzoate (EtBZ) over an acidic cation-exchange resin (Amberlyst-39). For the synthesis of ethyl benzoate, a Langmuir-Hinshelwood-Hougen-Watson (LHHW) activity ($a_i = \gamma_i x_i$) based kinetic model is employed which can be written as:

$$-r_1 = m_{cat}\left\{\frac{3.0532\times10^{13}\exp\left(\frac{-9620}{T}\right)\left[a_1\,a_2 - 19.08\times10^{3}\,\exp\left(\frac{541.48}{T}\right)a_3\,a_4\right]}{\left[1+0.08154\,a_1+1.6308\,a_2+0.3793\,a_3+9.1747\,a_4\right]^2}\right\} \quad (7.1)$$

This LHHW model gives the best representation for the kinetic behaviour of the global system and therefore, this reaction model is used in this work.

7.3.2 Phase Equilibrium (VLE)

The calculations of vapour and liquid molar enthalpies and thermodynamic properties for the production of ethyl benzoate are same as those presented in chapter five. The saturated pressure (P^{sat}) of the pure constituents is computed as a function of temperature through the Antoine's equation:

$$Log_{10}P_i^{sat} = A + \frac{B}{T} + C\,log_{10}T + DT + ET^2 \qquad (7.2)$$

Where A, B, C, D, E are the regression coefficients (with appropriate units) for the Antoine's equation and T is the temperature in Kelvin. All coefficients for the Antoine's equation used in this work were taken from (Yaws, 1997) and are summarised in Table 7.2.

Table 7.2 Antoine Parameters for Equation 7.2

Antoine Coefficients	BeZ	EtOH	EtBZ	H_2O
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^{-1}]	6.2611E+1	-5.0474	-1.1793E+1	-7.3037
D [K^{-1}]	-6.5321E-2	3.7448E-11	4.0697E-3	2.4247E-9
E [K^{-2}]	2.4596E-5	2.7361E-7	-1.2372E-13	1.8090E-6

The NRTL model was used to calculate the liquid-activity parameters (VLE) with the binary constants were taken from Lee et al. (2005). The enthalpy of vaporization and the vapour enthalpy coefficients are taken from Aspen Plus, and (Holland, 1981; Mackay et al., 2006; and VDI Atlas, 2010), respectively.

7.4 Formulation of Dynamic Optimization Problem

In the present work, the optimisation problems for CBD, and i-CBD systems can be stated as follows:

Given:	The batch configurations, the feed mixture, vapour load to the condenser, desired amount of EtBZ product and quality condition.
Determine:	Reflux ratio (R_{CBD}) (for CBD process) Reflux ratio ($R_{i\text{-}CBD}$), recycled rate (S_{EtOH}) (for i-CBD process)
So as to:	Minimize the overall operating batch time
Subject to:	Process model, and Process constraints

Mathematically, the optimization problem (OP1) can be represented as:

$$\begin{array}{llr} OP1 \quad \underset{R_{CBD}}{Min} \quad t_F & \text{(For CBD Column)} & \\ \quad\quad Or & & (7.3) \\ \quad R_{i\text{-}CBD}(t),\ S_{EtOH}(t) & \text{(For i-CBD Column)} & \\ \text{Subject to :} & & \\ \quad B_{EtBZ} \geq B^{*}_{EtBZ} & \text{(Inequality Constraints)} & \\ \quad x_{EtBZ} \geq x^{*}_{EtBZ} & \text{(Inequality Constraints)} & \end{array}$$

Where B_{EtBZ}, and x_{EtBZ} are the quantity of bottom product and concentration of ethyl benzoate at the end of batch time t_F in the still pot (B^{*}_{EtBZ}, and x^{*}_{EtBZ} are specified). R_{CBD} and $R_{i\text{-}CBD}$ are the reflux ratios, and S_{EtOH} the recycle rate of ethanol (in case of i-CBD column) which is optimized.

7.5 Results and Discussions

7.5.1 Traditional Batch Reactor-Batch Distillation Scheme

In a small laboratory fixed bed reactor system, Lee et al. (2005) utilized a feed rate of 9.15×10^{-6} kmol/hr with molar ratio of 5:1 for (Ethanol: Benzoic Acid) resulting in feed concentration of 0.167 (BeZ), 0.833 (EtOH), 0.0 (EtBZ), and 0.0 (H_2O) mole fraction. They obtained 90.20% conversion rate of acid resulting in the reactor outlet molar concentration of 0.016 (BeZ), 0.683 (EtOH), 0.150 (EtBZ), and 0.150 (H_2O). The residence time for the fixed bed reactor was 13.23 hours. For the TRBD process in this work, the total amount of catalyst loading was scaled up to 3886 kg, the total amount of feed to the reactor 5 kmol and assumed the same residence time of 13.23 hrs.

The reactor converted 90.20% of BeZ resulting in the same final product concentration as achieved by Lee et al. (2005) in the fixed bed reactor.

Therefore, this concentration was used as the initial feed concentration for the conventional batch distillation part. Note, in TRBD mode, no further reaction takes place in the distillation column.

The synthesis of ethyl benzoate is carried out in a batch column with ten plates (including condenser and pot drum) with (2.5 kmol/hr) of overhead vapour condenser load at the atmospheric pressure. The total column holdup is considered to be four percent of the total feed charge. Fifty percent of total column holdup is taken for reflux drum and the rest for the column stages (equally divided).

Ideally, if all of the ethyl benzoate (desired product) in the feed could be recovered at 100% concentration, the maximum desired product quantity would be 0.75 kmol. However, this will not be possible as BeZ is the heaviest component in the mixture. Hence, ideally if all ethanol and water have been removed by distillation column and no water is left in the pot drum after the depletion of ethanol, 0.830 kmol of bottom product will remain with concentration of 90.36% (mol %) of benzoate. The optimization results in terms of optimal reflux ratio, reactor time, and column batch time, as well as the total operation time for a range of desired product quality considerations (0.855 mole fraction onward) are shown in Table 7.3. For both cases, the product quantity to be accomplished is set as 0.83 kmol (to explore if EtBZ concentration of 90.36% is possible to obtain). The results of Table 7.3 indicate that the reflux ratio and operating time, increase gradually with increasing EtBZ mole fraction in the still drum. It is noticed also form Table 7.3 that no results were achieved at product quality beyond 0.86 mole fraction due to the removal of some of the EtBZ in trays above the pot tank due to separation.

Table 7.3 Optimal Operation results for the EtBZ production for TBRD system

Product Purity, x^*_{EtBZ}	Optimal Reflux Ratio (-----)	Reactor time, t_{FBR}, (hr)	Column time, t_{CBD}, (hr)	Total Batch time, t_{tot}, (hr)
0.855	0.202	13.23	1.99	15.22
0.860	0.285	13.23	2.22	15.45
> 0.870	---[a]	---[a]	---[a]	---[a]

[a] Infeasible.

7.5.2 The Performance of CBD and i-CBD Systems with Excess Ethanol

Having considered the traditional batch operation in section 7.5.1, the effectiveness of reactive distillation will be investigated for the reaction scheme concerned. In both cases, the feed concentration (0.167 BeZ, 0.833 EtOH, 0.0 EtBZ, and 0.0 H_2O mole fraction) is kept the same as in Lee et al. (2005) and the quantity of product in the still is kept constant at 0.83 kmol (same as TRBD system) for making fair comparison.

7.5.2.1 Case A: CBD Mode

Table 7.4 summarizes the optimum operation results for CBD mode in terms of reflux ratio, maximum conversion of BeZ, minimum batch time, and the total energy consumption for a range of product quality requirements (mole fraction of 0.860 to 0.925).

Table 7.4 Optimal Operation results for the production of EtBZ for CBD

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

It can be seen from Table 7.4 that, in all cases, the reflux ratio, and the operating time together with the thermal energy usage decrease progressively with increasing the desired concentration conditions. The reason for this reduction is that the batch column gets rid of water and ethanol faster and so a large amount of water and ethanol was removed from the reboiler drum to the distillate tank to meet product specifications. Reduced reflux ratio assists the removal of water (as it is being produced) thus pushing the chemical reaction more forward. Although, ethanol is the lightest, it will also be removed with water, but due to excess ethanol being used, the remaining ethanol in the pot drum is sufficient to convert more of the benzoic acid and thus improves the concentration of the desired product (ethyl benzoate). It can be observed from the results that the conversion rate of acid increase gradually and thus increases the product purities. This is clear as higher composition of EtBZ dictates more conversion of BeZ. A comparison of the results between the conversion of benzoic acid using CBD system and the TRBD approach conversion shows that for the same amount of EtBZ product (0.83 kmol) CBD column can synthesis more ethyl benzoate at a much higher concentration (0.925 compared to 0.860) and can convert more acid (96.11% as opposed to 90.20%).

7.5.2.2 Case B: i-CBD Mode

The optimal results for the i-CBD column are listed in Table 7.5, including the optimal reflux ratio, optimal recycle rate of ethanol, the BeZ conversion, minimum batch time, and total energy consumption, as well as total amount of ethanol recycle for four product purity specifications. It can be noticed from these results that the all reflux ratios, the conversion level of BeZ, batch time and the total energy usage rate, and quantity of recycled EtOH progressively increase with increasing EtBZ quality constraints (unlike those observed in a CBD process in Table 7.4).

Table 7.5 Optimal Operation results for the production of EtBZ for i-CBD

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

Obviously, the recycled stream has significant amount of water with ethanol, which pushes the reaction reverse. Thus, it takes significantly more batch time (compared to CBD column) to yield the same amount of product for a given concentration. Increasing the production time can lead to a considerable increase the conversion rate of acid. Note, although the recycle rate of ethanol increased for the last case, higher reflux ratio and operating time and more energy consumption rate are demanded to convert more BeZ into EtBZ and to achieve the product purity specification as compared to other product purities.

Note, comparison of the results in Table 7.5 with those in Table 7.4 illustrates that the use of CBD column is more beneficial option for the production of EtBZ than the i-CBD operation in terms of operating batch time and total energy usage. As in the example, an overall operating time reduction of 64.50% and energy consumption reduction of 65.51% at EtBZ composition of 0.925 mole fraction are possible by applying the two-reflux interval policy instead of one reflux interval policy.

However, the i-CBD process is found to be better than the CBD process in terms of maximum achievable conversion due to more ethanol recycled back to the reboiler, which can have further reaction with the unreacted benzoic acid. It is noted that 2.53% of conversion rate of BeZ can be upgraded at 0.925 of product concentration as compared to that obtained by employing the CBD column.

7.5.3 Performances of CBD, and i-CBD Systems with Equimolar Feed

Lee et al (2005) used excess alcohol in their reactor and the mass balance will show that it decreases the amount of desired product massively (as can be seen in section 7.5.1 and 7.5.2). The question that arises here is whether it is essential to have excess alcohol and whether there is a scope for increasing the amount of desired product for the same product quality. In this section, therefore, equimolar reactant ratio (EtOH: BeZ) of 5 kmol of initial feed charge to the reboiler is examined in all batch reactive columns (CBD, and i-CBD). For all case studies, the desired product quantity in the reboiler was set to 2.4 kmol.

7.5.3.1 Case C: CBD Column

Table 7.6 shows the optimization results (reflux ratio, the conversion of BeZ into EtBZ minimum operating time, and total energy usage) for each bottom product (EtBZ) quality. As before, the results of Table 7.6 demonstrate that for all cases, reflux ratio, batch time, and the total energy consumption reduce progressively with increasing concentration of the product. Although the conversion of acid increases with the increasing EtBZ purity compared to CBD with excess feed (Table 7.4), the maximum concentration of ethyl benzoate that could be accomplished 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 assists the removing of ethanol (as it is being lightest component) thus pushing the reaction more forward. However, since there is no excess ethanol in this case, the remaining ethanol in the still pot is not enough to convert more of the benzoic acid and thus cannot enhance the composition of ethyl benzoate. As it can be observed, the CBD process operates in a small reflux mode to achieve the maximum possible the product purity of 0.73 mole fraction. Also, it can be seen that it is difficult to achieve higher conversion rate of acid using a conventional batch reactive column at the equimolar feed ratio.

Table 7.6 Optimal Operation results for the production of EtBZ for CBD column

Product Purity, x^*_{EtBZ}	Optimal Reflux Ratio, R_{CBD}	Conversion of BeZ (%)	Final Batch time, t_F, hr	Energy Usage, Q_{tot}, GJ
0.700	0.227	71.47	1.24	0.170
0.710	0.186	72.41	1.18	0.164
0.720	0.130	73.42	1.10	0.157
0.730	0.022	74.38	0.98	0.145
> 0.730	---[a]	---[a]	---[a]	---[a]

[a] Infeasible.

7.5.3.2 Case D: i-CBD Process

As mentioned before in sections 7.5.1 and 7.5.2, the use of excess alcohol in the feed can only improve the conversion level of benzoic acid, which reduces the product quantity considerably. Here, the i-CBD configuration is suggested to enhance the product amount in the pot drum at the equimolar ratio case. Two scenarios are studied, Scenario-A with single-reflux strategy of operation (NCI=1), and Scenario-B with two-reflux intervals (NCI=2). Note that, the purity of EtBZ product requirement is changed from 0.730 onward in each scenario whilst the product amount in the bottom tank remains the same at 2.4 kmol.

7.5.3.2.1 Scenario-A: Optimal Operation using of One-Reflux Interval

The optimal operating results (optimal ethanol recycle rate, reflux ratio, the conversion of BeZ into EtBZ, and minimum operating time together with the thermal energy usage, and the total quantity of ethanol recycled over the batch time) for different bottom product concentrations of EtBZ are summarized in Table 7.7.

Unlike CBD process (Table 7.6), the results in Table 7.7 clearly show that i-CBD can yield higher purity product (0.925 mole fraction of EtBZ). This is due to the fact that the recycled stream has significant amount of water to enhance the reversible 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 7.7). This consequently increase the production batch time and the total energy demand.

As expected, an increase in the operating time results in the increase of BeZ conversion. Figure 7.1 shows the processing batch time and energy consumption rate for all reflux ratio values in the one-control i-CBD operation. It is clear from Table 7.7 that the higher reflux ratio, the higher batch time required and the higher energy usage rate at 0.925 of EtBZ concentration compared to the others to suppress the travel of benzoate up the column further and to meet the product quality specification (Figure 7.1).

Note that, there is a sharp increase in processing-batch time and thus total energy consumption (Table 7.7) to increase the EtBZ concentration from 0.730 to 0.925 (mole fraction). For this case (0.925 mole fraction), the distillation column operates at higher reflux mode and higher operating batch time to decrease the depletion of ethanol from the top of column and to improve the conversion of BeZ into EtBZ to fulfil the product consideration as shown in Table 7.7.

It is noted from the results of Table 7.7 that i-CBD column can produce ethyl benzoate at a much higher quality (0.925 mole fraction) and can convert more benzoic acid (93.57%) as compared to those achieved (74.38%) by using the CBD column (see Table 7.6). Note, the i-CBD with equimolar ratio (Table 7.7) needed higher operating batch time and more energy usage compared to the i-CBD column with excess ethanol (Table 7.5).

A higher amount of total ethanol recycling was required for the i-CBD with equimolar feed compared to that for i-CBD with excess feed. Since a higher product amount of 2.4 kmol was specified to be attained in the i-CBD at the equimolar ratio, the removal of higher quantity from the reboiler in this case demanded a longer batch time.

Table 7.7 Optimal Operation results for the production of EtBZ for i-CBD column at equimolar ratio using NCI = 1

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

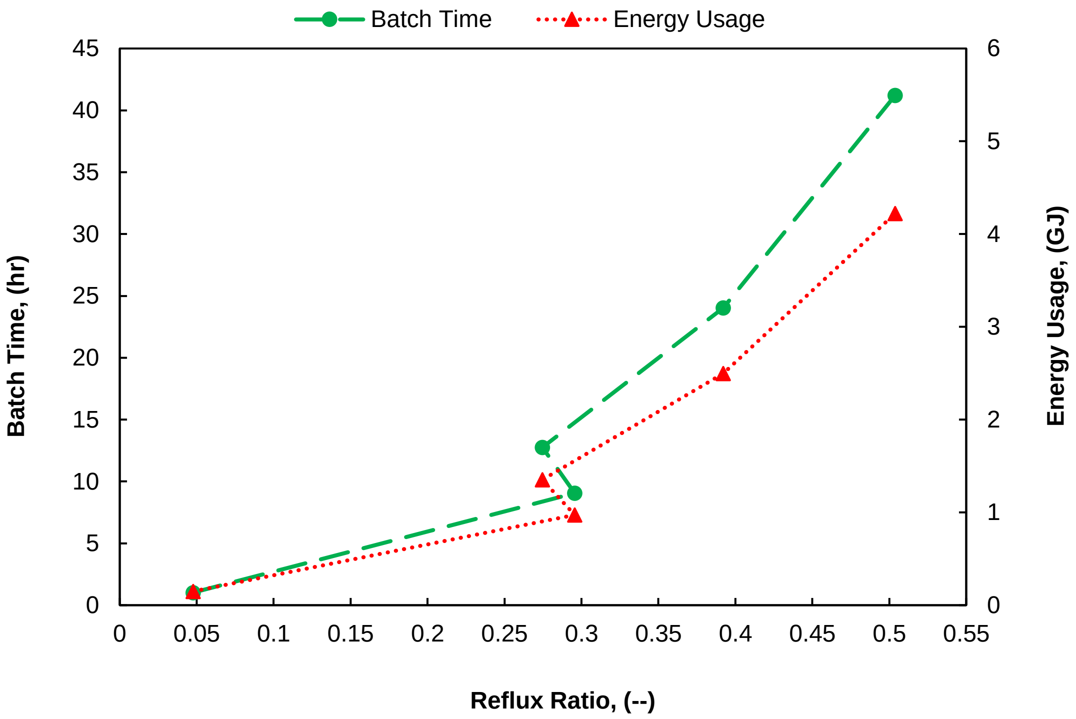

Figure 7.1 The final batch time and energy demand profiles for i-CBD system

The mixture composition profiles in the accumulator drum and in the reboiler are given in Figures 7.2 and 7.3, respectively for the EtBZ concentration (x^*_{EtBZ} = 0.925). The concentration of water (2nd boiling component) in the still rises from zero and reaches a maximum value and then drops down to almost zero. This is thought to be due to its removal in the accumulator receiver (Figure 7.2).

Ethanol (the lightest component in the mixture) is gradually consumed through the reaction with benzoic acid at the bottom of the column, producing a higher improvement in the conversion of BeZ at the end of the operation (as shown in Figure 7.3, Table 7.7). As long as the reaction continues, the composition of ethanol progressively decreases in the pot drum due to its lowest boiling point, which is collected at the top of column (see Figure 7.2).

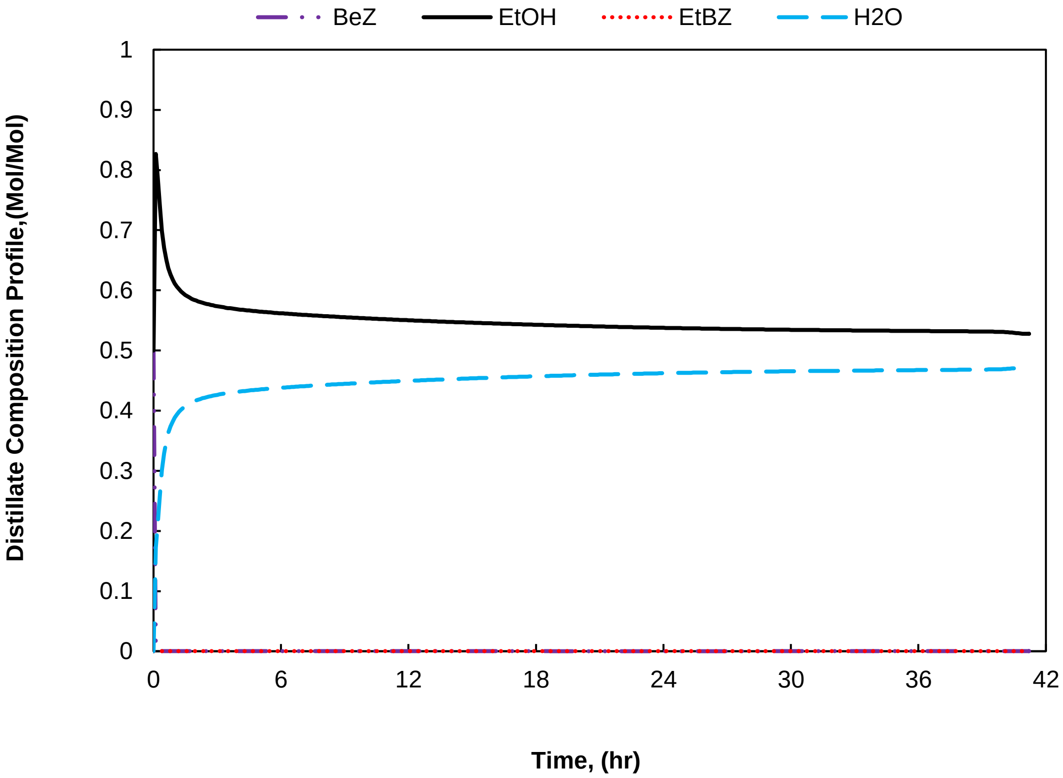

Figure 7.2 The distillate composition of i-CBD, One Control Interval

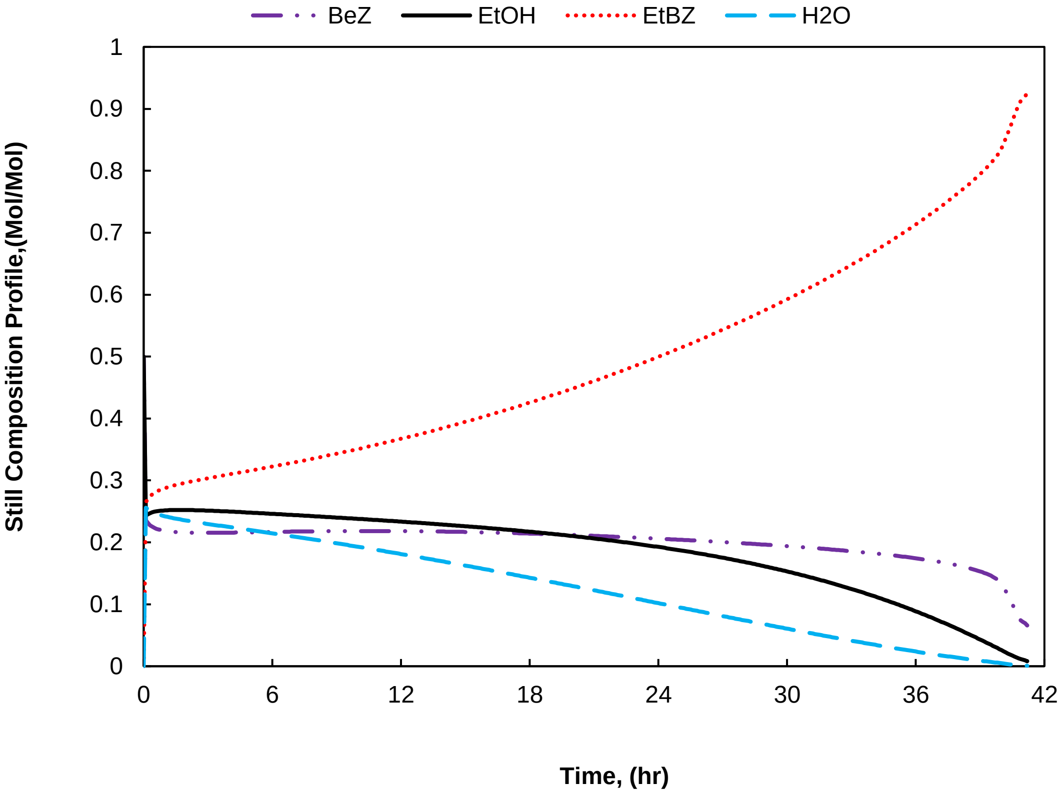

Figure 7.3 The still composition of i-CBD, One Control Interval.

7.5.3.2.2 Scenario-B: Optimal Operation using of Two-Reflux Intervals

The optimal ethanol recycled rate and reflux ratio for each interval batch time, optimal time intervals, the total minimum batch time, the total amount of ethanol recycled over the production time, the maximum conversion of BeZ, and the total energy consumption using two-control intervals strategy to achieve the product quality are provided in Table 7.8. It can be noted from Table 7.8 that the significant savings in the production batch time (by about 81.12%), and the total energy demand (by almost 80.25%), and maximum improvement in the conversion of acid is by 1.97%, respectively at the 0.925 more fraction of EtBZ employing multi-control strategy compared to one-control strategy i-CBD operation (scenario-A).

Table 7.8 Optimal Operation results for the production of EtBZ for i-CBD column at equimolar ratio using NCI = 2

Product Purity, x^*_{EtBZ}	Optimal Recycle Rates S_1, S_2	Optimal Reflux Ratios R_1, R_2	Batch Time Intervals t_1, t_2, hr	Final Batch time, t_P, hr	EtOH Recycle Amount, kmol	Conversion of BeZ (%)	Energy Usage, Q_{tot}, GJ
0.730	0, 0.12	0.033, 0.000	0.62, 0.38	1.00	0.05	74.51	0.147
0.860	0, 1.47	0.641, 0.061	0.56, 2.16	2.72	3.17	88.42	0.326
0.875	0, 1.53	0.660, 0.067	0.71, 2.25	2.96	3.45	90.07	0.352
0.900	0, 1.67	0.704, 0.085	1.49, 2.10	3.59	3.50	92.90	0.420
0.925	0.2, 1.77	0.633, 0.199	1.16, 6.62	7.78	11.91	95.45	0.834

It can be seen from Table 7.8 that multi-reflux operation resulted a potential reduction in the operating batch time and the energy required compared to single-reflux policy. This obviously shows the benefit of using multi-control intervals approach. It can be also noticed that, total recycled amount of ethanol can be saved at using two-control process (reduction by about 75.55% compared to the one-control policy). Multi-control policy for the i-CBD column is found to have ability to secure more batch time and thermal energy savings, and to upgrade the maximum achievable conversion compared to single-control for the i-CBD operation (scenario-A). It can be realized form Table 7.8 that the column operates at higher reflux mode and lower operating batch time for the first interval to push the water up to the distillate drum and then at lower reflux ratio and higher recycle rate of ethanol in the second-time interval to keep both reactants (BeZ and EtOH) in the pot tank to have further reaction to fulfil the required product (EtBZ) purity. More ethanol is separated from the bottom of column at higher concentration in the first interval but is not recycled leading to some amount of benzoic acid in the reboiler and possibly having reverse reaction (see Figure 7.5, Table 7.8). While, in the second interval, ethanol is recycled converting most of the benzoic acid and producing ethyl benzoate.

The mixture composition profiles in the distillate receiver and the reboiler drum of i-CBD column at product quality constraint (x^{*}_{EtBZ} = 0.925) are shown in Figure 7.4 and 7.5 for two-control intervals. In the pot drum, as the reaction progresses, initially the compositions of reactants (benzoic acid and ethanol) decrease progressively, whereas, the concentration of ethyl benzoate rises. It can be seen from Figure 7.5 that although the composition of benzoic acid increases in the first-time interval and then decreases in the second-time interval due to its consumption by chemical reaction with ethanol resulting in higher conversion ratio of acid at the end of reaction, the concentration of ethanol reduces gradually due to large difference between the boiling temperatures of the feed mixture. Ethyl benzoate reached the desired quality at shorter batch time for two-control policy than the one-control case (Figure 7.5).

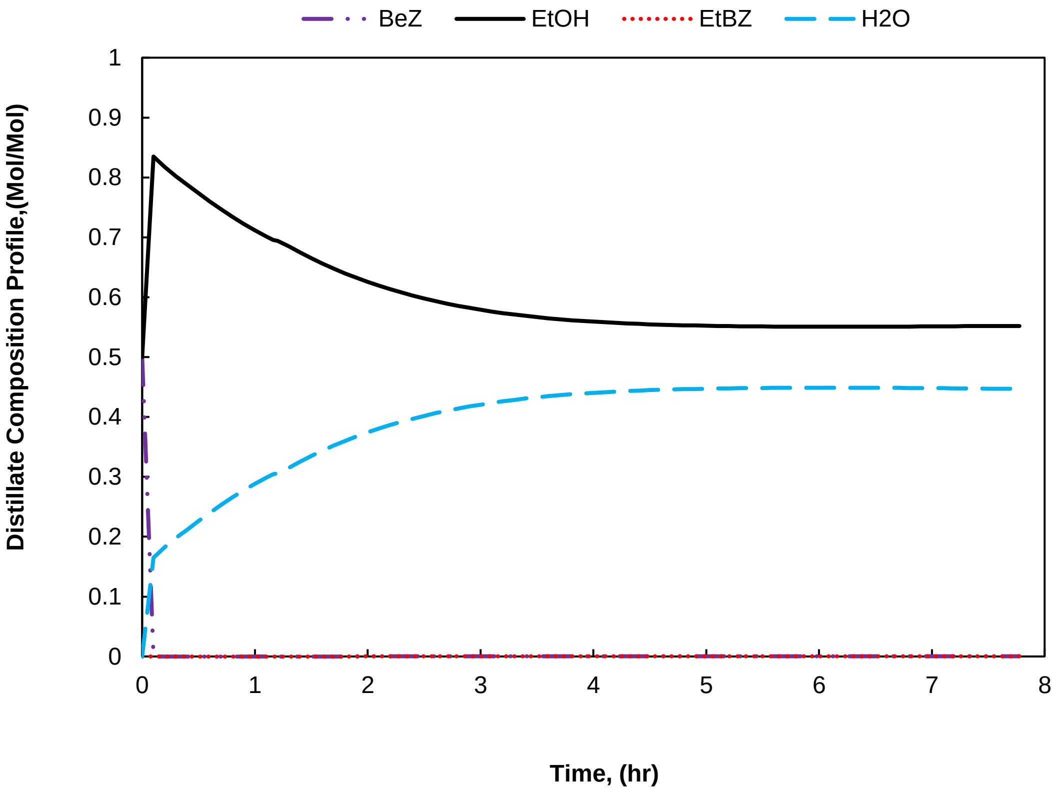

Figure 7.4 The distillate composition of i-CBD, multi-control intervals

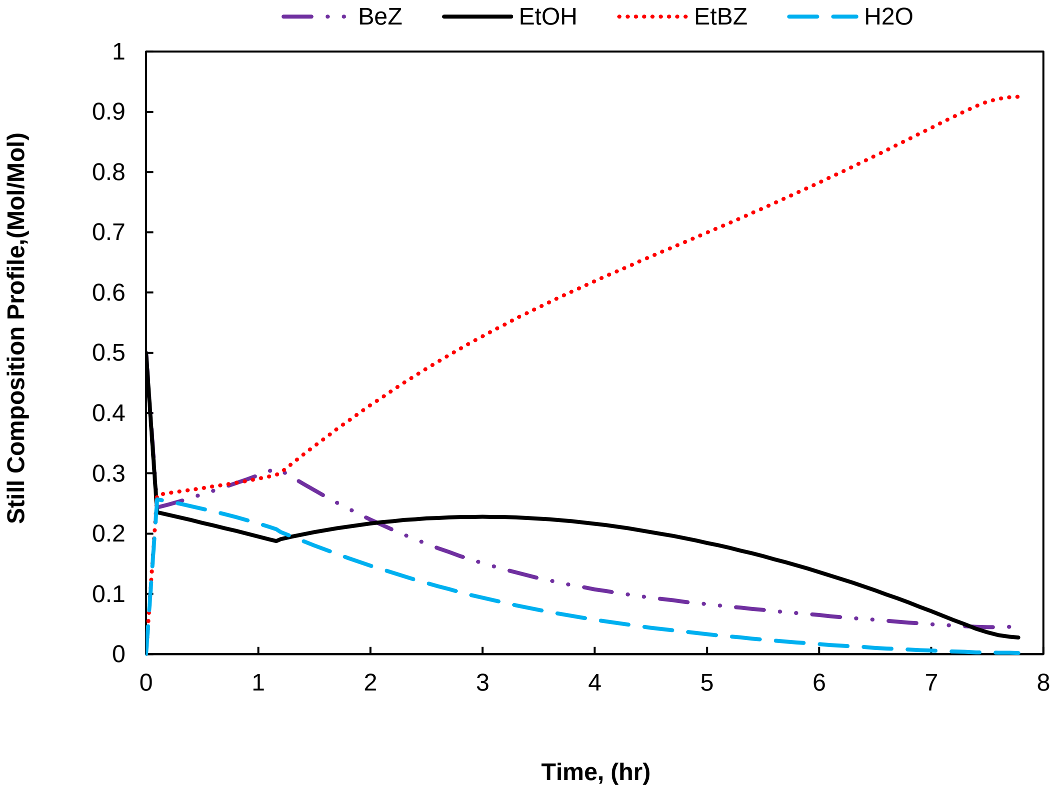

Figure 7.5 The still composition of i-CBD, multi-control intervals

7.6 Conclusions

For the first time, the optimum operation of conventional and integrated (CBD and i-CBD) batch distillation configurations are evaluated using model-based techniques for the synthesis of ethyl benzoate through the esterification of benzoic acid and ethanol. However, first, the classical batch reactor-batch distillation approach is explored to find the concentration of benzoate and maximum possible amount that can be achieved by using non-reactive batch distillation system. It is found that the efficiency of using the TRBD mode is very restricted in terms of product amount and quality. Next, the reactive distillation columns (CBD and i-CBD) are considered with excess ethanol to investigate if the conversion of benzoic acid and the product composition can be enhanced. Clearly, the reactive distillation system is found to perform the traditional TRBD mode to achieve higher ethyl benzoate product specifications with the lower production time and the higher achievable conversion rate. However, with excess ethanol, the performance of CBD column was superior to the i-CBD column in terms of conversion of benzoic acid, purity of ethyl benzoate, operating batch time, and thus energy demand. Remarkably, with equimolar reactants ratio in the feed mixture, the use of i-CBD system significantly improves the process efficiency in terms of reaction conversion, operation time, and energy consumption rate compared to those obtained by using CBD process. In addition, equimolar ratio case increases the amount of product significantly. Note also, the optimization results for a defined separation task demonstrate that multi-control strategy can considerably improve the process efficiency compared to that attained by using one-reflux interval for the i-CBD operation.

Chapter Eight

Optimization of Acetic Acid Esterification Process

8.1 Introduction

This chapter deals with optimal operation of different types of batch reactive distillation (middle-vessel, inverted, and conventional) columns in terms of minimum operating time for an esterification of acetic acid (AA) with benzyl alcohol (BzOH) to produce benzyl acetate (BzAC) and water (H_2O). A detailed model for the system is developed within gPROMS.

The amount of BzAC and its purity are utilised as inequality constraints. Reflux ratio for middle-vessel and conventional columns and reboil ratio for inverted column are utilised as control variables.

8.2 Benzyl Acetate Production

Benzyl acetate (BzAC) is a colorless liquid having a characteristic odor with a molecular weight of 150.18 g/mol. In general, benzyl acetate is produced by esterification of acetic acid and benzyl alcohol.

It can be used in a wide range of applications, across many industries, including:

- As flavouring agents and preservatives in the food industry.
- As solvents in the perfume and cosmetics industries.
- As solvents, resin, cellulose acetate, leather finishes, and paints.

Benzyl acetate is the heaviest boiling component and water the lightest boiling component in the mixture. The removal of benzyl acetate from the bottom tank in middle-vessel and inverted batch columns will also shift the reaction forward.

Finally, the removal of water in a regular batch column will shift the reaction forward.

8.3 Model Equations

The mathematical models for MVD, IBD, and CBD modes can be seen in Chapter 4.

8.3.1 Kinetic Modelling and Phase Equilibrium

Three kinetic models (a pseudo-homogeneous (PH), Eley-Rideal (ER), and Langmuir-Hinshelwood-Hougen-Watson (LHHW)) were examined by Ali and Merchant (2009) to correlate the kinetic experimental data of synthesis of benzyl acetate to obtain the general kinetic model.

For the formation of benzyl acetate, a LHHW activity ($a_i = \gamma_i x_i$) based kinetic model is used which can be written as:

$$- r_1 = m_{cat} \left\{ \frac{13.01\times10^5 exp\left(\frac{-6855.91}{T}\right) \left[a_1\, a_2 - 906.87\; exp\left(\frac{-1279}{T}\right) a_3\, a_4\right]}{[1+ 2.15\, a_1 + 1.21\, a_2 + 0.10\, a_3 + 3.25\, a_4]^2} \right\} \qquad (8.1)$$

This kinetic model predicts the esterification reaction of acetic acid with benzyl alcohol and therefore, this reaction scheme is employed here.

8.3.2 Vapour-Liquid Equilibrium (VLE)

The calculations of liquid and vapour enthalpies and thermodynamic properties for the production of benzyl acetate are same as those shown in Chapter Five. The vapour-liquid equilibrium equation is calculated from the following form:

$$y_i = \frac{P_i^{sat}\, x_i\, \gamma_i}{P} \qquad (8.2)$$

Where, *P* (mmHg) is the operating pressure, y_i and x_i are the concentration of the vapour and liquid phases, respectively, γ_i represents the activity coefficient of component *i* which was computed using the NRTL equation. The saturation vapour pressure (P^{sat}) of pure components has been calculated by using the Antoine equation (see equation 7.2).

The NRTL binary interaction coefficients were taken from the data bank of Aspen Plus and the Antoine parameters were taken from Yaws (1997). The physical and thermodynamic properties data and enthalpy parameters for all pure components (Table 8.1) are taken from the data bank of Aspen Plus and Yaws (1997), respectively.

Table 8.1 Physical and thermodynamic properties and Antoine constants

Physical Properties	AA	BzOH	BzAC	H_2O
T_C [K]	592.7	677.0	699.0	647.3
λ_b [kJ/kmol]	23330	51660	44580	39500
M_{wt} [kg/kmol]	60.05	108.14	150.18	18.01
A [--]	28.3756	-36.2189	46.1904	29.8605
B [K]	-2.9734E+3	-3.3475E+3	-4.6053E+3	-3.1522E+3
C [K^{-1}]	-7.0320	2.3337E+1	-1.2820E+1	-7.3037
D [K^{-1}]	-1.5051E-9	-4.4600E-2	1.6574E-10	2.4247E-9
E [K^{-2}]	2.1806E-6	2.1443E-5	2.5462E-6	1.8090E-6

8.4 Dynamic Optimization Problem

In this work, the optimum operations of MVD, IBD and CBD columns are evaluated in terms of maximum yearly profit for a given product amount and desired purity of BzAC.

8.4.1 Maximum Profit Problem

The optimization problem can be described as follows:

Given:	The column configurations, feed mixture, vapour load to the condenser, desired amount of product and purity.	
Determine:	Reflux ratio (R) and reboil ratio (r_b)	(for MVD process)
	Reboil ratio (r_b)	(for IBD process)
	Reflux ratio (R)	(for CBD process)
So as to:	Maximize the annual revenue (P)	
Subject to:	Model equations, and Process constraints	

Mathematically, the optimization problem (OP1) can be written as follow:

$$\begin{array}{lll} OP1 & \underset{R(t),\ r_b}{Max}\ P & \text{(For MVD Column)} \\ & r_b & \text{(For IBD Column)} \\ & R(t) & \text{(For CBD Column)} \end{array} \qquad (8.3)$$

Subject to :

$$B_{BzAC} \geq B^{*}_{BzAC} \qquad \text{(Inequality Constraints)}$$

$$x_{BzAC} \geq x^{*}_{BzAC} \qquad \text{(Inequality Constraints)}$$

For a given separation task, the minimization of batch time will increase the number of batches (N_B) and thus will increase the total yearly revenue.

Therefore, the maximum annual profit problem of those operations can be converted into minimum production batch time problem as presented below.

Note, the profit function equations for all MVD, IBD and CBD configurations and constants utilized in this work, are same as those shown in section 5.5.2.

8.4.2 Minimum Operating Time Problem

In mathematical terms, the optimization problem (OP2) can be represented as follow:

$$
\begin{array}{llll}
OP2 & \underset{R(t),\ r_b}{Min}\ t_f & \textit{(For MVD Column)} & \\
 & \quad r_b & \textit{(For IBD Column)} & (8.4) \\
 & \quad R(t) & \textit{(For CBD Column)} &
\end{array}
$$

Subject to :

$$B_{BzAC} \geq B^{*}_{BzAC} \qquad \textit{(Inequality Constraints)}$$

$$x_{BzAC} \geq x^{*}_{BzAC} \qquad \textit{(Inequality Constraints)}$$

Where, $B_{BzAC}$and x_{BzAC} are the amount of bottom product (2.5 kmol for all columns), and concentration of benzyl acetate, respectively at the final batch time t_f (denotes that the B^{*}_{BzAC}, x^{*}_{BzAC} are specified). Note, all prices of both reactants (AA and BzOH) were taken from Alibaba Trade (2018) and the costs of benzyl acetate at other qualities are evaluated based on the exponential trend method used in (Mujtaba and Greaves, 2006). The prices of chemical reactants (AA and BzOH) and product (BzAC) at various product compositions values are listed in Table 8.2.

Table 8.2 The costs of reactant and product reaction

The price constants	Cost ($/kmol)
AA Reactant Cost at 100% purity	18.20
BzOH Reactant Cost at 100% purity	25.43
Benzyl Acetate Price at 82.5% purity	114.90
Benzyl Acetate Price at 83% purity	125.20
Benzyl Acetate Price at 83.5% purity	141.60
Benzyl Acetate Price at 84% purity	179.60
Benzyl Acetate Price at 84.5% purity	210.00

8.5 Results and Discussions

8.5.1 Problem Specifications

The synthesis of benzyl acetate has taken place in a ten-tray column (including a condenser and a still drum) with condenser vapour load of 2.5 kmol/h for three batch systems (MVD, IBD, and CBD). Four percent of the total initial feed is the total column holdup. This strategy of column holdups has been used only for CBD, and IBD columns. For CBD column, fifty percent of this total holdup is taken as the condenser holdup and the rest is taken as the tray holdup (equally divided). While, the reboiler holdup is 50% of the total column holdup and the rest is equally divided on the plates for IBD column. For MVD column, the total column holdup is 6% of the initial feed (of which 33.33% is taken as the condenser hold up, 33.33% is taken as the reboiler hold up and the rest is equally divided in the plates to make plate holdup). Similar distributions of column holdups were applied by a number of scholars (Mujtaba, 2004; Edreder et al., 2011; Mujtaba et al., 2012; Edreder et al., 2015). The total initial amount of feed is 5 kmol with the feed composition as AA, BzOH, BzAC and H_2O as: 0.5, 0.5, 0.0 and 0.0, respectively. The column is operated at total reflux/reboil during initial start-up mode until a steady-state is reached. This steady-state is the end of the start-up procedure.

8.5.2 MVD Column

Table 8.2 shows the optimum operation policy; including reboil ratios, reflux ratios, the minimum batch time, the conversion level of AA into BzAC, the total number of batches, yearly production rate, as well as the maximum achievable revenue for the MVD operation. As can be noted form Table 8.3 that increasing the quality of BzAC product increases the optimum reflux, reboil ratios, and the processing-batch time. Obviously, increasing the operating batch time can lead to increase the conversion rate of acetic acid. It can be observed also from Table 8.3 that as the product purity and production batch time increase, the total number of batches produced over the year and total annual production gradually reduce (see equations 5.18 and 5.22 in section 5.5.2). As the bottom product concentration consideration increases form (0.825 to 0.835 mole fractions) together with cost of BzAC product, the yearly profit increases gradually. However, it was not possible to accomplish benzyl acetate > 0.840 mole fraction using a MVD operation. This is due to reverse reaction being active and a quick separation of alcohol form acid reactant in the feed tank due to the big gap in boiling points of reactants. Note, higher operating batch time and lower product quality obtained make MVD uncompetitive column (compared to others) and hence the recommended IBD and CBD systems.

Table 8.3 Summary of Optimization Results for MVD Column

Product Quality of BzAC	Optimal Reboil Ratio, r_b	Optimal Reflux Ratio, R	Final Batch time, t_F, hr	Conversion of AA (%)	Number of Batches, batch/yr	Product Demand PD, kmol/yr	Total Annual Profit, $/yr
0.825	0.941	0.951	17.73	88.33	439	1097	133
0.830	0.956	0.965	24.44	88.81	321	802	235
0.835	0.969	0.975	35.04	89.31	225	563	387
0.840	---[a]	---[a]	---[a]	---[a]	---[a]	---[a]	---[a]

[a] Infeasible.

8.5.3 IBD Column

Theoretically, most of the chemical reaction will start at the feed tank (condenser drum) at the beginning of operation. As water and benzyl acetate are formed, water will remain in the condenser drum, benzyl acetate and then benzyl alcohol will travel down the column. Water with some trace of acid will be trapped at the condenser drum and internal plates. After a certain time, the reacting volume will shift from the condenser drum to probably in middle to lower plates. The conversion level of acid will be a quite limited and the rate of reaction will be slow due to the holdup amount in plates is small. As before, the concentration of BzAC product is varied from 0.830 to 0.845 mole fraction in each case, whereas, the product amount in the bottom tank is kept constant at 2.5 kmol so that the performance comparison of IBD column can be made with MVD column in terms of highest achievable conversion of acetic acid, and maximum annual revenue. The optimization results in terms of reboil ratio, which maximizes the process profitability via the minimization of the batch time subject to constraints on the amount and quality of BzAC at the final batch time are summarized in Table 8.4. It was found that all values of optimum reboil ratio, and the batch time with the maximum composition of BzAC, as well as total yearly profit, increase gradually with increasing the BzAC purities.

A comparison of the results between the BzAC concentration and the net annual revenue using the IBD mode and the MVD column (Table 8.3) shows that for the same product quantity in the bottom tank (2.5 kmol), the IBD mode produced BzAC at a higher quality (0.845 compared to 0.835 mole fraction) and acquired more profit (107936 as opposed to only 387 $/yr).

Table 8.4 Summary of Optimization Results for IBD Column

Product Quality of BzAC	Optimum Reboil Ratio, R	Conversion of AA (%)	Final Batch time, t_F, hr	Number of Batches, batch/yr	Product Demand PD, kmol/yr	Total Annual Profit, $/yr
0.830	0.931	84.05	12.57	612	1530	27857
0.835	0.937	84.39	13.85	557	1394	45552
0.840	0.942	84.72	15.38	504	1259	86113
0.845	0.948	85.06	17.27	450	1125	107936

8.5.4 CBD Column

A series of maximum profitability problems were solved at different values of bottom product quality and the effect of time dependent reflux ratio strategy on the product purity, and the operating batch time, as well as the maximum achievable revenue. Note, two cases are considered here, one (Case 1) with one-reflux interval and the second one (Case 2) with two-reflux intervals strategy of operation. The quality of BzAC product is varied from 0.830 to 0.845 mole fraction in each case, whereas, the product amount in the reboiler drum remains the same at 2.5 kmol so that the performance comparison of CBD mode can be made with IBD mode in terms of maximum achievable conversion of acetic acid, operation batch time, and highest annual revenue.

8.5.4.1 Case 1: Optimal Operation using Single-Control Interval

For the bottom product concentrations considered, the summary of optimization results including optimum reflux ratios profile, the processing-batch time, the conversion ratio of acid, the number of batches, and yearly product demand, and the annual profit for the CBD mode are shown in Table 8.5. It is obvious form Table 8.5 that the employ of CBD column is found to outperform the IBD column in many aspects.

For example, at 0.845 molefraction quality, the savings in the operating batch time is almost 15.56%, and the enhancement in conversion level is about 7.97%, as compared to IBD column. It is realised form Table 8.5 that the total yearly product demand improved is around 15.12% at product concentration of 84.50% compared to that obtained by the IBD process. In addition, for the 0.845 of BzAC purity case, comparison of the maximum annual profit for the CBD mode with those obtained using IBD shows 18.57% more profit due to lower production time required to achieve the desired composition constraints. However, for 0.845 of product purity, there is a sharp decrease in the product profit due to significant increase in the reflux ratio and operating batch time (compared to others). This makes even CBD using single-reflux strategy uncompetitive operation at maximum BzAC purity and hence the suggested multi-reflux strategy.

Table 8.5 Summary of Optimization Results for CBD Column using NCI = 1

Product Quality of BzAC	Optimal Reflux Ratio, R	Final Batch time, t_F, hr	Maximum Conversion of Acid (%)	Number of Batches, batch/yr	Product Demand PD, kmol/yr	Total Yearly Revenue, $/yr
0.830	0.390	1.51	88.00	3986	9965	347991
0.835	0.541	2.01	88.70	3192	7980	403510
0.840	0.755	3.76	89.87	1879	4697	403605
0.845	0.937	14.58	92.43	530	1326	132552

Table 8.6 summaries the results (for MVD, IBD, and CBD columns) in terms of optimal operating time and maximum achievable revenue for each product purity using single control operation. Figure 8.1 shows the total minimum batch time for different product compositions using three batch columns. From Table 8.6 and Figure 8.1, it can be seen that the CBD process is more effective operation than IBD and MVD columns in terms of operating batch time and annual profit.

Table 8.6 Summary of the Results for MVD, IBD, and CBD columns

	MVD Column		IBD Column		CBD Column	
Purity of BzAC	Batch time, t_F, hr	Annual Profit, $/yr	Batch time, t_F, hr	Annual Profit, $/yr	Batch time, t_F, hr	Annual Profit, $/yr
0.830	24.44	235	12.57	27857	1.51	347991
0.835	35.04	387	13.85	45552	2.01	403510
0.840	---[a]	---[a]	15.38	86113	3.76	403605
0.845	---[a]	---[a]	17.27	107936	14.58	132552

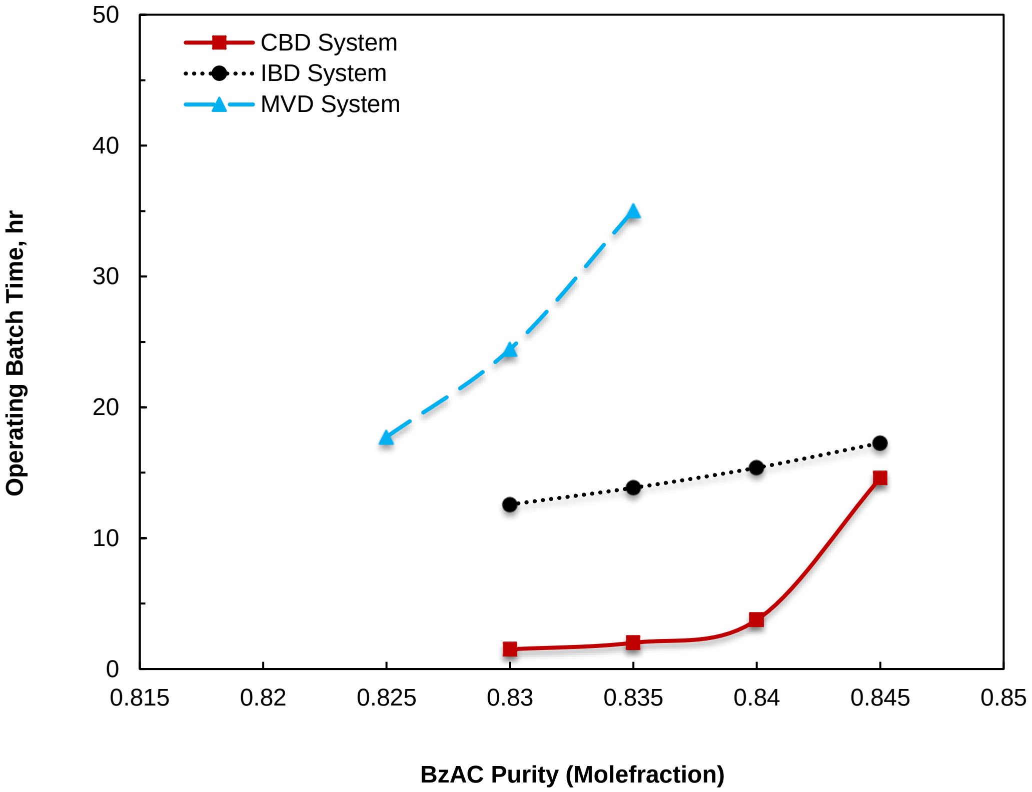

Figure 8.1 The operating batch time profile for three different batch systems

The mixture concentration profiles in the distillate tank and still pot are shown in Figures 8.2, and 8.3 for the BzAC composition (x^*_{BzAC} = 0.845 mole fraction) for the CBD process using a single-control policy. As it can be noted from Figure 8.3 that the mole fraction of water (the lower boiling component) increases from zero and reaches the maximum point and then drops to almost zero due to its removal in the accumulator tank (see Figure 8.2).

As can be seen form Figure 8.2 that, it is mainly water and trace amount of acetate in the distillate tank. Benzyl alcohol reactant (2nd heaviest boiling component) is gradually consumed by the reaction with acetic acid in the still pot tank. As the operating time proceeds, more benzyl acetate (BzAC) is formed at the bottom of distillation column as the heaviest boiling product (Figure 8.3).

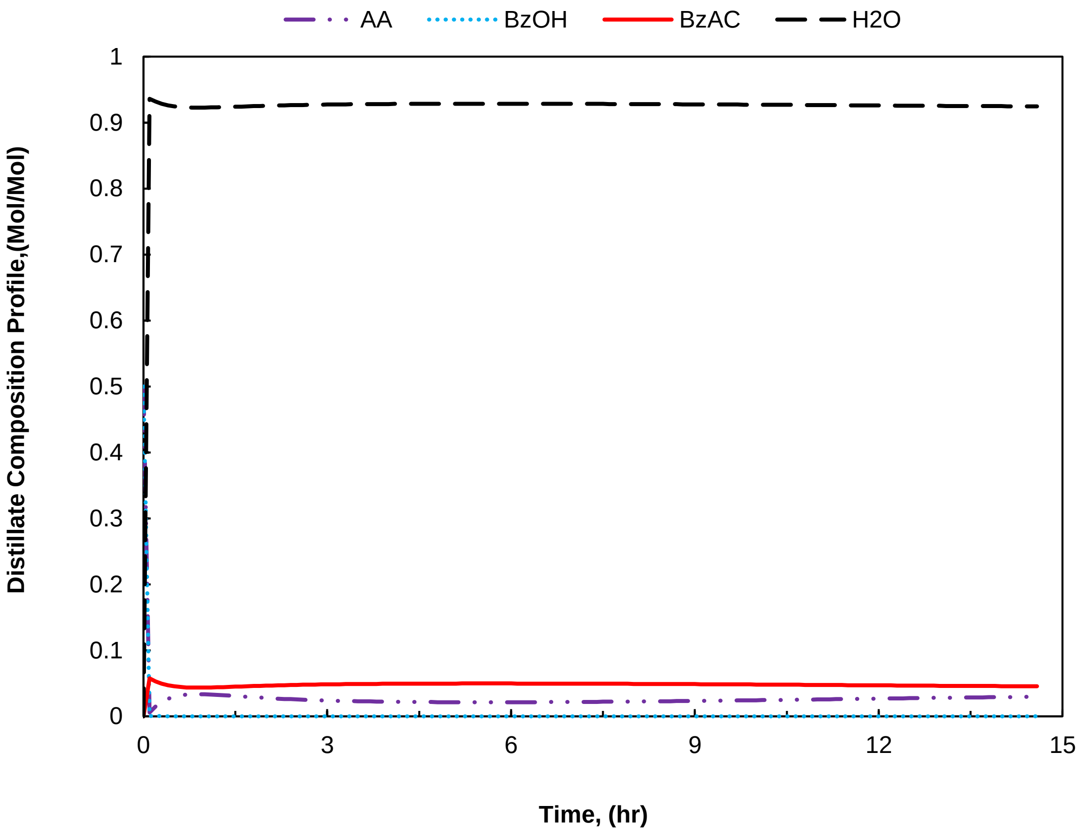

Figure 8.2 The distillate composition of CBD, one-control interval

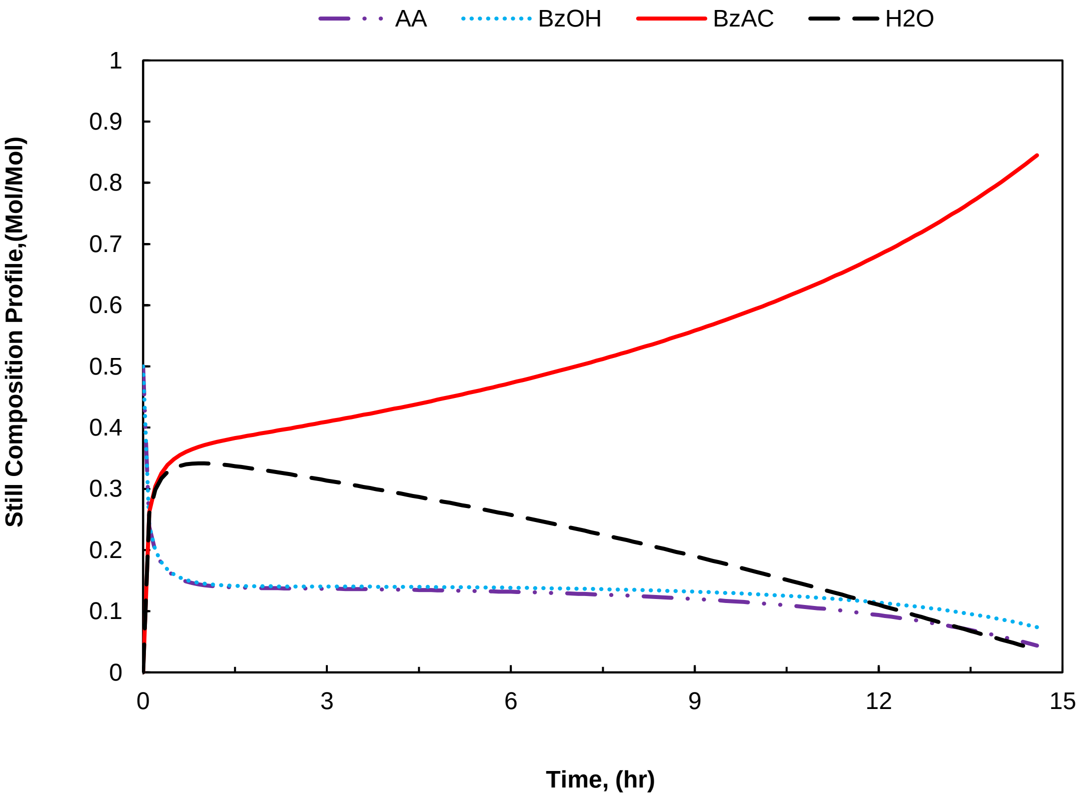

Figure 8.3 The still composition of CBD, one-control interval

8.5.4.2 Case 2: Optimal Operation using Two-Control Intervals

Two reflux intervals policy of operation is used in this work. For each purity consideration, Table 8.7 shows the optimum operation results in terms of reflux ratios, switching time, conversion rate of acetic acid, total batch time, the total number of batches produced over year, and annual production rate, as well as the total yearly profit to meet the product within the specifications. It is clear from Table 8.7 that the use of multi-reflux policy resulted considerable reduction in the operating batch time, and higher improvement in the process revenue as compared to the one-reflux CBD operation (Table 8.5).

For example, at 0.845 mole fraction concentration the saving in batch time is nearly 35.96%, and the improvement in maximum yearly profit is around 39.55%, as compared to one-control CBD system. It is noticed from Table 8.7 that the total annual product demand improved is about 34.76% at product composition of 84.5% compared to that obtained by the one-control CBD column. It can be seen from Table 8.7 that for each quality requirement, the CBD operation operates at lower reflux ratio for the first-time interval to remove water as quickly as it is produced as the distillate product. Higher reflux ratio is required in the second interval to retain both reactants benzyl alcohol and acetic acid in the reaction region to have further reaction.

Table 8.7 Summary of Optimization Results for CBD Column using NCI = 2

Product Quality of BzAC	Optimal Reflux Ratios R_1, R_2	Batch Time Intervals t_1, t_2, hr	Conversion of acid (%)	Final Batch time, t_P, hr	Number of Batches, batch/yr	Product Demand PD, kmol/yr	Total Yearly Revenue, $/yr
0.830	0.335, 0.685	1.30, 0.18	87.98	1.48	4048	10119	353851
0.835	0.463, 0.993	1.71, 0.10	88.62	1.81	3459	8648	439854
0.840	0.680, 0.996	2.87, 0.13	89.60	3.00	2287	5717	497804
0.845	0.891, 0.989	8.34, 1.00	91.69	9.34	813	2032	219289

Figures 8.4 and 8.5 present the concertation profiles in the accumulator tank and reboiler drum at the BzAC composition (x^{*}_{BzAC} = 0.845 mole fraction) for CBD process using two-control policy.

As the operating time increases, benzyl acetate is synthesised in the still pot and water is removed more quickly from the bottom tank.

For the two control intervals, Figure 8.5 shows clearly that the maximum concentration of benzyl acetate attained is 0.845 mole fraction at 9.34 hours against 0.845 mole fraction of benzyl acetate shown in Figure 8.3 for one-control interval, which was attained at a much later time of about 14.58 hours.

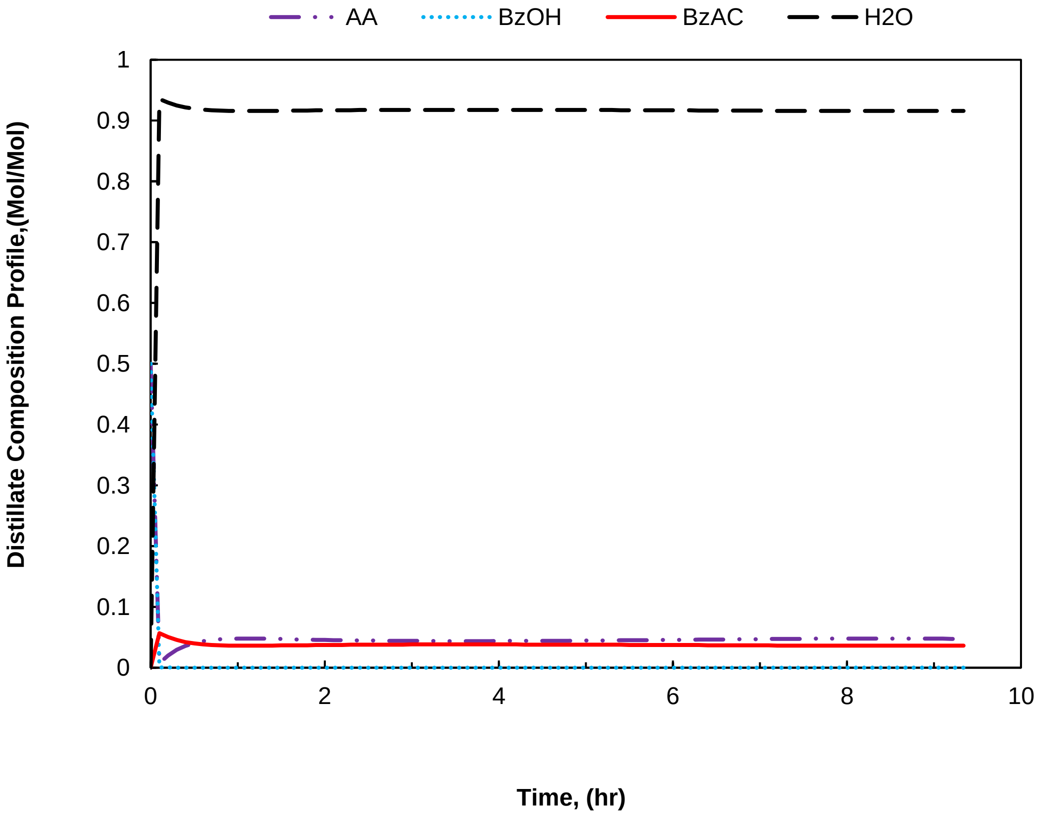

Figure 8.4 The distillate composition of CBD, two-control intervals

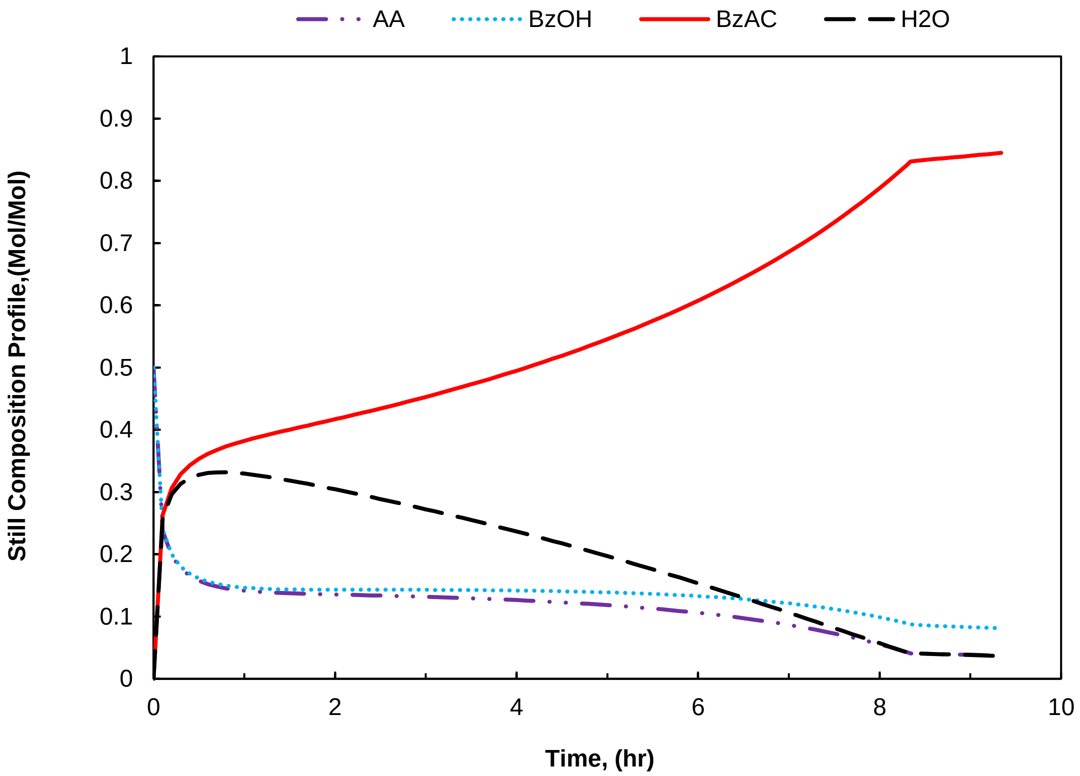

Figure 8.4 The still composition of CBD, two-control intervals

8.6 Conclusions

In this chapter, the performances of different types of batch reactive column configurations are evaluated in terms of maximum profitability via minimisation of production time under single and multi-reflux intervals modes for the synthesis of benzyl acetate through the esterification reaction of acetic acid and benzyl alcohol. Control variables (reflux ratio and/or reboil ratio) are used as a piecewise constant, which are discretised using CVP method.

A dynamic optimization problem is developed incorporating the process model within gPROMS software. The product amount and its purity are employed as operating constraints.

Observation results using single-reflux strategy (for CBD) and reboil ratio (for IBD and MVD) show that CBD is more suitable than both MVD and IBD columns in terms of minimum operating time, maximum conversion rate, and maximum annual revenue.

In addition, the optimization results clearly demonstrate that the use of two-control operation is more promising option compared to the single-control interval in CBD system in terms of minimum batch time and maximum achievable profit improvement.

Chapter Nine

Conclusions and Future Work

9.1 Conclusions

This work focused on the modelling and optimisation of conventional and unconventional batch distillation systems for the synthesis of a number of esters (such as methyl lactate, methyl decanoate, ethyl benzoate, and benzyl acetate) via the esterification reaction. The main factors investigated in this research were:

1. Minimizing the operating batch time.
2. Maximizing the profitability.
3. Minimizing the energy consumption rate.

The four esterification reaction schemes were studied in this work as shown in Table 9.1.

Table 9.1 The reaction scheme for all esterification reactions

Methyl Lactate Scheme

Lactic Acid + Methanol <==> Methyl Lactate + Water

Methyl Decanoate Scheme

Decanoic Acid + Methanol <==> Methyl Decanoate + Water

Ethyl Benzoate Scheme

Benzoic Acid + Ethanol <==> Ethyl Benzoate + Water

Benzyl Acetate Scheme

Acetic Acid + Benzyl Alcohol <==> Benzyl Acetate + Water

The synthesis of methyl lactate via the esterification of lactic acid with methanol was carried out using conventional, integrated conventional, semi-batch, and integrated semi-batch distillation columns. The synthesis of methyl decanoate via esterification of decanoic acid with methanol was carried out using different types of batch reactive systems (such as conventional, integrated conventional, semi-batch, integrated semi-batch, divided-wall, split reflux divided-wall, and integrated divided-wall distillation columns). The synthesis of ethyl benzoate via esterification of benzoic acid with ethanol was carried out using conventional, and integrated conventional batch distillation processes. The synthesis of benzyl acetate via the esterification of acetic acid and benzyl alcohol was carried out using middle-vessel, inverted, and conventional batch distillation operations. Different types of dynamic optimisation problems were formulated which included a detailed process model and was transformed into non-linear programming (NLP) problem by Control Vector Parameterisation (CVP) method, which is solved using a SQP-based technique within gPROMS software (2017).

The following conclusions are drawn from this work.

Chapter Five

The synthesis of methyl lactate via the esterification of lactic acid and methanol was carried out using both conventional and semi-batch distillation processes. Due to the separation of methanol from lactic acid in a conventional batch column because of the wide difference in boiling points between the reactants, the use of conventional batch distillation column was limited. With the loss of methanol (one of the forward reaction elements), the backward reaction was being activated along the process decreasing conversion of acid massively. Therefore, a semi-batch distillation column was used to overcome interaction between the reactants and to improve the conversion level. The optimum operations of conventional and semi-batch distillation modes were evaluated in terms of minimum operating batch. It was found clearly that the semi-batch distillation column outperformed the classical regular batch column in terms of higher product purity and maximum conversion ratio of lactic acid.

Two new integrated conventional and integrated semi-batch column configurations were considered to maximise the profitability for the optimal synthesis of methyl lactate. Both piecewise constants reflux ratio together with the rate of methanol feed were considered. It was found that the integrated semi-batch distillation process performed better than the integrated conventional batch distillation process to accomplish the maximum product purity of methyl lactate with lower batch time and energy usage, and maximum achievable annual profit. The multi reflux operation was found to be more effective than single-reflux operation in terms of batch time and energy savings, with highest achievable revenue in the i-SBD operation.

Chapter Six

Different types of batch reactive distillation systems (e.g. conventional and unconventional configurations) for the synthesis of methyl decanoate were considered. The conventional distillation columns include regular, integrated conventional, and semi-batch distillation columns; whereas, the unconventional columns are divided-wall, split reflux divided-wall, and integrated divided-wall batch distillation. The performance of these column configurations was evaluated in terms of minimum energy expense under single and multi-control intervals strategies. For the conventional batch systems, it was found from the results that the integrated conventional batch mode performed better than the semi-batch distillation column at the excess feed ratio, while, the semi-batch distillation operation performed better than the integrated conventional batch column at the equimolar feed ratio to fulfil the specified product constraints with the shorter batch time and total energy usage. Also, at high heat duty and catalyst loading amount, big reductions in the operating time can be accomplished for both column configurations.

In unconventional modes, the results showed that the integrated divided-wall batch operation outperformed all the classical conventional, divided-wall, and split reflux divided-wall batch configurations by achieving the highest product quality of methyl decanoate and maximum conversion rate of acid. For all batch modes, the results indicated that the multi-control operation helped retaining reactants in the column leading to further reaction conversion and production of methyl decanoate compared to the cases with single-control interval.

Chapter Seven

The synthesis of ethyl benzoate via esterification reaction of benzoic acid and ethanol was carried out using both conventional and integrated conventional batch distillation processes. Two case studies were considered with different feed concentrations. However, the classical traditional reactor-batch distillation system was used to achieve the desired product specifications. The optimization problem was formulated in terms of minimum batch time for a defined separation task. The optimization results showed that, the reactive distillation operation was found to outperform the traditional reactor-batch distillation mode by accomplishing higher conversion rate of benzoic acid, and higher quality of ethyl benzoate with lower batch time and less energy demand. Also, the performance of a conventional batch distillation column was superior to the integrated conventional batch distillation column at the excess ethanol in the feed in terms of batch time and energy usage rate, as well as the conversion rate of acid. While, with the equimolar feed ratio, the use of integrated conventional batch distillation process improved significantly the process proficiency by achieving maximum product purity and higher conversion ratio as compared to those obtained by using conventional batch distillation operation. Furthermore, the multi-control policy was found to be more effective than single-control operation for the integrated conventional batch distillation column.

Chapter Eight

The esterification of acetic acid and benzyl alcohol producing benzyl acetate and water was considered using middle-vessel, inverted, and conventional batch distillation columns for the first time. The profitability via the minimisation of batch time was used as a performance measure. Piecewise constants: the reflux ratio (for middle-vessel, and conventional columns) and reboil ratio (for middle-vessel, and inverted columns) were optimised. The optimisation results indicated that the conventional batch distillation process was more powerful than other operations in terms of minimum production time and maximum yearly profit. In addition, the lower reflux operation for conventional mode was good enough to keep the chemical reactants in the reaction region; higher reboil operation was needed for the inverted mode for the same purpose. For the certain benzyl acetate quality, thus inverted column required more operating batch time.

9.2 Future Work

Although, significant progress has been reported in this thesis, there still remains some suggestions for future work, which are outlined below.

- The impact of reaction kinetics and phase equilibria models available in the literature for chosen esterification schemes employing rigorous and simple models should be investigated further for future work.
- The effect of total catalyst amount on the overall process performance should be investigated.
- Only reversible reaction systems were considered in this work. Irreversible reaction systems can be studied in future work.
- gPROMS Process Builder can be the next-generation advanced process modelling environment for control studies and optimization of the operations of process plants.
- The optimal operation policies of batch distillation columns were studied based on a single objective function problem. However, different types of optimization techniques such as Neural Network, MINLP, and Genetic Algorithm can be investigated in future.
- The use of computational fluid dynamics (CFD) can also be employed in this study.
- The use of Aspen Plus/Hysys can also be employed in future work.
- Optimization of column configurations in terms of minimum batch time/thermal energy usage or maximum profitability for the esterification

processes has been studied. Minimum total annual cost problem for such reaction schemes can also be considered in future work.

- The integrated divided-wall batch column has been used only for the optimal synthesis of methyl decanoate as a promising option. This type of column configuration can be further utilised for different reaction systems.

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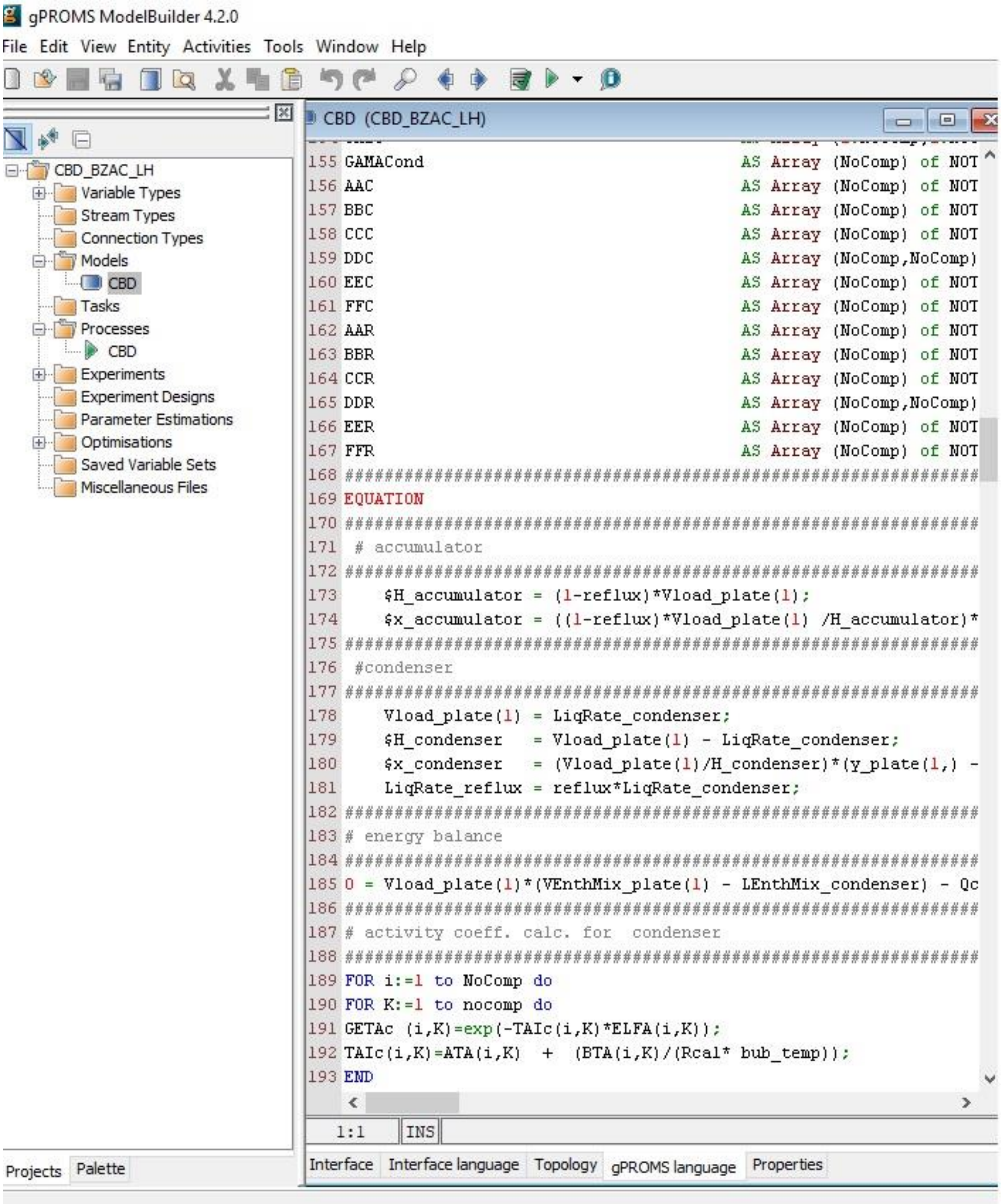
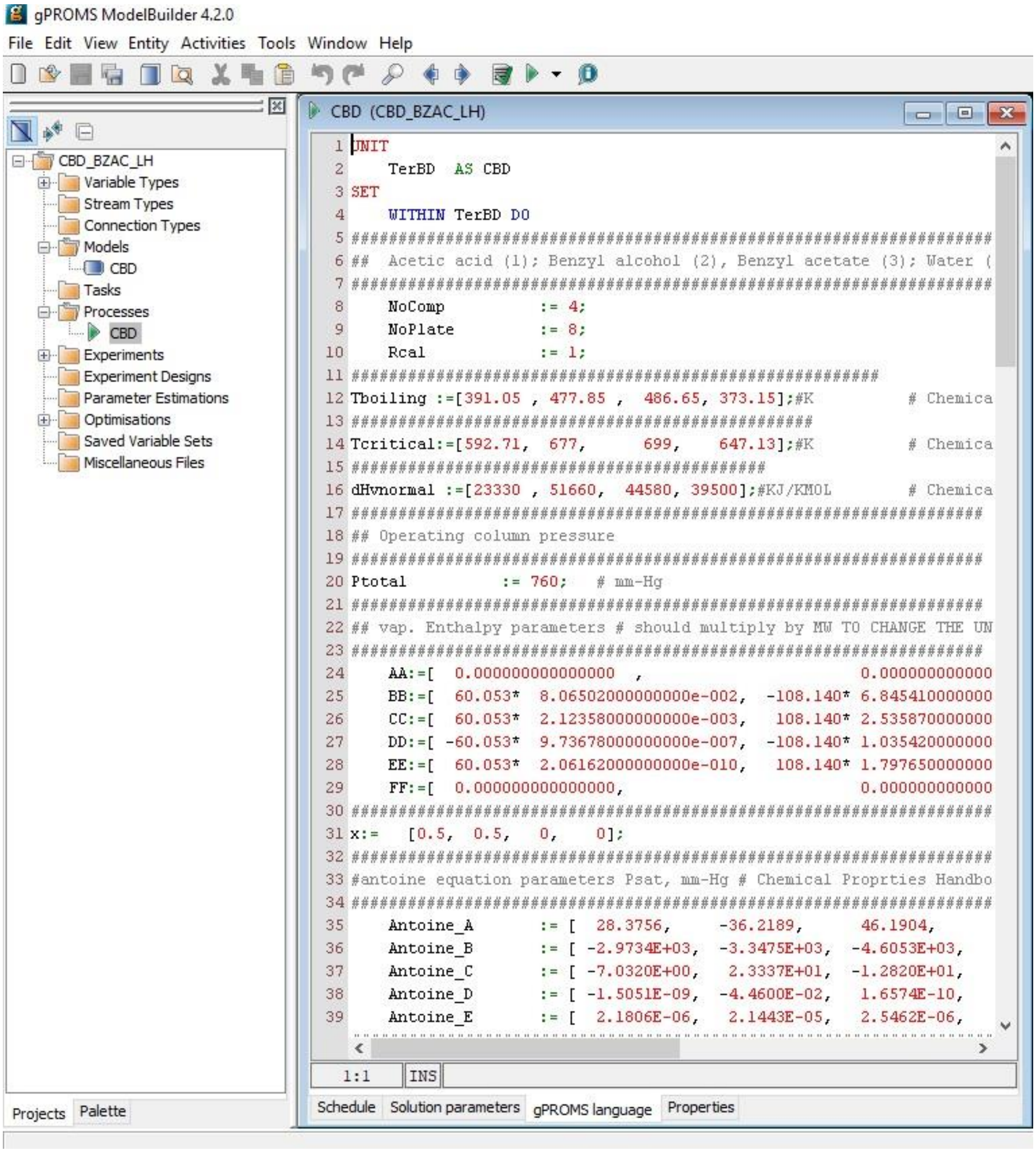
Appendix A

gPROMS Platform for the Batch Process Model



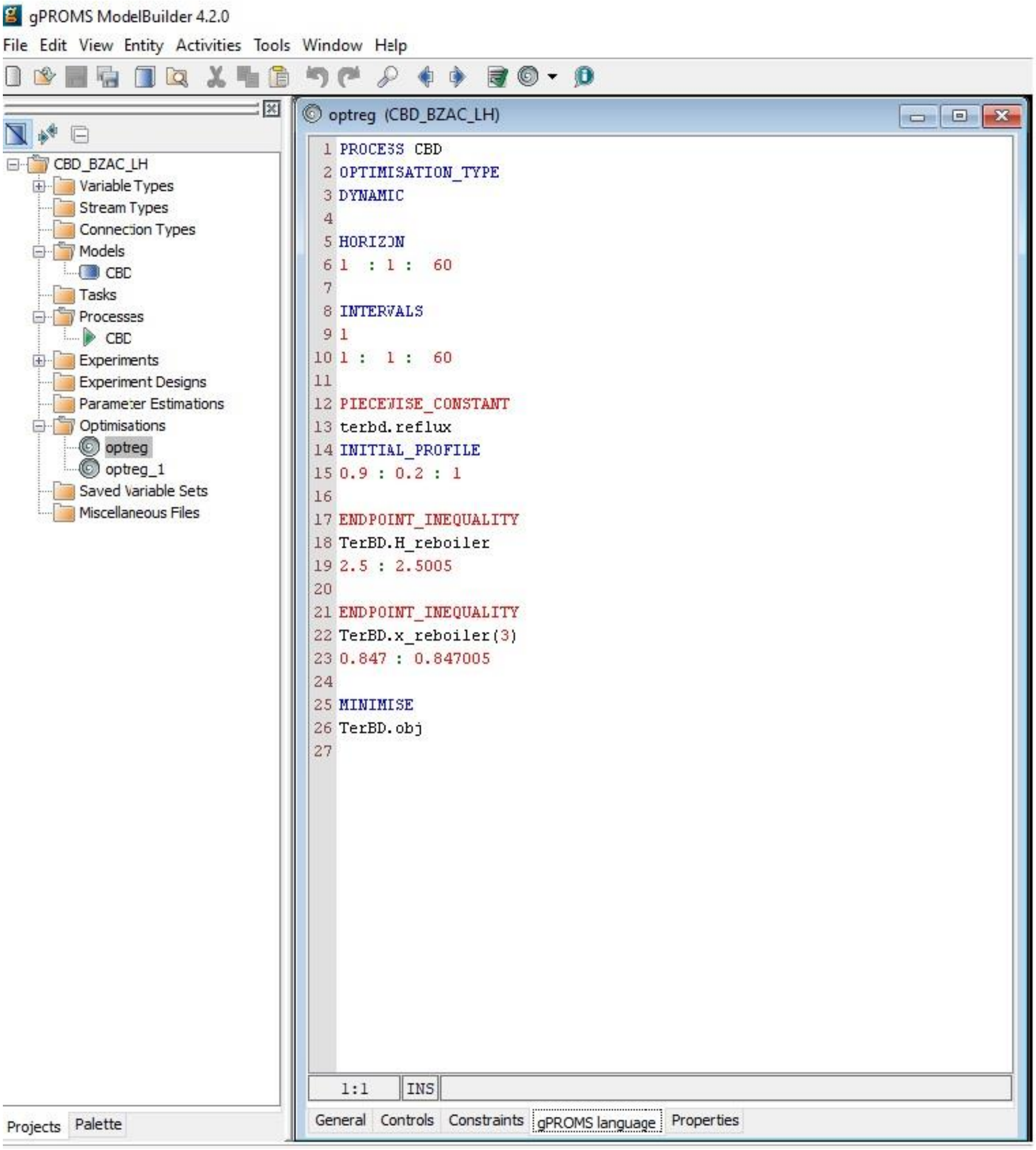
```
GAMACond                                AS Array (NoComp) of NOT
AAC                                     AS Array (NoComp) of NOT
BBC                                     AS Array (NoComp) of NOT
CCC                                     AS Array (NoComp) of NOT
DDC                                     AS Array (NoComp,NoComp)
EEC                                     AS Array (NoComp) of NOT
FFC                                     AS Array (NoComp) of NOT
AAR                                     AS Array (NoComp) of NOT
BBR                                     AS Array (NoComp) of NOT
CCR                                     AS Array (NoComp) of NOT
DDR                                     AS Array (NoComp,NoComp)
EER                                     AS Array (NoComp) of NOT
FFR                                     AS Array (NoComp) of NOT
################################################################
EQUATION
################################################################
 # accumulator
################################################################
    $H_accumulator = (1-reflux)*Vload_plate(1);
    $x_accumulator = ((1-reflux)*Vload_plate(1) /H_accumulator)*
################################################################
 #condenser
################################################################
    Vload_plate(1) = LiqRate_condenser;
    $H_condenser   = Vload_plate(1) - LiqRate_condenser;
    $x_condenser   = (Vload_plate(1)/H_condenser)*(y_plate(1,) -
    LiqRate_reflux = reflux*LiqRate_condenser;
################################################################
# energy balance
################################################################
0 = Vload_plate(1)*(VEnthMix_plate(1) - LEnthMix_condenser) - Qc
################################################################
# activity coeff. calc. for  condenser
################################################################
FOR i:=1 to NoComp do
FOR K:=1 to nocomp do
GETAc (i,K)=exp(-TAIc(i,K)*ELFA(i,K));
TAIc(i,K)=ATA(i,K)  +  (BTA(i,K)/(Rcal* bub_temp));
END
```

Figure A.1 Screenshot showing the gPROMS model entity for the production of BzAC



```
UNIT
    TerBD  AS CBD
SET
    WITHIN TerBD DO
####################################################################
##  Acetic acid (1); Benzyl alcohol (2), Benzyl acetate (3); Water (
####################################################################
    NoComp          := 4;
    NoPlate         := 8;
    Rcal            := 1;
########################################################
Tboiling :=[391.05 , 477.85 ,  486.65, 373.15];#K          # Chemica
#################################################
Tcritical:=[592.71,  677,      699,    647.13];#K          # Chemica
############################################
dHvnormal :=[23330 , 51660,  44580, 39500];#KJ/KMOL        # Chemica
###################################################################
## Operating column pressure
###################################################################
Ptotal          := 760;   # mm-Hg
###################################################################
## vap. Enthalpy parameters # should multiply by MW TO CHANGE THE UN
###################################################################
    AA:=[  0.000000000000000  ,                          0.000000000000
    BB:=[  60.053*  8.06502000000000e-002,  -108.140* 6.845410000000
    CC:=[  60.053*  2.12358000000000e-003,   108.140* 2.535870000000
    DD:=[ -60.053*  9.73678000000000e-007,  -108.140* 1.035420000000
    EE:=[  60.053*  2.06162000000000e-010,   108.140* 1.797650000000
    FF:=[  0.000000000000000,                          0.000000000000
####################################################################
x:=   [0.5,  0.5,   0,    0];
####################################################################
#antoine equation parameters Psat, mm-Hg # Chemical Proprties Handbo
####################################################################
    Antoine_A       := [  28.3756,     -36.2189,      46.1904,
    Antoine_B       := [ -2.9734E+03,  -3.3475E+03,  -4.6053E+03,
    Antoine_C       := [ -7.0320E+00,   2.3337E+01,  -1.2820E+01,
    Antoine_D       := [ -1.5051E-09,  -4.4600E-02,   1.6574E-10,
    Antoine_E       := [  2.1806E-06,   2.1443E-05,   2.5462E-06,
```

Figure A.2 Screenshot showing the gPROMS process entity for the production of BzAC



```
PROCESS CBD
OPTIMISATION_TYPE
DYNAMIC

HORIZON
1  : 1 :  60

INTERVALS
1
1 :  1 :  60

PIECEWISE_CONSTANT
terbd.reflux
INITIAL_PROFILE
0.9 : 0.2 : 1

ENDPOINT_INEQUALITY
TerBD.H_reboiler
2.5 : 2.5005

ENDPOINT_INEQUALITY
TerBD.x_reboiler(3)
0.847 : 0.847005

MINIMISE
TerBD.obj

```

Figure A.3 Screenshot showing the gPROMS optimization entity for the production of BzAC

Appendix B

Author's Publications Made from This Work

1. Aqar, D.Y., Rahmanian, N. and Mujtaba, I.M., **2016**. Methyl lactate synthesis using batch reactive distillation: Operational challenges and strategy for enhanced performance. Separation and Purification Technology, 158, pp.193-203.
2. Aqar, D.Y., Rahmanian, N. and Mujtaba, I.M., **2016**. Integrated batch reactive distillation column configurations for optimal synthesis of methyl lactate. Chemical Engineering and Processing: Process Intensification, 108, pp.197-211.
3. Aqar, D.Y., Rahmanian, N. and Mujtaba, I.M., **2016**. Optimal design and operation of semi-batch reactive distillation for methyl lactate synthesis with fixed product demand. In Computer Aided Chemical Engineering (Vol. 38, pp. 895-900). Elsevier.
4. Aqar, D.Y., Rahmanian, N. and Mujtaba, I.M., **2017**. Synthesis of methyl decanoate using different types of batch reactive distillation systems. Industrial & Engineering Chemistry Research, 56(14), pp.3969-3982.
5. Aqar, D.Y., Rahmanian, N. and Mujtaba, I.M., **2017**. Feasibility of integrated batch reactive distillation columns for the optimal synthesis of ethyl benzoate. Chemical Engineering and Processing: Process Intensification, 122, pp.10-20.
6. Aqar, D.Y., Rahmanian, N. and Mujtaba, I.M., **2017**. Significant Profitability Improvement for Methyl Decanoate Production using Different Types of Batch Distillation. Chemical Engineering Transactions, 57.

7. Aqar D.Y., Rahmanian N., Elmahboub E., Mansour E., Mujtaba I.M., **2017**. Exploitation of Integrated Batch Reactive Distillation Columns for a Number of Chemical Reaction Systems. Proceedings of the International Conference on Chemical Engineering (ICChE2017), Dhaka, Bangladesh.
8. Aqar, D.Y., Rahmanian, N. and Mujtaba, I.M., **2018**. Feasibility of novel integrated dividing-wall batch reactive distillation processes for the synthesis of methyl decanoate. Separation and Purification Technology, 202, pp.200-215.
9. Aqar, D.Y., Rahmanian, N. and Mujtaba, I.M., **2018**. Investigation about Profitability Improvement for Synthesis of Benzyl Acetate in Different Types of Batch Distillation Columns. Chemical Engineering Transactions, 70.