

การออกแบบไมซ์หอกลั่นแบบเบตซ์ที่มีปฏิริยาภายใต้ขอบเขตกระบวนการเพื่อลดการใช้พลังงาน



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OPTIMIZATION OF A BATCH REACTIVE DISTILLATION COLUMN WITH
PROCESS CONSTRAINTS FOR SAVING OF ENERGY CONSUMPTION



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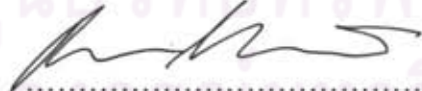
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กระบวนการกลั่นที่รวมเอาปฏิริยาเคมีและหอกลั่นเข้าด้วยกันได้รับความสนใจใน
อุตสาหกรรมอย่างแพร่หลาย เนื่องจากมีข้อดีที่เหนือกว่าการกลั่นแยกแบบธรรมดาหลายประการ
ต่อมาจึงมีการนำเทคนิคการออกแบบมาประยุกต์ใช้ร่วมกับการกลั่นเพื่อประโยชน์ในหลายด้าน
เช่น เพิ่มปริมาณผลิตภัณฑ์ ลดการใช้วัตถุดิบ ลดของเสียต่างๆที่มีผลกระทบต่อสิ่งแวดล้อม และ
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ในหลายปีที่ผ่านมา การใช้พลังงานไม่ได้ถูกพิจารณาพร้อมกับกระบวนการออกแบบหอกลั่น
ของหอกลั่นแบบแบดซ์ที่มีปฏิริยา ส่งผลให้ค่าใช้จ่ายเพิ่มสูงขึ้นและผลิตภัณฑ์ที่กลั่นได้มีความ
บริสุทธิ์เพียง 80 เปอร์เซ็นต์เท่านั้น ดังนั้นงานวิจัยนี้จึงศึกษาการออกแบบหอกลั่นแบบ
แบดซ์ที่มีปฏิริยาเคมี โดยให้ความร้อนแก่ระบบคงที่ตลอดการดำเนินงานเป็นเวลา 16 ชั่วโมง
เพื่อหาสภาวะที่เหมาะสมของรีฟลักซ์และพลังงานความร้อน ที่ทำให้ได้ปริมาณผลิตภัณฑ์มาก
ที่สุด ในขณะที่ใช้พลังงานความร้อนน้อยที่สุด ภายใต้เงื่อนไขความบริสุทธิ์ของเอทิลอะซิเตท
สูงกว่า 90 เปอร์เซ็นต์ จากการออกแบบพบว่า จำนวนช่วงเวลา ฟังก์ชันวัตถุประสงค์ และ
จำนวนตัวแปรตัดสินใจ ล้วนเป็นปัจจัยที่มีผลต่อปริมาณผลิตภัณฑ์และพลังงานความร้อนที่ใช้
ทั้งสิ้น โดยจำนวนช่วงเวลาของตัวแปรตัดสินใจเพิ่มขึ้น ส่งผลให้ปริมาณผลิตภัณฑ์สูงขึ้น ทำให้
ระบบใช้พลังงานความร้อนลดลง รวมทั้งได้ผลกำไรเพิ่มขึ้นด้วย และเมื่อเปรียบเทียบปัญหา
ทั้งหมดพบว่าการออกแบบหอกลั่นของปัญหาผลิตภัณฑ์สูงสุด ในขณะที่ใช้พลังงานความร้อนน้อยที่สุด
ใช้สัดส่วนรีฟลักซ์และความร้อนจากหม้อต้มเป็นตัวแปรตัดสินใจสำหรับ 8 ช่วงเวลา ใช้พลังงาน
ความร้อนต่อมวลของผลิตภัณฑ์น้อยที่สุด ในขณะที่ปัญหาผลิตภัณฑ์สูงสุด ใช้สัดส่วนรีฟลักซ์
และความร้อนจากหม้อต้มเป็นตัวแปรตัดสินใจสำหรับ 16 ช่วงเวลา ได้ผลิตภัณฑ์ปริมาณมาก
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BENJAMARD SACHARERN : OPTIMIZATION OF A BATCH
REACTIVE DISTILLATION COLUMN WITH PROCESS
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The hybrid process integrating chemical reaction with the distillation column has been increasingly received much interest in many industries because it has many advantages. The optimization technique is applied with a batch reactive distillation for increased efficiency of the production system such as increased products, decreased raw material, reduced waste and reduced energy consumption.

In many past year, the energy consumption is not be considered in the optimization process with a batch reactive distillation column leading to increased cost operation and the distilled product with only 80% maximum by mole of the ethyl acetate. Thus, this work presents the optimization of a batch reactive distillation column by operating constant heat duty for 16 hr. The aims of optimization are to compute the optimal reflux ratio and the heat duty in order to obtain the maximization amount of ethyl acetate by saving heat energy consumption subject to 90% of product purity and fixed batch time. The number of time interval, the objective function and the number of decision variable are the factors affecting the amount of desired product and the energy consumption. The amount of the desired product increases and the profit increases whereas the energy consumption decreases when a number of intervals increase. In addition, the maximum product and minimum heat duty problem by manipulating reflux ratio and heat duty for 8 intervals uses the minimum of energy consumption per amount of desired product whereas the maximum product by manipulating heat duty for 16 intervals achieves the maximum amount of desired product.

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LIST OF ABBREVIATIONS

a, b, c, d, e	=	Specific heat of liquid constant for each component
A_d, B_d	=	Correlation constants for each component
B_0	=	initial amount of the reboiler charge (kmol)
C_{pL}	=	heat capacity of liquid (kJ/kmol.K)
h_j^V	=	enthalpy of vapor leaving n th plate (kJ/kmol)
h_j^L	=	enthalpy of liquid leaving n th plate (kJ/kmol)
H_a	=	amount of product in accumulator (kmol)
H_c	=	amount of product in condenser (kmol)
H_j	=	amount of product j th plate (kmol)
H_N	=	amount of product in reboiler (kmol)
k	=	rate constants
k_r	=	array of reaction rate constants
K	=	vapor-liquid equilibrium constant
L	=	flow rate of liquid (kmol/h)
L_1	=	flow rate of liquid feed back (kmol/h)
L_D	=	flow rate of liquid to accumulator (kmol/h)
MW	=	molecular weight (kg/kmol)
P	=	pressure (bar)
Q_C	=	condenser duty (kJ/h)
Q_R	=	reboiler heat duty (kJ/h)
r	=	reaction rate (1/h)
R, r_f	=	internal reflux ratio
t	=	batch time (h)
T	=	temperature (K)
T_c	=	critical temperature (K)
V_1	=	flow rate of vapor in condenser (kmol/h)

V	=	flow rate of vapor (kmol/h)
x	=	mole fraction of liquid
x_{B0}	=	mole fraction of liquid in the reboiler charge
x_a	=	mole fraction of liquid in accumulator
x_D	=	mole fraction of liquid in condenser
y	=	mole fraction of vapor

Greek Letters

ω_i	=	acentric factor of component i
ρ_i	=	density of component i (g/cc.)
Δn	=	total of reaction (1/h)

Subscript and Superscript

i	=	component number (1,2,...,n)
j	=	plate number (1,2,...,N)
N	=	reboiler
B	=	the bottom
C	=	the condenser
1	=	acetic acid
2	=	ethanol
3	=	ethyl acetate
4	=	water

CHAPTER I

INTRODUCTION

1.1 Importance and Reasons for Research

A batch distillation is the oldest liquid mixtures separation using the difference of boiling points of matters. A batch distillation is often carried out for chemical industries under conditions of production such as low capacity, small amounts, high value and uncertain season over many years. To improve effectiveness of the batch process, the reactor and the distillation column are combined into one column called the *batch reactive distillation column*. It has the potential to reduce the capital investment cost, operating costs and the environmental emissions. Moreover, this process yields large quantities of desired products separated immediately and continuously when the reaction takes place in the column. The column is used in many industries such as the fine chemical industry, the pharmaceutical industry, the polymer industry, the biotechnological industry, and the food industry. A batch reactive distillation is an inherent complexity and a nonlinear dynamics. Consequently, the optimal control of the process is the function of times that the optimal criterion have a number of forms depending on a defined objective function. Also, the decision variables in optimization problem can be chosen, the most impacted on the system.

Optimization problem of a batch distillation process has many different formulations discussed in the literature: the maximum product problem (Mujtaba, 1999, Fernholz et al., 2000), the maximum distillate problem (Converse and Gross, 1963) and the minimum time problem (Cowerd, 1967, Kerkhof and Visser, 1978, and Logsdon et al., 1990). Generally, the problem is formulated in form of the maximum distillation without computing the optimal heat duty resulting on causing some problems in the process. For examples, when constraints of heat duty are not considered for maximum product problem, it leads to high energy consumption. In addition, those papers show a distilled product with only 80% maximum by mole of the ethyl acetate. Therefore, the optimization problem for the maximum product

and the minimum heat duty problem to produce ethyl acetate purity of 90% is developed in this thesis.

This study deals with the production of ethyl acetate via ethanol esterification and acetic within a batch reactive distillation column. Details of the research are divided into two sections. Firstly, it is the study of the dynamic behavior of the column consisting of a different operations and a sensitivity analysis. Secondly, it is the solving of dynamic optimization problem that involves both the maximum product and the minimum heat duty using the reflux ratio and the reboiler heat duty as control variables to give the product purity of 90% by mole of ethyl acetate.

1.2 Objectives of Research

1. Suitable profile of reflux ratios and heat duty are computed by fixed batch time to give maximum product and minimum heat duty.
2. Factor effecting to amount of product and energy consumption is studied.

1.3 Scope of Research

1. A rigorous model with chemical reaction in the research of Mujtaba and Maccheitto (1997) is applied.
2. Programs written to simulate and optimize the process are based on the MATLAB program.
3. Optimization problem of a batch reactive distillation column is studied.

1.4 Activity Plan

1. Study the relevant information regarding :
 - Literature review of batch reactive distillation

- Optimization techniques
 - Model base control strategy
2. Study MATLAB programming software for using to solve the optimization problem.
 3. Study the dynamic behavior of a batch reactive distillation.
 4. Optimize the problem for finding the optimal operation conditions of internal reflux ratio and heat duty.
 5. Analyze and summarize the result of the research.

1.5 Expected Benefits

1. The development of optimization problem for a batch reactive distillation column.
2. The suitable conditions of the optimal for the process.
3. The effective application of MATLAB for solving complex problems.

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CHAPTER II

LITERATURE REVIEW

2.1 Batch Reactive Distillation

A batch distillation is industrially important process operations. Composition monitoring and composition control play an essential role in these plants because the fine and specialty chemicals must be manufactured according to high and well defined the purity specifications. Depending on the market conditions and economic incentives, the kinds and the amounts of products can be readily changed with these operations. For increasing the efficiency of batch distillation, the chemical reaction and a distillation are combined into a single column called Batch REactive Distillation (BREAD), which is firstly patented by Backhaus since 1921. Several reviews, which have been published in the last decade, give an excellent introduction and overview of BREAD processes (Doherty and Buzad, 1992, Taylor and Krishna, 2000, Sakuth et al., 2001, and Worz and Mayer, 2001). They offered several advantages such as: increasing yield due to overcoming of chemical and thermodynamic equilibrium limitations, increasing selectivity through suppression of undesired consecutive reactions, reducing energy consumption via direct heat integration in case of exothermic reactions, avoidance of hot spots by simultaneous liquid evaporation, separation of close boiling components. These advantages become especially useful when the system under consideration involves reversible reactions, azeotropes and undesired product formations. Moreover, they can reduce capital investment and operating costs that were mentioned in research of Kim and Diwekar (2001), Venkateswarlu and Kumar (2006).

In many reactive batch distillation processes, the chemical reaction rates are the dominant factor in determining the process performance. The product formation and the composition profiles of reactive batch distillation change with the operating conditions over a wide range of values. The product withdrawal or the slop cut removal during the course of operation is taken based on the desired purity

specifications for the product. According to the operation, Venkateswarlu and Kumar (2006) found that batch process involves dynamic behavior from the beginning to the end.

2.2 Mathematical Model and Simulation

Batch process is a dynamic process with no steady state operating condition. Problems in the process are particularly difficult due to the dynamic interaction of thermodynamic properties, mass and heat transfer. Because of these difficulties, the simulating actual operation of the process has been the subject of research for half a century. Usually, the main interest is to develop the model (consisting of mass and energy balance, hydraulic model, physical properties, etc.) that could best predict the operation of the process.

Simple modelling of batch distillation, Rayleigh Model began to be well known (Rayleigh, 1902). The main issues was composed of the development of high speed digital computers and modelling. To simulate the actual operation of the columns, the modelling included energy balance, column holdup, plate hydraulics, accurate physical properties. After that, the modelling has been developed until the rigorous model was achieved. This model explains the actual operation widely used in many research of batch distillation. Details of the model, such as chemical reaction, mass and energy transfer, can be varied according to many assumptions.

Meadows (1963) developed the first rigorous multi-component batch distillation model based on assumptions of equilibrium stages, perfect mixing of liquid and vapor phases at each stage, negligible vapor holdup and constant molar holdup. In 1986, Distefano (1968) presented a rigorous model in the batch distillation which include consideration of column dynamics together with the reboiler and condenser dynamics. He analysed a detail of the characteristic of differential mass and energy balance associated with the complete dynamics of a multicomponent batch distillation. Distefano (1968) found that the system of equations presented for batch distillation is much more difficult to solve than continuous distillation due to several factors. For example, in case of batch distillation, plate hold up is generally much

smaller than reboiler hold up, while in continuous distillation the ratio of the reboiler hold up to plate hold up is a little different. In addition in batch distillation severe transients can occur, unlike continuous distillation, where variations are relatively small.

Moreover, Boston (1981) extended the model, provided a variety of practical sets of specifications, and utilized modern numerical procedures and equation formulations to handle efficiently the nonlinear and often stiff nature of multicomponent batch distillation problem. After that, rigorous models are used to predict the concentration profile, to specify the optimal switching time from products and to slop cuts for nonlinear dynamic modeling of multi-component batch distillation by Jimenez et al. (2002).

For the analysis of a batch reactive distillation model in a staged column, it was first published by Cuille and Reklaitis (1986). They considered the simulation of reactive batch distillation with reaction occurring on the plates in the condenser and in the reboiler. They considered the esterification of 1-propanol with acetic acid but the example was not suitable for use in batch distillation. Since 1-propanol (one of the reactants) is the more volatile component in the system, the removal of species by distillation causes the removal of reactant from the column thus decreasing conversion. In 2003, the rigorous model was applied with Elgue et al. (2003). The model consists of total and component material balances, total energy balance, negligible vapor holdup, and constant liquid holdup for a batch reactive distillation. The model was equally used to solve the differential equations by Euler method.

The heterogeneously catalyzed batch reactive distillation (BRED) of methyl acetate was studied by Noeres et al. (2004). Dynamic reactive distillation experiments at pilot plant scale were performed using the catalytic structured packing MULTIPAK. A rigorous model was developed and this model contained hydrodynamic effects as liquid holdup, liquid back mixing and pressure drop as well as reaction kinetics describing the process behavior accurately. Five years later, Kathel and Jana (2009) studied a heterogeneous esterification reaction between the acetic acid and butanol taking place in a batch reactive distillation column. The process model was formulated considering variable liquid holdup, UNIQUAC model

for thermodynamic property predictions, nonlinear Francis weir formula for tray hydraulics, pseudohomogeneous model to represent the reaction kinetics and rigorous energy balance. A structured and simple iterative approach was devised to compute the vapor flows with the fast convergence, under the rigorous energy balance.

Recently, simulation of a batch reactive multistage multicomponent distillation was presented by Nakkash et al. (2010). Rigorous model was used to build the simulation program using MATLAB version 6.5 to solve this equations. The validity and the accuracy of the developed program were checked with previous work for the esterification of acetic acid with methanol to produce methyl acetate and water using sulfuric acid as a homogeneous catalyst.

Since the system of differential equations in a rigorous model is difficult to analyse, the numerical solution techniques should be applied. The governing differential equations of batch distillation often fall into the category of stiff differential equations constraints which contributes very little to the solution but can cause errors accumulated over time, resulting in an incorrect solution. In the study of Boston et al. (1983) and Diwekar and Madhavan (1991). They claimed that most batch distillation models used stiff numerical methods based on a backward difference formula (BDF) for batch distillation model and used a one of the well-known BDF techniques known as the Livermore Solver for ordinary differential equations (LSODE).

2.3 Dynamic Optimization

The dynamic optimization has been attracted the attention in many centuries because in competition, it is a natural choice for reducing production costs, improving product quality, meeting safety requirements and environmental regulations (Srinivasan et al., 2003) and these are applied in many researchs.

Converse and Gross (1963), Converse and Huber (1965), Murty et al.(1980), Diwekar et al. (1987) and Mujtaba (1989) considered an optimization problem which maximized the amount of distillate product (of specied purity) for a given time of

operation. This type of operation is often useful when a fixed period is assigned to a particular batch unit for a particular job. In 1990, Logsdon et al. (1990) presented a simultaneous optimization strategy for the design and operation of batch distillation columns undergoing both single and multiple separation duties (defined in Mujtaba and Macchietto, 1996). They defined an objective function in terms of net profit, which was maximised during optimisation.

Farhat et al. (1991) considered multicomponent mixtures. For the maximum distillate problem, an optimal policy for linear time-dependent reflux was determined for each distillation period. From three examples involving binary and ternary mixtures, they appear that the Lagrangian procedure is an efficient tool for solving batch distillation problems.

Logsdon and Biegler (1993) solved maximum distillate problem with path constraints. Instead of satisfying the product purity at the end of batch time, the product proportion was collected at a constant ratios. The maximum amount product achieved using this approach was reduced by about 8% compared with maximum product without by specifying the product purity. Moreover, Sorensen et al. (1996) studied several aspects of the optimal control of a reactive batch distillation process with reference to a specific industrial application. The control objective is either to maximise profitability or to minimise operating time. There are constraints on the maximum allowable reboiler temperature to avoid thermal decomposition of the product and on the maximum loss of volatile reactant in the distillate. Manipulated variables for control are the heat input to the reactor and the internal reflux ratio, Q_R and R , respectively. It is assumed that the condenser duty, Q_c , is used for pressure control and the distillate flow, D , for condenser level control.

According to these researches concerning the dynamic optimization, we can see that the quantity and the purity are the essential keys for products. However, the energy consumption which is, in fact, important for the process should be taken into the consideration. So, we should be aware of the energy consumption during the operation in order to avoid losing too many resources.

The batch process is nonlinear and its optimization can be applied in many methods but the the popular one is the successive quadratic programming method (SQP) because of its advantages stated in the research of Arpornwichanop et al. (2005). One advantage in the sequential approach is that only the parameters that are used to discretize the control variable profile are considered as the decision variables. The optimization formulated by this approach is a small scale nonlinear programming (NLP) that makes it attractive to apply for solving the optimal control with large dimensional systems that are modeled by a large number of differential equations. In addition, this approach can take the advantage of available initial value problem (IVP) solvers. This method has been used for solving nonlinear optimization problems of batch process with many researches, for example: Diwekar et al. (1987) solved the maximum distillation problem whereas in 1997 Mujtaba and Macchietto (1997) solved the optimal reflux flow rate for maximum profit in batch distillation. However, both researches used the same method: the successive quadratic programming method. For the semi-batch reactive distillation column, Fernholz et al. (2000) used the method to compute the optimal operation of a semi-batch reactive distillation column and this method is also applied to the pervaporative membrane reactor in the research of Moolasartorn (2002) for determining the optimal temperature policy for maximizing product problem.

CHAPTER III

THEORY

This chapter is divided into three main sections. The first section describes details of a batch distillation process and a batch reactive distillation in part background. In the second section discusses the mathematical models of the research. The third section shows details of dynamic optimization problem.

3.1 Batch Distillation

Distillation has been widely accepted for product separation purification and waste removal in chemical process industries. Depending on whether the industry is handling petrochemicals, bulk chemical, specialty chemicals, or pharmaceuticals, the distillation process can be divided into two categories: (1) batch distillation, which is mainly used in specialty chemical, biochemical, and pharmaceutical industries; and (2) continuous distillation, which is primarily implemented in the petrochemical and bulk chemical industries. In a conventional batch distillation column, the feed is initially charged into the reboiler at the beginning of the operation. After the total reflux operation (i.e., all condensates are recycled to the column), the distillate is continuously drawn while the bottom residue with a high-boiling-temperature component is concentrated, making this a time-varying process.

Batch distillation is the oldest separation process and the most widely used unit operation in the batch industry. Batch distillation is highly preferable to continuous distillation when high-value-added, low-volume chemicals must be separated. It is also widely used in chemical processing industries where small quantities of materials are to be handled in irregularly or seasonally scheduled periods, and it is implemented when the feed composition varies widely from period to period or where completely different feed stocks have to be handled.

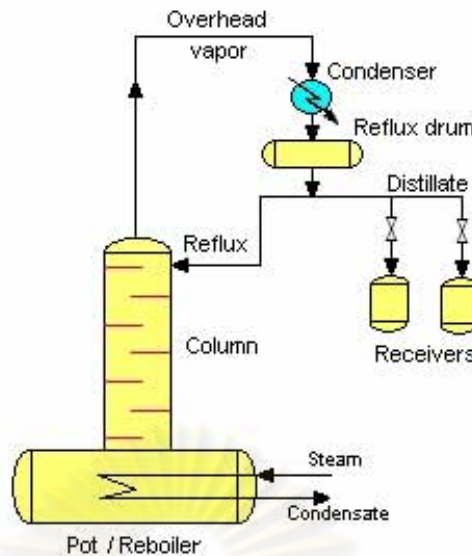


Figure 3.1 Diagram of a Batch Rectifier (Kim and Diwekar, 2006)

The principle of a batch distillation is divided into three formats as follows: the simplest and most frequently used batch distillation configuration is the *batch rectifier* (Figure 3.1), including a pot (or reboiler), rectifying column, a condenser, some means of splitting off a portion of the condensed vapor (distillate) as reflux, and one or more receivers. The other simple batch distillation configuration is the *batch stripper* (Figure 3.2). The batch stripper consists of the same parts as the batch rectifier. However, in this case, the charge pot is located above the stripping column. A third feasible batch column configuration is the *middle vessel column*. The middle vessel column consists of both a rectifying and a stripping section and the charge pot is located at the middle of the column.

The most outstanding feature of batch distillation is its flexibility in operation. This flexibility allows to deal with uncertainties in feed stocks or product specifications. In addition, one can handle several mixtures just by switching the operating conditions of the column. The basic difference between batch distillation and continuous distillation is that the feed is continuously entering the column, while in batch distillation the feed is charged into the reboiler at the beginning of the operation. The reboiler in batch distillation gets depleted over time, so the process has an unsteady-state nature.

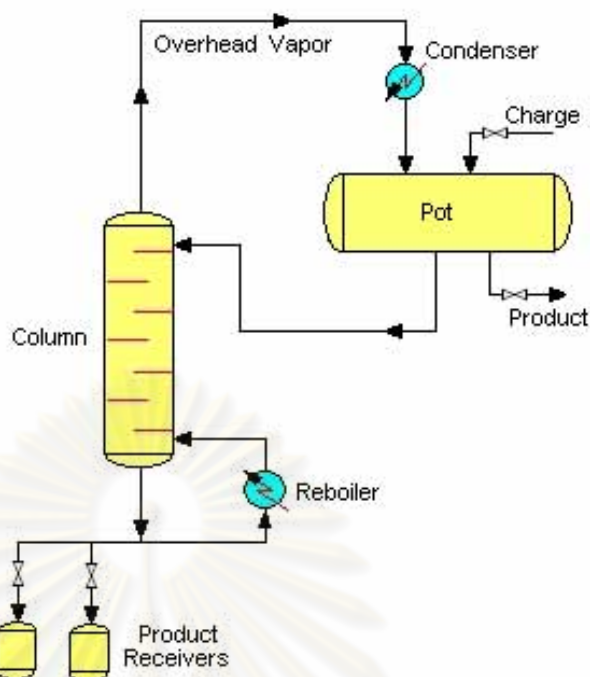


Figure 3.2 Diagram of a Batch Stripper (Kim and Diwekar, 2006)

3.2 Batch Reactive Distillation

Reactive Distillation processes combine the benefits of traditional unit operations with a substantial progress in reducing capital and operating costs and environmental impact (Taylor and Krishna, 2000).

Traditionally, as in many chemical industries, reaction and separation take place separately (Figure 3.3) in a batch reactor followed by a batch distillation column. Therefore, the distillation of desired species cannot influence the conversion of the reactants in the reactor.

However, conventional batch distillation with chemical reaction (reaction and separation taking place in the same vessel and hence referred to as *Batch REActive Distillation-BREAD*) is particularly suitable when one of the reaction products has a lower boiler point than other products and reactants. The higher volatility of this product results in a decrease in its concentration in the liquid phase, therefore increasing the liquid temperature and hence reaction rate, in the case of irreversible reaction. With reversible reactions, elimination of products by distillation favors the

forward reaction. In both cases, higher conversion of the reactants is expected than reaction alone. Therefore, in both cases, higher amount of distillate with desired purity is expected than by distillation alone (as in traditional approach) (Mujtaba (2004)).

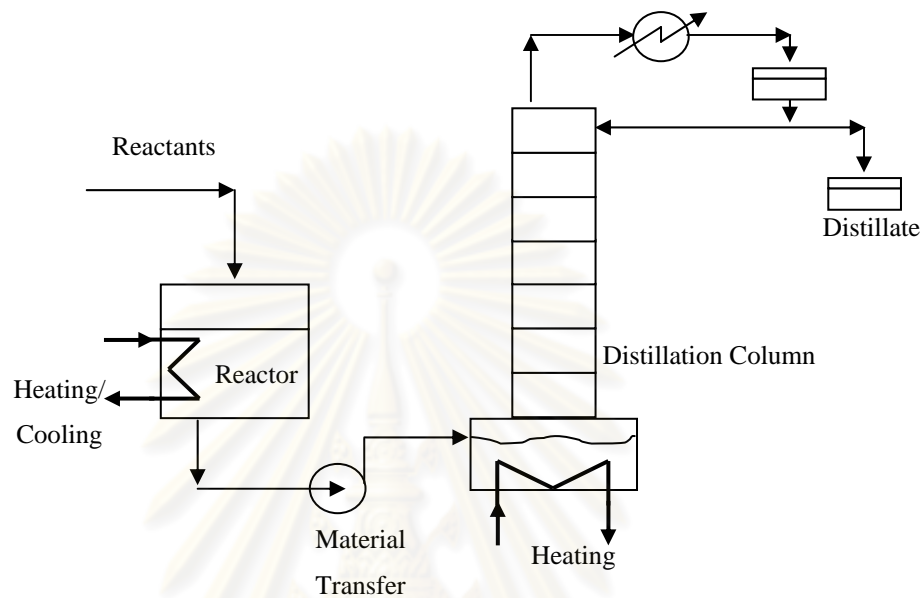


Figure 3.3 Traditional Batch Reactive-Distillation System (Mujtaba, 2004)

3.2.1 Features of conventional batch distillation column

The essential features of a conventional batch distillation column are as follows:

- a) A bottom receiver or reboiler which is charged with feed to be processed and which provides the heat transfer surface.
- b) A rectifying column (either a tray or packed column) superimposed on the reboiler, coupled with either a total condenser or a partial condenser system.
- c) A series of product accumulator tanks connected to the product streams to collect the main and or the intermediate distillate fractions.

Operation of such a column involves carrying out the fractionation until a desired amount has been distilled off. The overhead composition varies during the

operation and usually a number of cuts are made. Some of the cuts are desired products while others are intermediate fractions that can be recycled to subsequent batches to obtain further separation. A residual bottom fraction may or may not be recovered as product.

3.3 Dynamic Process Models

Grosser et al. (1987), Stevanovica et al. (1992), Abufares and Douglas(1995), Schrans et al. (1996), Singh et al. (2005), and Khaledi and Young (2005) developed dynamic modelling and simulation.

A batch reactive distillation is herently a dynamic process and the results to optimal control or dynamic optimisation problems (unless batch distillation task is carried out in a continuous distillation column).

Dynamic model plays a central role in the subject of process dynamics and control. The models can be used to:

1. *Improve the understanding of the process:* Dynamic models and computer simulation allow transient process behavior to be investigated. Computer simulation allows valuable information about dynamic and steady state process behavior to be acquired even before the plant is constructed.
2. *Train plant operating personnel:* Process simulators play a critical role in training plant operators to run complex unit and to deal with emergency situations. By interfacing a process simulator to standard process control equipment, a realistic training environment is created.
3. *Develop a control strategy for a new process:* A dynamic model of the process allows alternative control strategies to be evaluated.
4. *Optimize process operating conditions:* It can be advantageous to recalculate the optimum operating conditions periodically in order to maximize cost. A

steady-state process model economic information can be used to determine the most profit operating conditions.

3.3.1 A systematic approach for developing dynamic models

State the modeling objectives and the end use of the model. Then determine the required levels of model detail and model accuracy.

1. Draw a schematic diagram of the process and label all process variables.
2. List all of the assumptions involved in developing the model. Try to be parsimonious: the model should be no more complicated than necessary to meet the modeling objectives.
3. Determine whether special variations of process variables are important. If so, a partial differential equation model will be required.
4. Write appropriate conservation equations (mass, component, energy, and so forth).
5. Introduce equilibrium relations and other algebraic equations (from thermodynamics, transport phenomena, chemical kinetics, equipment geometry, etc.)
6. Perform a degree of freedom analysis to ensure that the model equations can be solved.
7. Simplify the model. It is often possible to arrange the equations so that the output variables appear on the left side and input variables appear on the right side. This model form is convenient for computer simulation and subsequent analysis.
8. Classify inputs as disturbance variable or as manipulated variable (Seborg et al., 2004).

3.4 Mathematical model of this work

The mathematical model of the conventional batch reactive distillation (figure 3.4) developed by Mujtaba and Macchietto (1997) is based on mass and energy balances.

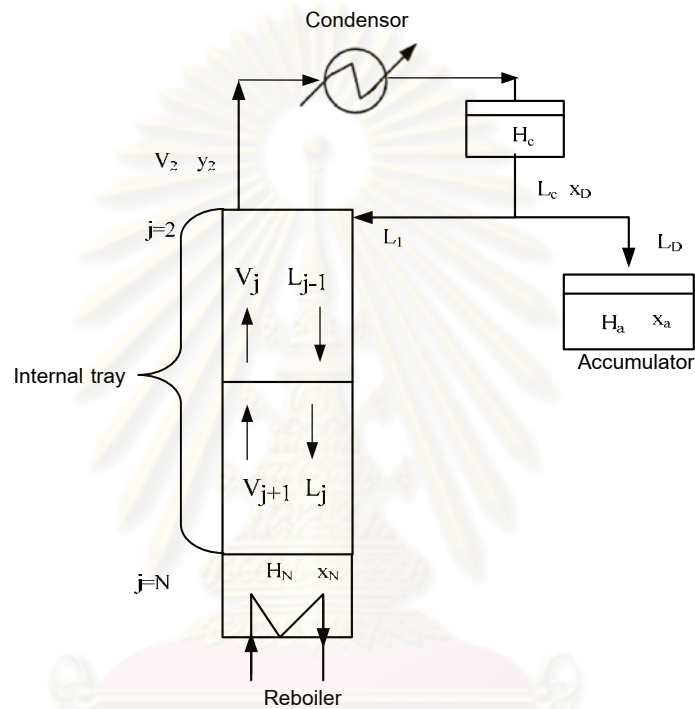


Figure 3.4 Schematic of A batch reactive distillation column

3.4.1 Assumption

To develop a dynamic model of BREAD for the esterification of reaction, the following assumptions have been made,

- The liquid volumetric holdups on trays and in condenser will be assumed to be constant.
- Condensed vapor is total condensation with no sub-cooling.

- The vapor-phase holdup is assumed to be negligible compared to the liquid-phase holdup on each phase.
- Liquid and vapour on trays is assumed to be perfect mixing.
- Heat losses is assumed to be negligible.
- Mixture is feed at its bubble point .
- The column is adiabatic trays.
- Energy dynamic is assumed to be fast.
- chemical reaction on trays, in reboiler and in condenser but not product accumulator.

3.4.2. Modeling Equations

Let us consider a batch reactive distillation column which vapor and liquid counter current flow as shown in Figure 3.4. Performing a mass and energy balance for system and component i in the column leads to the following equation:

3.4.2.1. Internal Trays: $j=2,N-1$

total mass balance;

$$0 = L_{j-1} + V_{j-1} - L_j - V_j + \Delta n_j H_j \quad (3.1)$$

component mass balance;

$$H_j \frac{dx_{ji}}{dt} = L_{j-1}x_{j-1,i} + V_{j+1}y_{j+1,i} - L_jx_{j,i} - V_jy_{j,i} + r_{j,i}H_j \quad (3.2)$$

energy balance;

$$0 = L_{j-1}h_{j-1}^L + V_{j+1}h_{j+1,i}^V - L_jh_{j,i}^L - V_jh_{j,i}^V \quad (3.3)$$

equilibrium equation;

$$y_{j,i} = K_{j,i}x_{j,i} \quad (3.4)$$

Restrictions;

$$\sum y_{ji} = 1 \quad (3.5)$$

relations defining physical properties and chemical reactions;

$$K_{j,i} = K_{j,i}(y_j, x_j, T_j, P) \quad (3.6)$$

$$h_j^L = h_j^L(x_j, T_j, P) \quad (3.7)$$

$$h_j^V = h_j^V(y_j, T_j, P) \quad (3.8)$$

$$r_{j,i} = r_{j,i}(k_r, x_j) \quad (3.9)$$

$$\Delta n_j = \sum r_{j,i} \quad (3.10)$$

3.4.2.2 Reboiler: $j = N$

total mass balance;

$$\frac{dH_N}{dt} = L_{j-1} + V_{j-1} - L_j - V_j + \Delta n_j H_j \quad (3.11)$$

component mass balance;

$$H_N \frac{dx_{Ni}}{dt} = L_{j-1}(x_{N-1,i} - x_{N,i}) - V_N(y_{N,i} - x_{N,i}) + r_{N,i}H_N - \Delta n_N H_N x_{N,i} \quad (3.12)$$

energy balance;

$$0 = L_{N-1}(h_{N-1}^L - h_N^L) - V_N(h_N^V - h_N^L) + Q_R \quad (3.13)$$

3.4.2.3. Condenser and Distillate Accumulator: $j = 1$

accumulator total mass balance;

$$\frac{dH_a}{dt} = L_D \quad (3.14)$$

component mass balance;

(a) accumulator

$$H_a \frac{dx_{a,i}}{dt} = L_D(x_{D,i} - x_{a,i}) \quad (3.15)$$

(b) condenser holdup tank

$$H_c \frac{dx_{D,i}}{dt} = V_2 y_{2,i} - (V_2 + \Delta n_1 H_c) x_{D,i} + r_{1,i} H \quad (3.16)$$

energy balance;

$$0 = V_2 h_2^V - (V_2 + \Delta n_1 H_c) h_1^L - Q_C \quad (3.17)$$

3.4.2.4. Other equations;

$$L_1 = r_f (V_2 + \Delta n_1 H_c) \quad (3.18)$$

$$L_D = (V_2 + \Delta n_1 H_c)(1 - r_f) \quad (3.19)$$

$$T_1 = T_1(x_{D,i}, P) \quad (3.20)$$

$$h_1^L = h_1^L(x_{D,i}, T_1, P) \quad (3.21)$$

3.4.2.5. Bubble point calculation

Bubble point temperature is calculated by Raoult's law for finding temperature and component of vapor in the column. For solving the vapor and liquid flow rates i.e. the energy balance equation, one requires the enthalpy data. And to calculate the enthalpy; temperature should be known. Therefore, it is necessary to have the temperature-composition correlation. The vapor-phase composition in equilibrium with the liquid-phase is given by,

equilibrium equation;

$$y_{j,i} = K_{j,i} x_{j,i}$$

Restrictions;

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

When $K_{j,i}$ is vapor liquid equilibrium data of component i in tray j

Table 3.1 Kinetic Data and Vapor-Liquid Equilibrium for Ethanol Esterification
(Mujtaba and Macchietto, 1997)

Kinetic Data

$$\text{Rate of reaction, gmol/(Lmin): } r = k_1 C_1 C_2 - k_2 C_3 C_4 \quad (3.22)$$

where rate constants are $k_1 = 4.76 \times 10^{-4}$ and $k_2 = 1.63 \times 10^{-4}$ and C_i stands for concentration in gmol/L for the i^{th} component

acetic acid + ethanol \leftrightarrow ethyl acetate + water

$$K_1 = (2.25 \times 10^{-2})T - 7.812 \quad T > 347.6K \quad (3.23)$$

$$K_1 = 0.001 \quad T \leq 347.6K \quad (3.24)$$

$$\log K_2 = \frac{-2.3 \times 10^3}{T} + 6.588 \quad (3.25)$$

$$\log K_3 = \frac{-2.3 \times 10^3}{T} + 6.742 \quad (3.26)$$

$$\log K_4 = \frac{-2.3 \times 10^3}{T} + 6.484 \quad (3.27)$$

3.4.2.6. Enthalpy

Vapor and liquid enthalpies are calculated using data from Reid (1977) (in Mujtaba and Macchietto (1997)).

Enthalpy of liquid calculate from

$$H^L = \sum_{i=1}^4 H_i^L \quad (3.28)$$

where

$$H_i^L = x_i C_{pLi} T \quad (3.29)$$

Enthalpy of vapor calculate from

$$H^V = \sum_{i=1}^4 H_i^V \quad (3.30)$$

where

$$H_i^V = y_i \times (H_i^L + \Delta H_i^V) \quad (3.31)$$

$$\Delta H_i^V = R \times T_{ci} \times 7.08 \times (1 - T_{ri})^{0.345} + 10.95 w_i \times (1 - T_{ri})^{0.456} \quad (3.32)$$

$$T_r(K) = \frac{T(K)}{T_c(K)} \quad (3.33)$$

3.4.2.7. Density

Density of mixture in the column can be calculated by Balasubramhanya and Doyle (2000) as follow:

$$\rho = \sum x_i \rho_i \quad (3.34)$$

where

$$\rho_i = A_d B_d^{-(1-T_r)^{2/7}} \quad (\text{g/cc}) \quad (3.35)$$

$$T_r(K) = \frac{T(K)}{T_c(K)} \quad (3.36)$$

In this work, the production of ethyl acetate via ethanol esterification reaction is used as a case study. The ethyl acetate (desired product) has lowest boiling point as shown below. Thus, only the first main-cut is considered.

	acetic acid	+	ethanol	\Leftrightarrow	ethyl acetate	+	water
	(1)		(2)		(3)		(4)
Boiling point (K)	391.1		351.5		350.3		373.2

Information regarding the column configuration, feed, feed composition, hold-up in condenser and tray, column pressure, etc., is given in Table 3.2.

Table 3.2 Batch Reactive Distillation Column specification

System	Acetic Acid, Ethanol, Ethyl Acetate, Water
Feed (kmol)	5
Feed composition	0.45,0.45, 0.0,0.1
Condenser Hold-up (kmol)	0.1
Internal tray Hold-up (kmol)	0.0125
Column pressure (bar)	1.013

3.4.3. Simulation algorithm

Modeling equations solved by a stepwise procedure is given below.

- Step1: Declare all the variables and initialize the start up phase liquid composition ($x_{j,i}$) and liquid hold up (H_j) on each tray.
- Step2: Calculate temperature (T_j) and vapor phase composition ($y_{j,i}$) on each tray ; bubble point calculation.
- Step3: Calculate rate of reaction of component i and sum rate of reaction in each tray in section with the help of density, molecular weight, holdup and tray specifications.
- Step4: Find the vapor and liquid enthalpy using equations (3.28) and (3.30) for all the component on each tray and then total liquid and vapor phase enthalpies by multiplying the respective compositions on each tray.

Step5: Find the liquid flow rates and vapor flow rates by solving the total mass and energy balance equations in tray (3.1, 3.3), reboiler (3.13), condenser (3.17) and other equation (3.18, 3.19).

Step6: Finally solve differential equation to find the liquid phase composition, liquid hold up on each tray through 16 hours.

From the system of differential equations of the system, we can easily see that the problem has no analytical solution, and we must resort to numerical solution techniques. The governing differential equations of batch distillation often fall into the category of stiff differential equations constraints a component that contributes very little to the solution but can cause errors that accumulate over time, resulting in an incorrect solution. Boston et al. (1983) and Diwekar and Madhavan (1991) use stiff numerical methods based on a backward difference formula (BDF) for batch distillation model. Thus the method for solving the dynamic simulation is ode15s algorithm in Matlab Toolbox. The ode15s is a variable order solver based on the numerical differentiation formulas (NDFs). Optionally, it uses the backward differentiation formulas (BDFs, also known as Gear's method) that are multistep solver (see in Appendix B).

3.5 Dynamic Optimization (Optimal Control)

Optimization is one of the major quantitative tools in the machinery of decision-making. A wide variety of problems in the design, construction, operation, and analysis of chemical plants (as well as many other industrial processes) can be resolved by optimization problems and their solution techniques, and describe some typical benefits and applications in the chemical and petroleum industries (Edgar et al. (1983)).

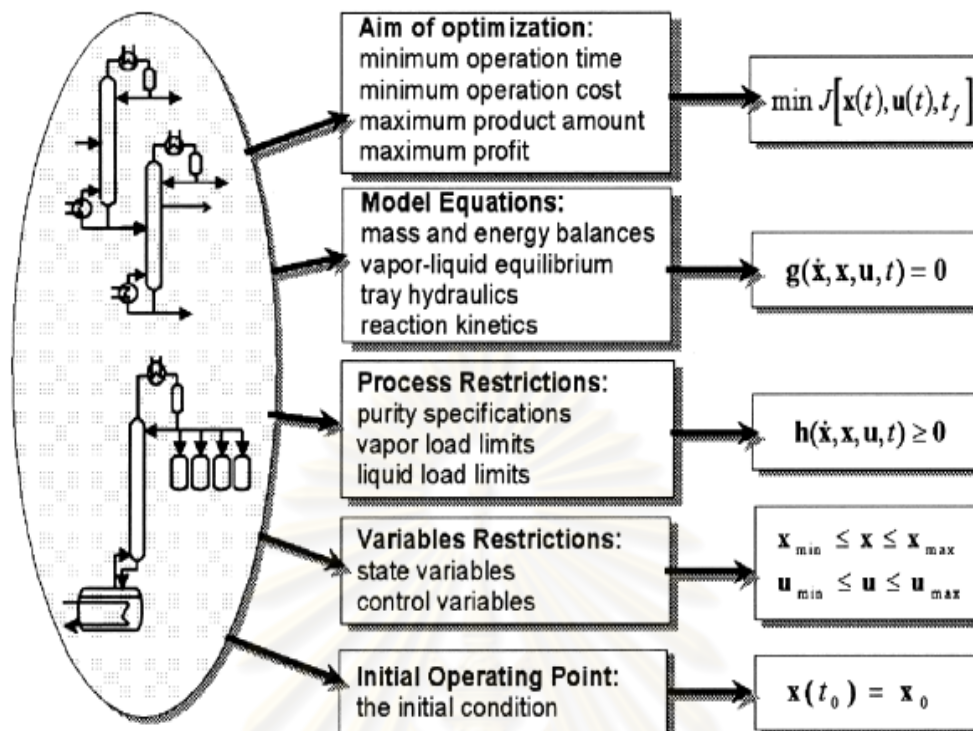


Figure 3.5 Formulation of process dynamic optimization problems
(Wozny and Li, 2000).

Behavior of a batch reactive distillation column is time-varying. Thus dynamic optimisation has been solved the problem. In general, the formulation of process dynamic optimization problem can be conclusion in Figure 3.5. Here we take thermal (continuous and batch) distillation columns as example processes. The formulated problem consists of objective function J , equality constraints vector g , inequality constraints vector h , variable constraints and the initial conditions x_0 , where x and u denote the state and control variables vectors, respectively. A large-scale nonlinear dynamic optimization problem is usually formulated (hundreds to thousands variables). The dynamic optimization problem is shown as follow:

consider a dynamic process model as in the form of an implicit function

$$f(t, \dot{x}(t), x(t), u(t), p) = 0; \quad [t_0, t_F] \quad (3.37)$$

with consistent initial conditions

$$f(t_0, \dot{x}_0, x_0, u_0, p) = 0 \quad (3.38)$$

where t is dependent variable (time), t_F is the batch time, $x(t)$ is the set of all state variables, $\dot{x}(t)$ denotes the derivative of $x(t)$ with respect to time, $u(t)$ is a vector of control variables, and p is a vector of time invariant parameters (design variable). Suitable initial conditions x are defined at time $t = t_0$. The time interval of interest is $[t_0, t_F]$ which is divided into a finite number of subintervals. The function f is assumed to be continuously differentiable with respect to all its arguments.

The system is subject to bounds on the controls as:

$$lb^u(t) \leq u(t) \leq ub^u(t); \quad t \in [t_0, t_F] \quad (3.39)$$

Where $lb^u(t)$ and $ub^u(t)$ are given continuous functions of time of $[t_0, t_F]$, and interior point or terminal constraints of from:

$$lb^f(t_p) \leq f(t_p, \dot{x}(t_p), x(t_p), u(t_p), p) \leq ub^f(t_p) \quad (3.40)$$

Where $f(t_p, \dot{x}(t_p), x(t_p), u(t_p), p)$ is continuously differentiable with respect to its arguments. At terminal point $t_p = t_F$, the system performance is measured in terms of a scalar objective function (J) to be minimized or maximized:

$$J = f(t_F, \dot{x}(t_F), x(t_F), u(t_F), p) \quad (3.41)$$

The optimal control problem is to choose and admissible at the final time, $u(t_F)$, to minimize the objective function, J , is subject to bounds on controls and constraints.

The time interval $[t_0, t_F]$ is divided into a finite number of subintervals (P). In each subinterval, the control $u(t)$ is represented by a set of basis functions involving a finite number of parameters

$$u(t) = g(t, z_j) \quad t \in [t_{j-1}, t_j] \quad \text{with } j = 1, 2, \dots, J \quad (3.42)$$

where $t_J = t_F$. The control profile is defined by the parameters z_j and switching times t_j . In this study, the piecewise constant control is assumed and used because the form of the solution is ideally suited for implementation on a digital computer. Thus the set of decision variables for the nonlinear program can be written as

$$y = \{z_1, z_2, \dots, z_J, t_1, t_2, \dots, t_J\} \quad (3.43)$$

3.5.1 Techniques for solution dynamic optimization

Computational techniques for solution dynamic optimization are mentioned in Arpornwichanop et al. (2005). There are a number of different techniques to solve the dynamic optimization problems. In general, they are mainly classified into three classes as follow:

The first one is based on a *classical variation method*. This approach is also known as an indirect method as it focuses on obtaining the solution of the necessary conditions rather than solving the optimization directly. Solution of these conditions often results in a two-point boundary value problem (TPBVP), which is accepted that it is difficult to solve (Ray, 1981). Although several numerical techniques have been developed to address the solution of TPBVP, e.g. control vector iteration (CVI) and single/multiple shooting method are usually inefficient (Renfro et al. ,1987). Another difficulty relies on the fact that it requires an analytical differentiation to derive the necessary conditions.

The second class of solutions is based on *dynamic programming*. Unlike the variation method, this approach applies the principle of optimality to formulate an optimization problem, leading to the development of the Hamilton–Jacobi–Bellman partial equations that determine the solution of the optimal control problem. However, this approach is quite limited to a simple control problem because of a difficulty in obtaining the solution of the optimality equations. Luus (1950) extended the idea of

the optimality principle to develop an alternative technique, named as iterative dynamic programming (IDP). Although the implementation of the IDP for solving many optimal control problems can be found in the literature, it is known that the IDP algorithm would be slower than most other gradient-based algorithms (Dadebo and Mcauley, 1995).

The last one is based on *discretization techniques*, received major attention and considered as an efficient solution method. The concept of this approach is to transform the original optimal control problem into a finite dimensional optimization problem, typically a nonlinear programming problem (NLP). Then, the optimal control solution is given by applying a standard NLP solver to directly solve the optimization problem. For this reason, the method is known as a direct method. The transformation of the problem can be made by using discretization technique on either only control variables (partial discretization) or both state and control variables (complete discretization).

Successive Quadratic Programming or Sequential Quadratic Programming (SQP) strategy is a type of discretization techniques that is carried out to solve the constrained nonlinear optimization problem in batch reactive distillation column (the details see in Appendix A). In SQP, at each iteration of optimization a quadratic program (QP) is formed using a local quadratic approximation to the objective function and linear approximation to nonlinear constraints. The resulting QP problem is solved to determine the search direction and this direction and with this direction, the next step length of the decision variable is specified. The feasible path optimization strategy is shown in Figure 3.6

In the feasible path approach, the process variables are partitioned into dependent variables and independent variables (optimization variables). For each choice of optimization variables (sometimes referred to decision variables) the simulator (model solver) is used to converge the process model equation (described by a set ODEs or DAEs). Therefore, the method includes two levels. The first level performs the simulation to converge all the equality constraints and to satisfy the inequality constraints and the second level performs the optimization. The resulting optimization problem is an unconstrained nonlinear optimization problem or a

constrained optimization problem with simple bounds for the associated optimization variables plus any interior or terminal point constraints (Mujtaba, 2004).

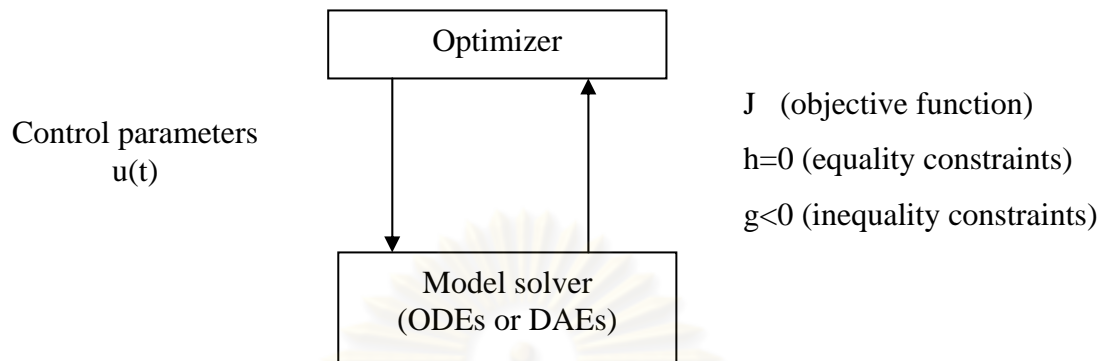


Figure 3.6 Feasible path optimization strategy (Mujtaba, 2004)

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Chapter IV

Discussion

A batch reactive distillation has many of the advantages for the chemical industry but its behavior is very complex. The behavior of batch process has been widely studied over many years and the mathematical models for best predicting the operation of the process have been proposed in the form of models were expressed in material and energy balances. In addition, an economic concept is applied with batch reactive distillation for increased efficiency of the production system such as decreased cost, saving product improvement and reduced energy consumption; thus the optimization problem is considered.

Optimization is included in order to reduce production costs, improve product quality, and meet safety requirements and environmental regulations. The optimization problem is solved by the best method to give fast convergence and correct results. Moreover, the reliability of the mathematical models, the objective functions assignment, the constraints definition and parameters selection are considered along with the optimization problem.

This chapter is divided into two parts; in the first part, the behavior of a batch reactive distillation is studied showing the dynamic behavior of the distillation column using different operations (operations such as constant heat duty and constant vapor load), using different trays (plate in distillation column) and analysing sensitivity of parameters and variables. In the second part, the optimization technique is described. This part discusses factors affecting the optimization problem, such as, objective function, decision variables and time intervals.

4.1 Dynamic Behavior

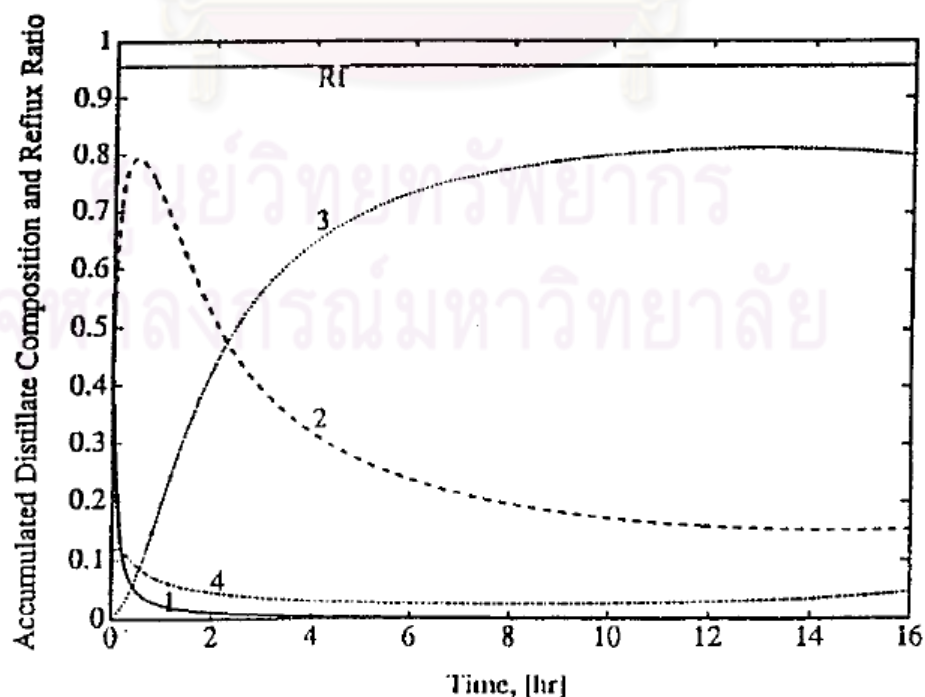
This section presents a study about the behavior of a batch reactive distillation by the mathematical models developed by Mujtaba and Maccheitto (1997). Details

regarding equations and step calculations are given in section 3.4. The method for solving the dynamic simulation is ode15s algorithm in Matlab Toolbox

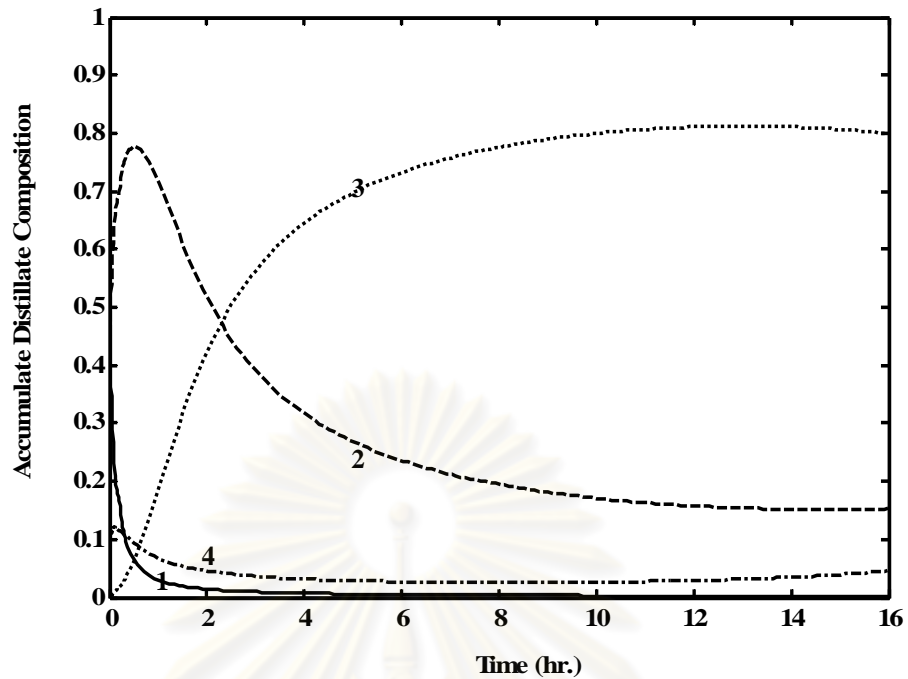
Dynamic simulation can be separated into two cases. First, the constant vapour load operation is studied for checking step calculation by comparing results of Mujtaba and Maccheitto (1997) before using the next part. Second, the constant reboiler heat duty operation is applied to replace the constant vapor load because it can be used with the actual plant.

4.1.1 Constant vapor load operation with 10 tray

The aim of the simulation in this section is to check the accuracy of step calculation, variables and parameters in the work by repeating Mujtaba and Maccheitto's (1997) results. For the simulation with constant vapor load operation, the calculation methods are shown in section 3.4. The column has ten stages. The first stage is the total condenser and the tenth stage is the reboiler. This column is operated with constant vapor load for 16 hours. The reflux ratio is 0.952 and vapor flow rate is constant at 2.5 kmol/hr. The simulation results from this work and Mujtaba and Maccheitto (1997) are illustrated in Figures below:

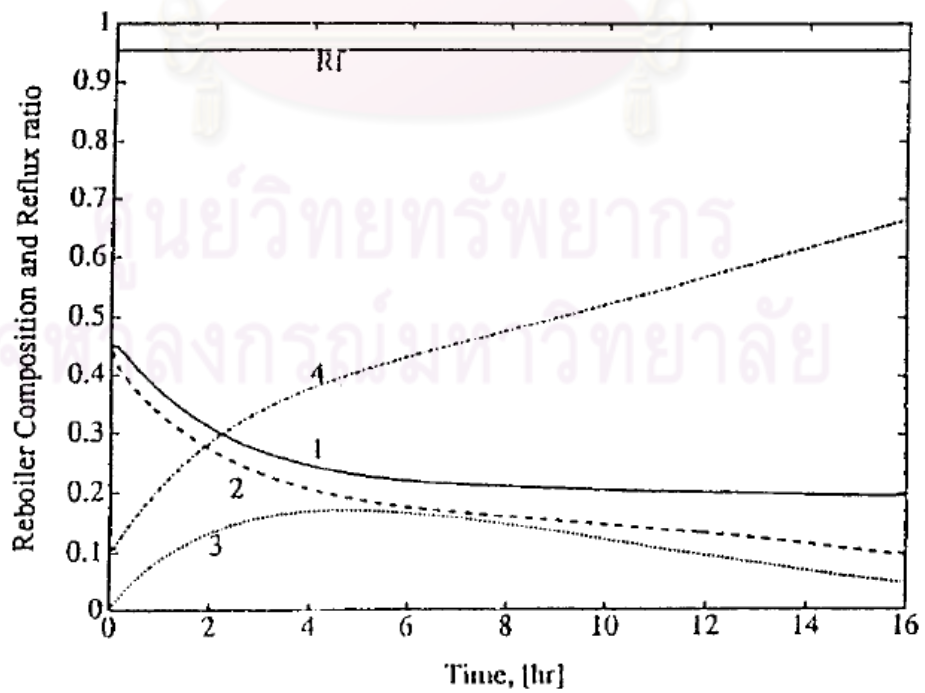


(a)

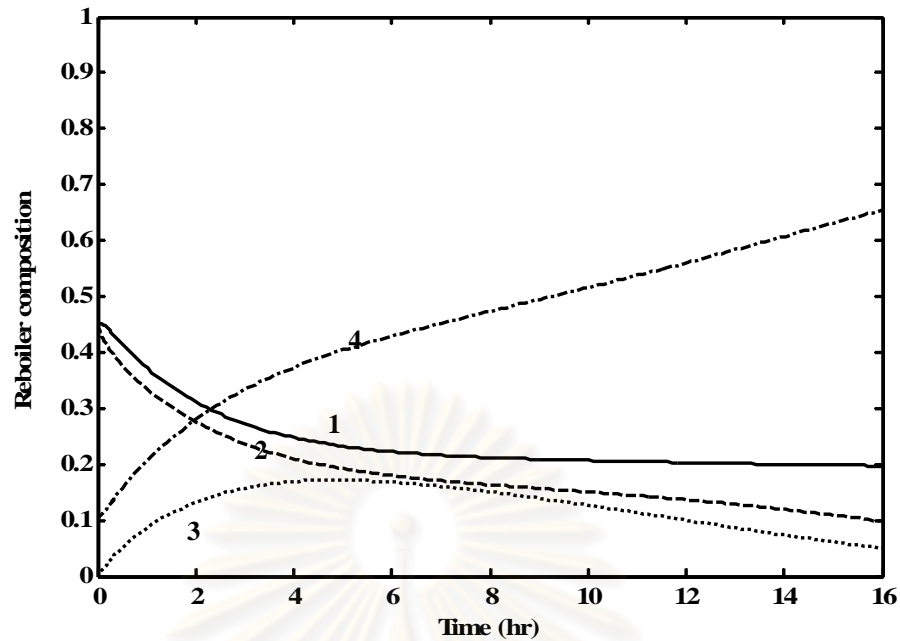


(b)

Figure 4.1 Composition profile of ethanol esterification in accumulator (a) Mujtaba and Maccheitto (1997) (b) Simulation of thesis: 1 acetic acid 2 ethanol 3 ethylacetate 4 water



(a)



(b)

Figure 4.2 Composition profile of ethanol esterification in reboiler (a) Mujtaba and Maccheitto (1997) (b) Simulation of thesis: 1 acetic acid 2 ethanol 3 ethylacetate 4 water

The comparison between the simulation results from Mujtaba and Maccheitto (1997) and this work are shown in Figure 4.1 – 4.2. For Figure 4.1(a) and Figure 4.2(a) are the Mujtaba and Maccheitto's (1997) results. For Figure 4.1(b) and 4.2(b) are the results from this work. As the process is carried out, the ethyl acetate concentration increases from initial condition to 80% at about 16 hours whereas the acetic acid, ethanol and water concentrations decrease in the accumulator. The composition of water increases whereas the other components decrease in the reboiler section. Since every components have different boiling points. Ethyl acetate (the least boiling points) is evaporated first at the top of the column while water (the highest boiling points) is remained at the bottom of the column. Furthermore, the reactant components (acetic acid and ethanol) are reduced in both sections after reactions takes place.

The simulation results between this work and Mujtaba and Maccheitto (1997) are compared and shown that the reboiler and accumulator compositions of this work are almost identical to those of the Mujtaba and Maccheitto's work. Thus, the parameters, the variables, the equations and the step calculation can be used in the next step.

4.1.2 Sensitivity analysis of constant vapor load operation

The dynamic behavior of the distillation column has been presented in the previous section. In this part, the product purity will be improved from 80 % to 90% mole of ethyl acetate by manipulating the reflux ratio. In addition, the reflux ratio is varied to 0.95, 0.97, 0.98 and 0.99, respectively to study the effect of the reflux ratio to the product purities. The result is shown in Figure 4.3.

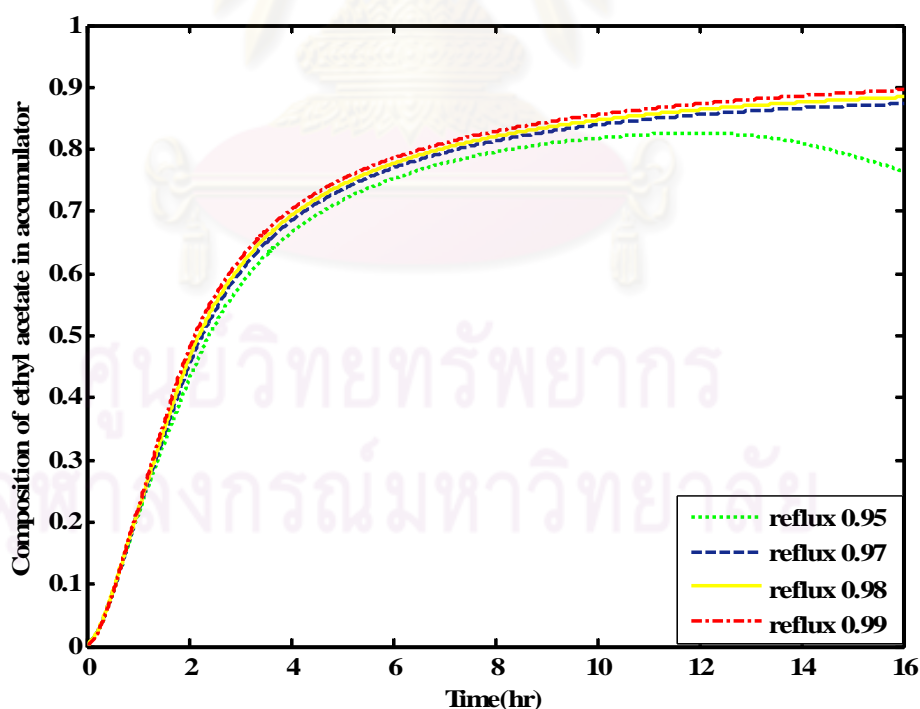


Figure 4.3 Composition of ethyl acetate in accumulator when changed of reflux

Table 4.1 The distillate composition in the accumulator at the final batch time with different reflux ratio

Reflux ratio	Ethyl acetate composition ($x_{a,3}$)
0.95	0.7650
0.97	0.8731
0.98	0.8843
0.99	0.8956

The distillate composition profiles when the reflux ratio is set constant through the operation, are shown in Figure 4.3. It has been found that the ethyl acetate concentration increases when the reflux ratio is increased to approximately total reflux. At the final batch time, the maximum purity of 89.56% by mole of ethyl acetate can be produced as shown in Table 4.1. However, the purity of 90.0% by mole of ethyl acetate cannot be achieved by fixing only one reflux ratio. Moreover, the constant vapor load operation cannot be applied with the real process (see details in constant reboiler heat duty) thus the operation is changed to the constant heat duty operation.

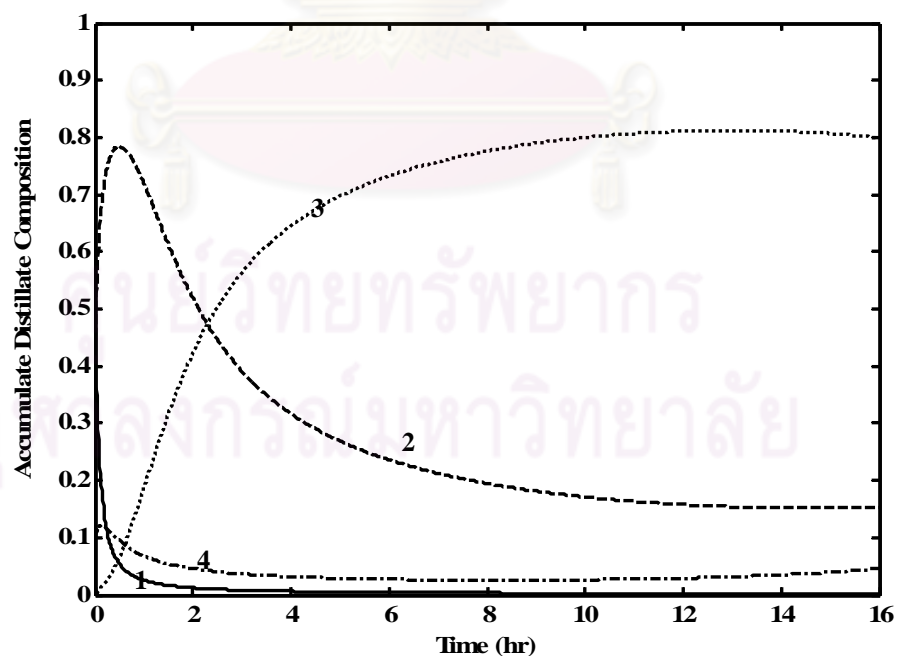
Constant reboiler heat duty operation

The constant vapor load operation by manipulating the reflux ratio cannot achieve the product specification. Moreover, a batch reactive distillation with constant vapour load operation concerns as a more complicated operation. For examples, it cannot control vapor load during the operation. Thus, the operation with constant reboiler heat duty is preferred for this work because it can directly define the value of heat duty to be supplied to the process and it can manipulate much more variables than the constant vapor load operation.

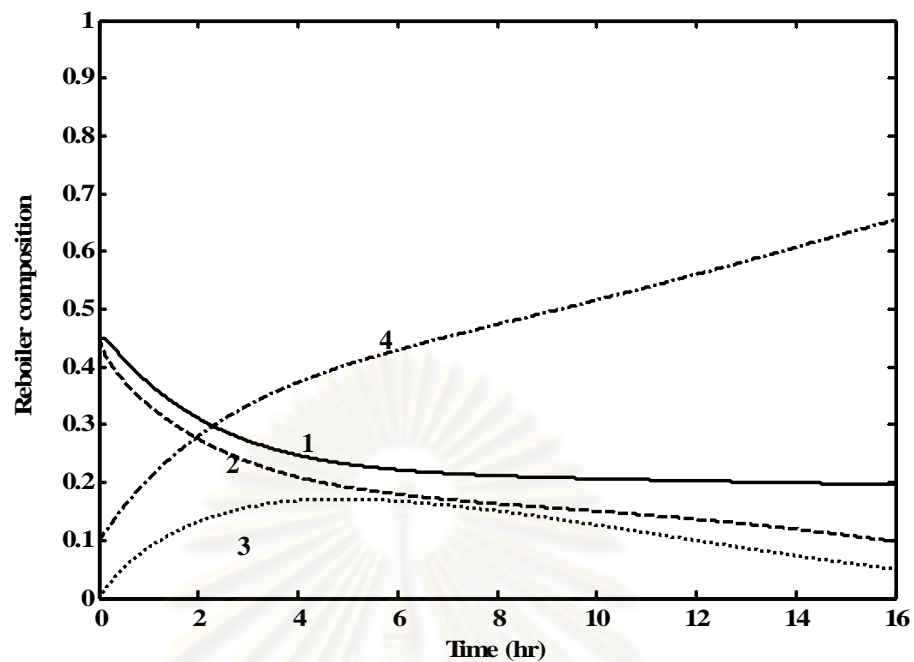
4.1.3 Constant reboiler heat duty operation with 10 tray

A batch reactive distillation of 10 trays and the reflux ratio of 0.952 is simulated with constant reboiler heat duty operation to study the dynamic behavior of the column. It has been found that the constant heat duty must be adjusted to achieve the composition profiles as same as those of Mujtaba and Macchietto (1997) (See Figure 4.1(a) and 4.2(a)).

When the reboiler heat duty is changed to 7.2×10^4 kJ/hr, the composition profiles obtained are identical to those of Mujtaba and Macchietto (1997). The composition profiles of the both sections are the same as the results from simulation with constant vapor load that the composition of acetic acid, ethanol and water decrease continuously whereas the distillate mole fraction of ethyl acetate reaches about 80% in the accumulator (Figure 4.4(a)) and the composition of acetic acid, ethanol and ethyl acetate decrease continuously whereas the distillate mole fraction of water reaches about 65% in reboiler (Figure 4.4(b)).



(a)



(b)

Figure 4.4 Composition profile of ethanol esterification of the constant heat duty operation with 10 trays (a) in accumulator (b) in reboiler: 1 acetic acid 2 ethanol 3 ethylacetate 4 water

4.1.4 Effect of reflux and heat duty to the product purity

The heat duty and the reflux ratio are main variables to improve the purity of the desired product to achieve 90%. In this study, the reflux ratio is fixed at the constant values of 0.95, 0.97 and 0.99, and the heat duty is varied from 1×10^4 to 3×10^4 , 5×10^4 , 7×10^4 and 9×10^4 kJ/hr.

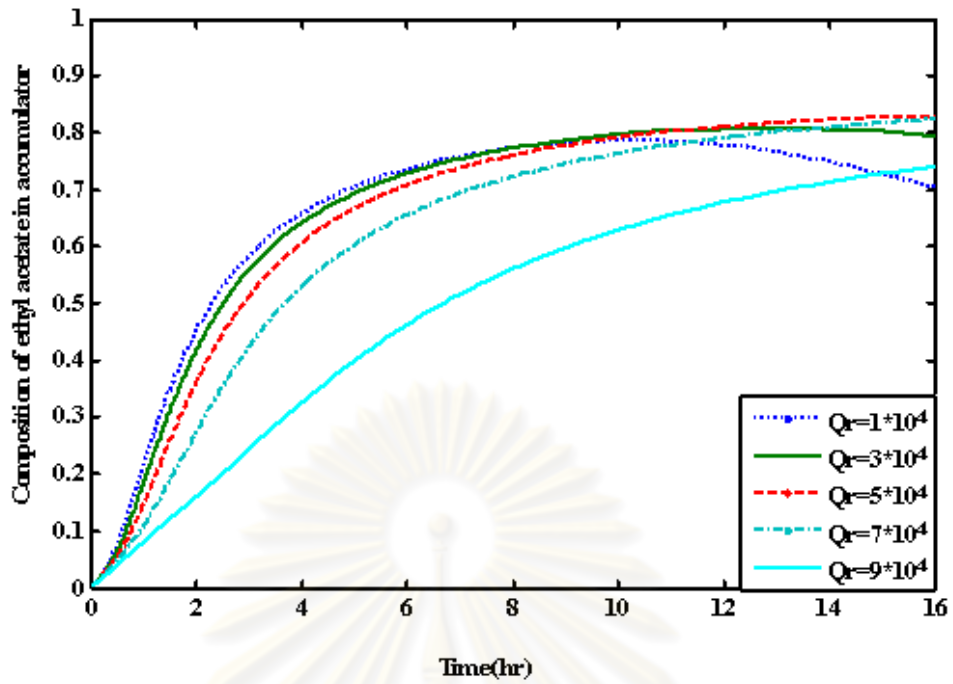


Figure 4.5 Concentration of ethyl acetate in accumulator when varied reboiler heat duty and reflux constant at 0.95

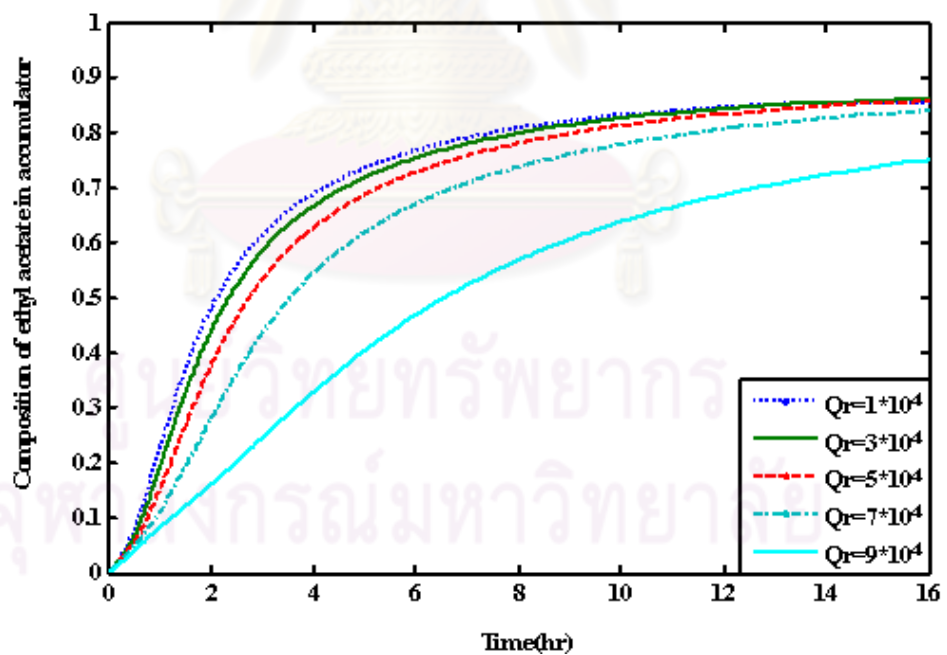


Figure 4.6 Concentration of ethyl acetate in accumulator when varied reboiler heat duty and reflux constant at 0.97

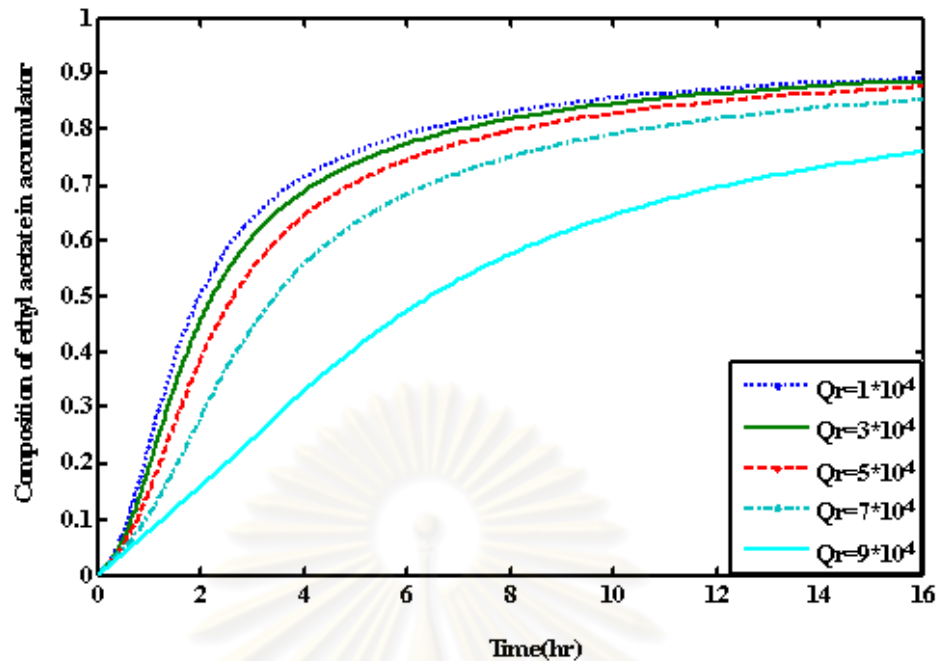


Figure 4.7 Concentration of ethyl acetate in accumulator when varied reboiler heat duty and reflux constant at 0.99

The simulation results (Table 4.2) have shown that the ethyl acetate concentration in distillate increases when the energy consumption is increased from 1×10^4 kJ/hr to 5×10^4 kJ/hr and the ethyl acetate concentration in distillate increases when the reflux ratio is increased to approximately total reflux. At the final time, the maximum purity of 82.81% by mole ethylacetate is achieved when the reflux ratio is fixed at 0.95 and the reboiler heat duty is used at 5×10^4 kJ/hr as shown in Figure 4.5. The maximum purity of 86.24% by mole ethylacetate is obtained when the reflux ratio is fixed at 0.97 and the reboiler heat duty is set at 3×10^4 kJ/hr as shown in Figure 4.6 whereas the maximum purity of 89.22% by mole ethylacetate is obtained when the reflux ratio is provided at approximately the total reflux and the heat duty is used at 1×10^4 kJ/hr as shown in Figure 4.7. However, the ethyl acetate purity has not reached to the desired purity of 90%. Thus, the number of tray is studied to find out the effect to the product purity in the next step.

Table 4.2 The distillate composition in the accumulator at the final batch time with different heat duty and reflux ratio

Heat duty (Q_r) kJ/hr	Ethyl acetate composition ($x_{a,3}$)		
	Reflux ratio=0.95	Reflux ratio=0.97	Reflux ratio=0.99
1×10^4	0.7405	0.7508	0.7588
3×10^4	0.8234	0.8407	0.8531
5×10^4	0.8281	0.8588	0.8762
7×10^4	0.7930	0.8624	0.8866
9×10^4	0.7049	0.8574	0.8922

4.1.5 Effect of changed the number of tray to the product purity

In section, the number of trays of a batch reactive distillation column with constant reboiler heat duty operation is studied to find out the the variation of the desired product purity. Here, the number of trays is varied from 10 to 12,15 and 20 trays and the reflux ratio is fixed at 0.952. The simulation result is compared in Figure 4.8.

In Figure 4.8, the simulation result has been found that the ethyl acetate concentration increases when the number of tray is increased from 10 to 20 trays . At the final time as shown in Table 4.3, the least ethyl acetate concentration is 80.03% for the column with 10 trays and the highest ethyl acetate concentration is 90.85% for the column with 20 trays because the number of trays increased leads to the increment of mass transfer.

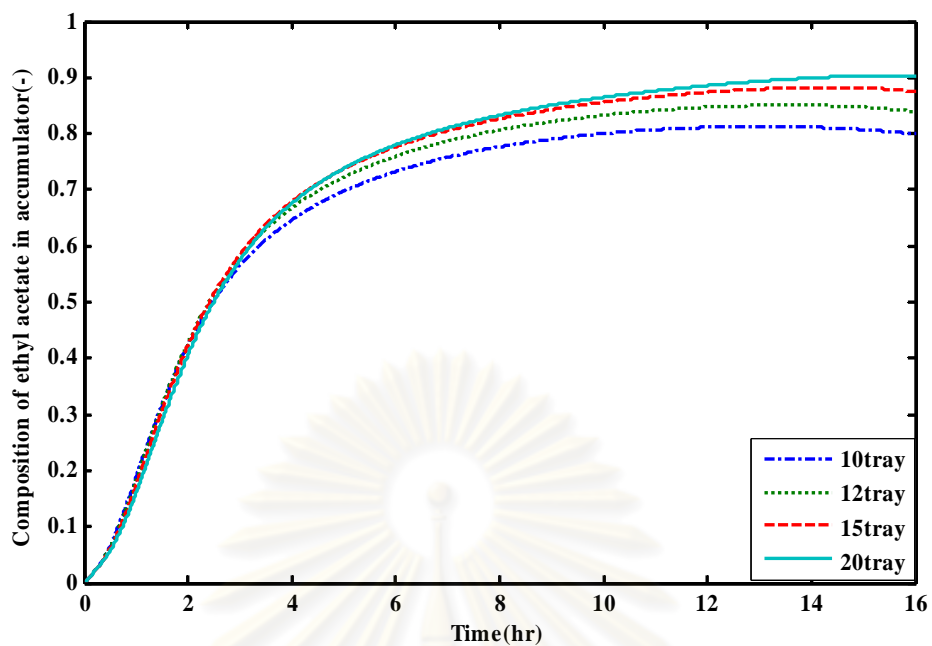


Figure 4.8 Concentration of ethyl acetate in accumulator with changed trays

Table 4.3 The distillate composition in the accumulator at the final batch time with the different number of trays

Number of tray (tray)	Ethyl acetate composition ($x_{a,3}$)
10	0.8003
12	0.8393
15	0.8762
20	0.9085

In this section, the other interesting point found is that in the first 30 seconds of operation, the ethyl acetate concentration for all case studies has the same profile as seen Figure 4.9. In addition, at one minute, the concentrations of each tray are slightly different in each case as seen Figure 4.10 and when the operation time reaches to half an hour the concentrations are rather different along the trays with rapidly reduced in the condenser section (tray 1) (Figure 4.11). This behavior occurred can be described that in the starting period of reaction, rate of reactions is very low leading to low evaporation and mass transfer and when the process is running about 30 min to the end of operation, the rate of reactions is high leading to high evaporation and mass transfer at the top of the column and therefore the column with higher trays have the product concentration higher than that of lower trays.

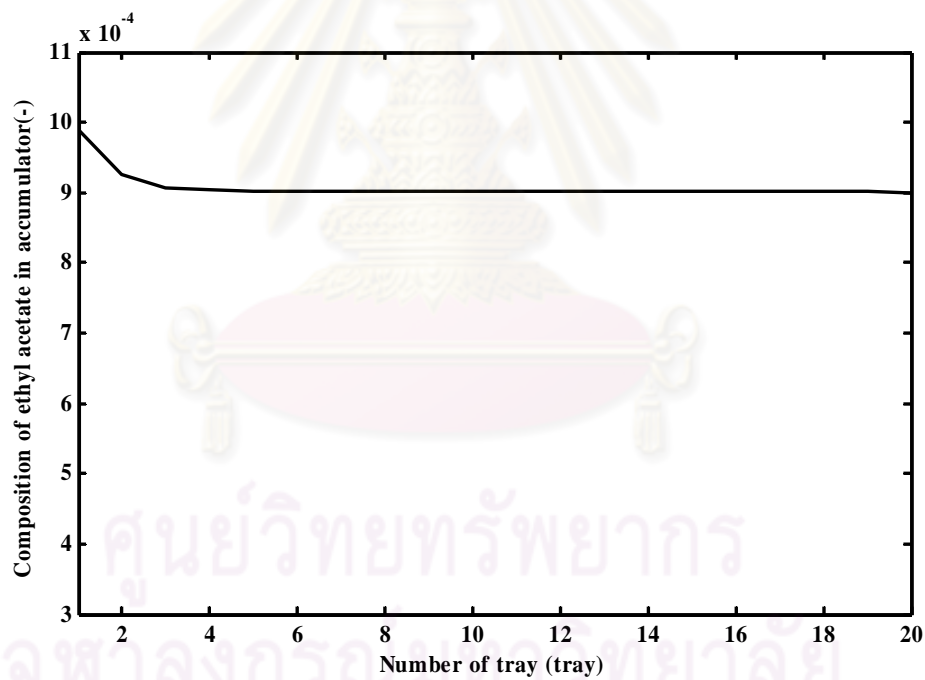


Figure 4.9 Concentration of ethyl acetate in each tray at 30 sec for column 10,12,15,20 trays

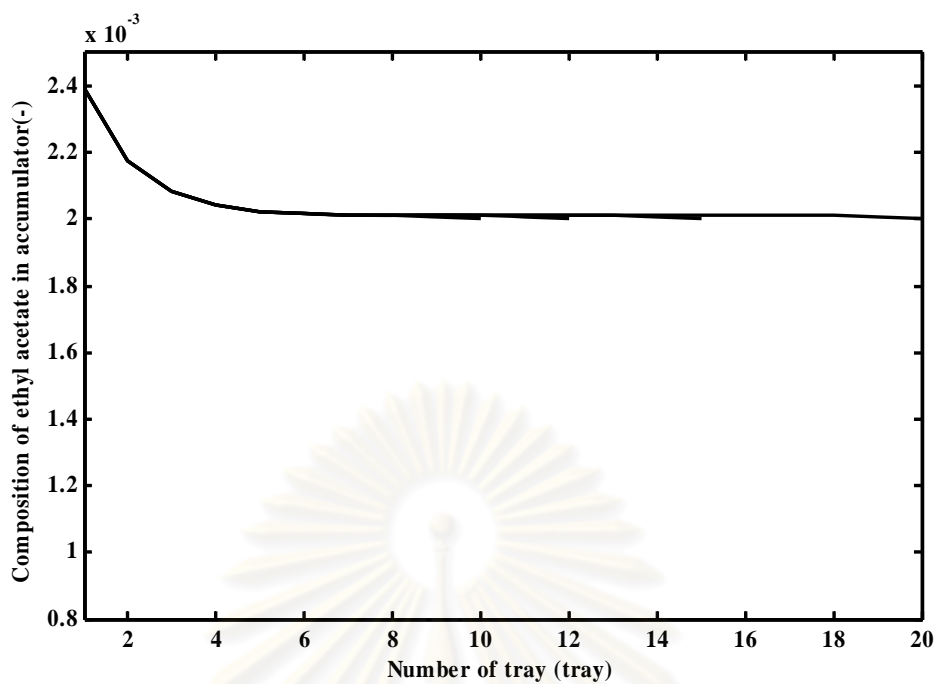


Figure 4.10 Concentration of ethylacetate in each tray at 1 min for column 10,12,15,20 trays

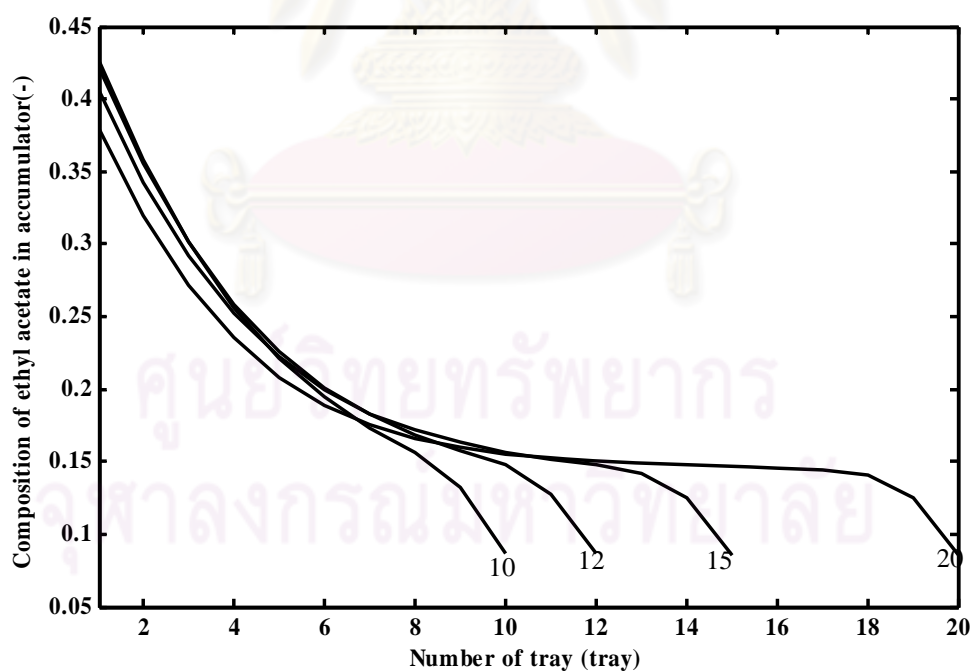


Figure 4.11 Concentration of ethylacetate in each tray at 30 min. for column 10,12,15,20 trays

4.1.6 The difference of the operation conditions

The different operation conditions of the heat duty, the number of trays and reflux ratio are studied to give the ethyl acetate concentration to 90% by operating constant reboiler heat duty. This section is compared the reflux ratio in each case for choosing the suitable number of tray in operation. For testing conditions, the reboiler heat duty is fixed at the constant values of 7.2×10^4 , 8.2×10^4 and 9.2×10^4 kJ/hr and the number of trays are varied from 12, 14, 16, 18 to 20 trays. Then the reflux ratio must be adjusted to achieve 90% by mole ethyl acetate. The results are shown in Figure 4.12 – 4.14.

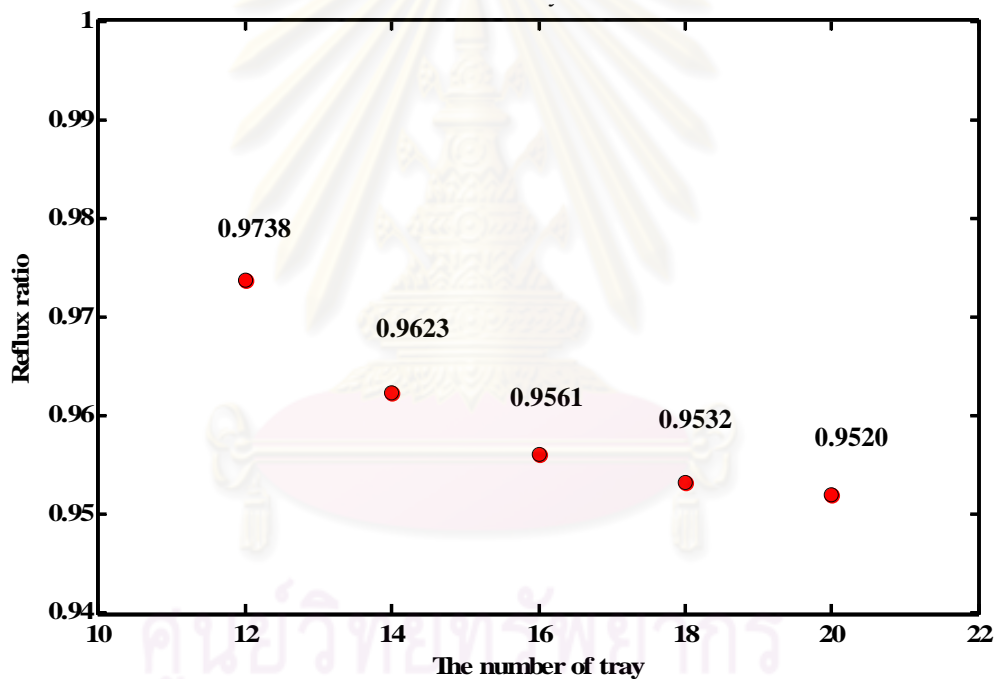


Figure 4.12 Reflux ratio of each column when the reboiler heat duty constant at 7.2×10^4 kJ/hr

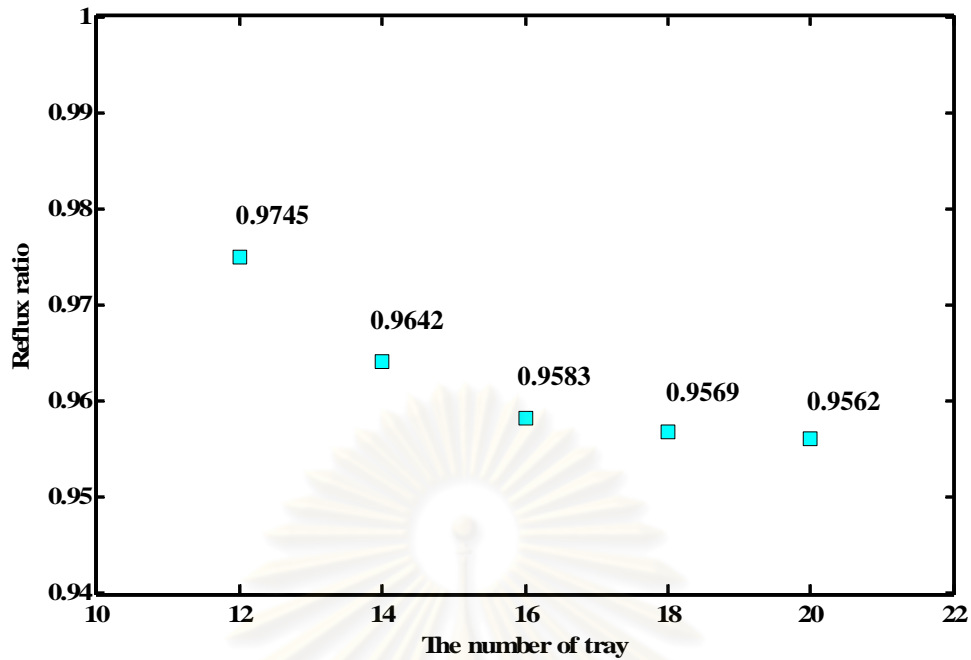


Figure 4.13 Reflux ratio of each column when the reboiler heat duty constant at $8.2 \cdot 10^4$ kJ/hr

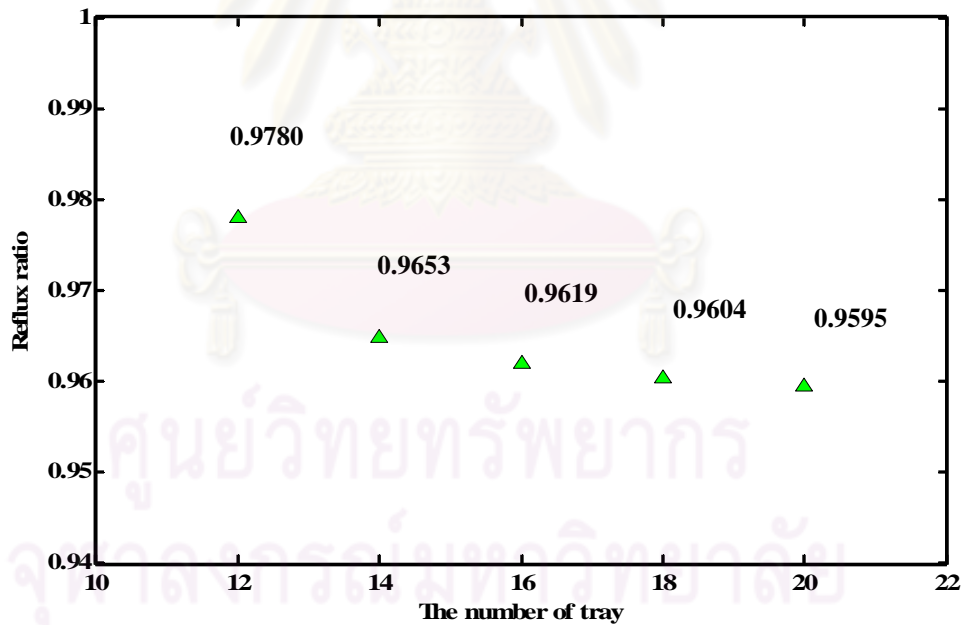


Figure 4.14 Reflux ratio of each column when the reboiler heat duty constant at $9.2 \cdot 10^4$ kJ/hr

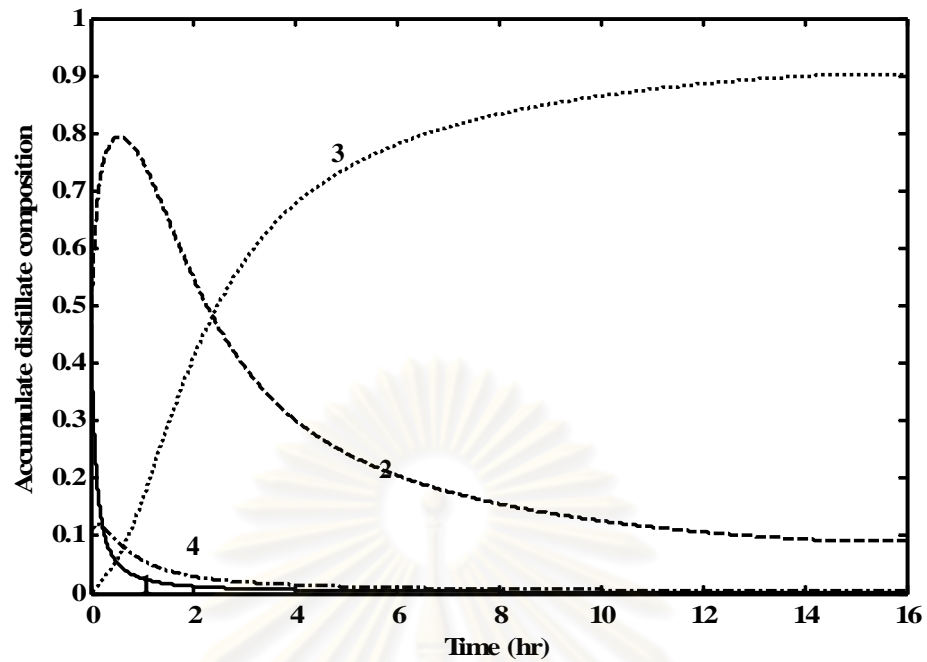
The ethyl acetate composition is defined to achieve 90% at 16 hours by manipulating different conditions of the operation. Simulation results have been indicated that in case of the column with the same tray, the reflux ratio must be

increased from 0.9520 to 0.9780 when the heat duty of operation is increased from 7.2×10^4 kJ/hr to 8.2×10^4 kJ/hr and 9.2×10^4 kJ/hr. In case of the column with 20 trays, the reflux ratio must be adjusted to 0.9520 when the reboiler heat duty is fixed at 7.2×10^4 kJ/hr. (Figure 4.12) whereas the reflux ratio is increased from 0.9520 to 0.9562, when the reboiler heat duty is increased from 7.2×10^4 kJ/hr to 9.2×10^4 kJ/hr (Figure 4.14). This is because when the heat supplied over the heat required for achieving the given product's purity, the other compositions evaporate leading to contamination to the desired product. Thus the reflux ratio must be increased to adjust the product purity back to its desired specification. In case of the column with the different trays, at constant heat duty, the reflux ratio is decreased from 0.99 to 0.95 when the number of tray is increased from 10 to 20 trays as shown in Figure 4.12-4.14. The minimum reflux ratio must be adjusted to 0.9520 for the column with 20 trays and the maximum reflux ratio must be adjusted to 0.9738 for the column with 12 trays as shown in Figure 4.12 because the number of trays increased leads to the increment of the product purity and the reflux ratio of the operation can be decreased.

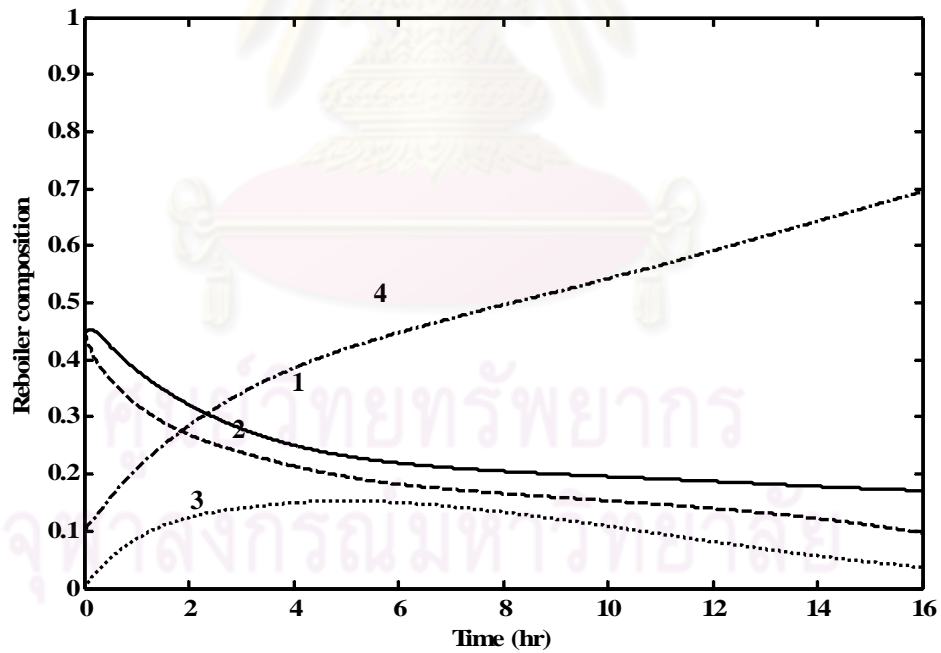
4.1.7 Constant reboiler heat duty operation with 20 tray

In this work, a batch reactive distillation column of 20 trays by constant reboiler heat duty at 7.2×10^4 kJ/hr and reflux ratio at 0.952 in previous section is chosen to study dynamic behavior for 16 hours in this section. The simulation results in both accumulator and reboiler are shown in figure 4.5:

The composition profiles of the both sections are the same as the 10 trays of constant heat duty operation as shown in Figure 4.4 but the 20 trays is achieved the product purity more than the 10 trays to 10% at the final time. In other words, the ethyl acetate concentration increases continuously and reaches to 90% whereas the other composition decrease in the accumulator section (Figure 4.15 (a)) and the composition of water increases whereas the other components decrease in the reboiler section (Figure 4.15 (b)). From these simulation results, the constant reboiler heat duty operation of a batch reactive distillation with 20 trays is optimized to reduce energy consumption subjecting to the product (ethyl acetate) purity of 90% by mole.



(a)



(b)

Figure 4.15 Composition profile of ethanol esterification of the constant reboiler heat duty operation with 20 tray (a) in accumulator (b) in reboiler: 1 acetic acid 2 ethanol 3 ethylacetate 4 water

4.1.8 Sensitivity Analysis

Before solving an optimization problem, process parameters and the variables must be tested to study the influence of the product purity. The parameters and the variables studied are density, specific heat capacity, liquid holds up, reaction rate constant, molecular weight, heat duty and reflux ratio. Thus, the parameters and the variables studied can be concluded as follows:

1. Reflux ratio.

In the study, the heat duty is fixed constant at 7.2×10^4 kJ/hr, and when reflux ratio is increased from 0.9000 to 0.9750, the product purity increases because the product impurity can be removed out of the product as shown in Figure 4.16.

2. Reboiler heat duty.

When the reflux ratio is fixed at a constant value of 0.952. and the reboiler heat duty is increased from 3×10^4 to 9×10^4 , the product purity will increase from 90 to 95% . This is because the endothermic reaction can take place at the condition with higher heat input much more than that with less one as shown in Figure 4.17.

3. Reaction rate constant (k_1)

In the study, when the reflux ratio and the heat duty are fixed at 0.952 and 7.2×10^4 respectively, the reaction rate constant is increased from 10 to 30% and decreased from -10 to -30%. It has been found that the desired product purity increases when reaction rate constant is increased to 92% (increase in the forward reaction). In contrast, the desired product purity decreases when the reaction rate constant is decreased to 87% (increase in the backward reaction) as shown in Figure 4.18.

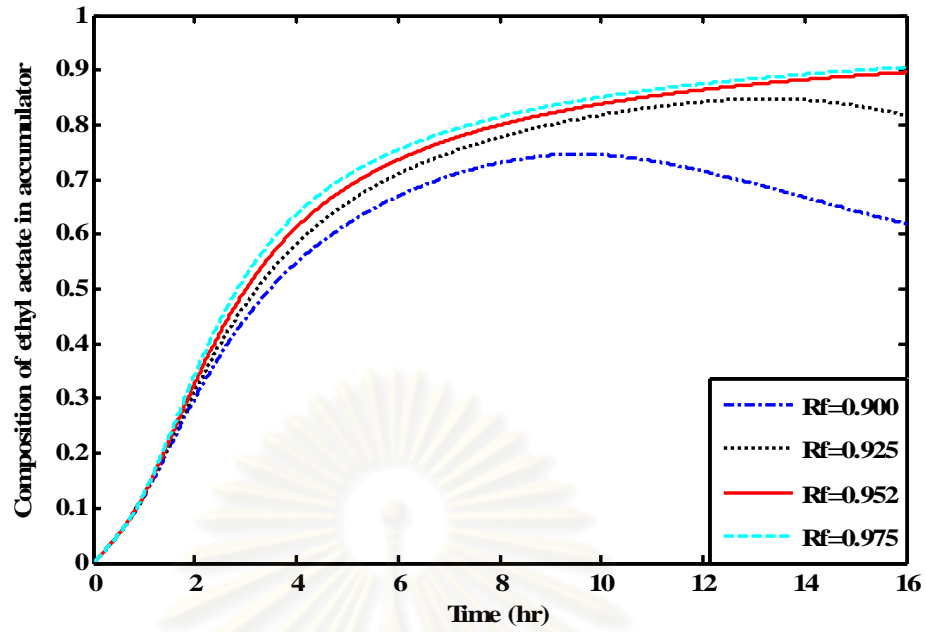


Figure 4.16 Concentration of ethyl acetate in accumulator at different reflux ratio

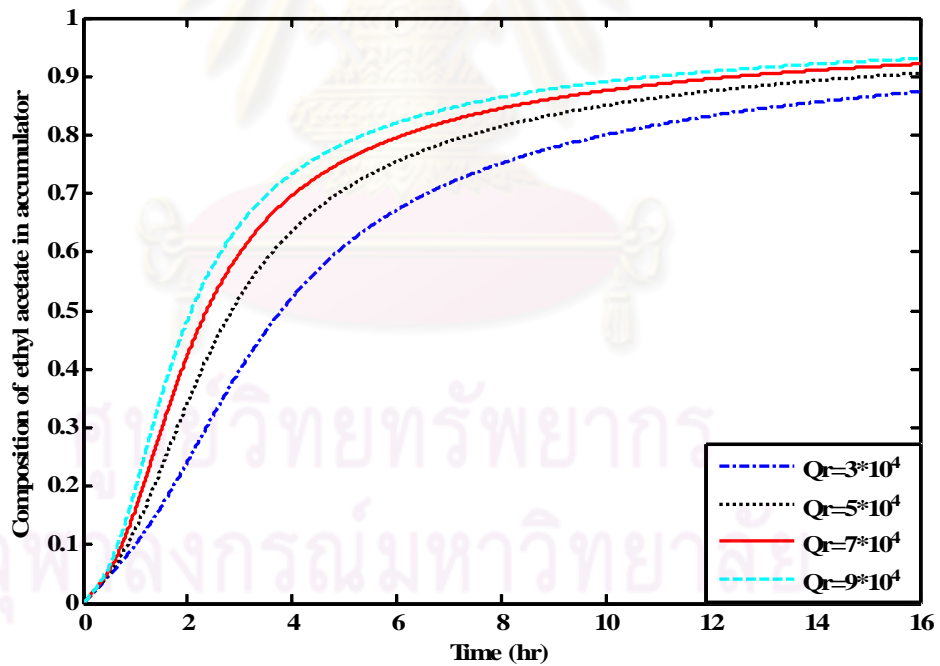


Figure 4.17 Concentration of ethyl acetate in accumulator at different reboiler heat duty

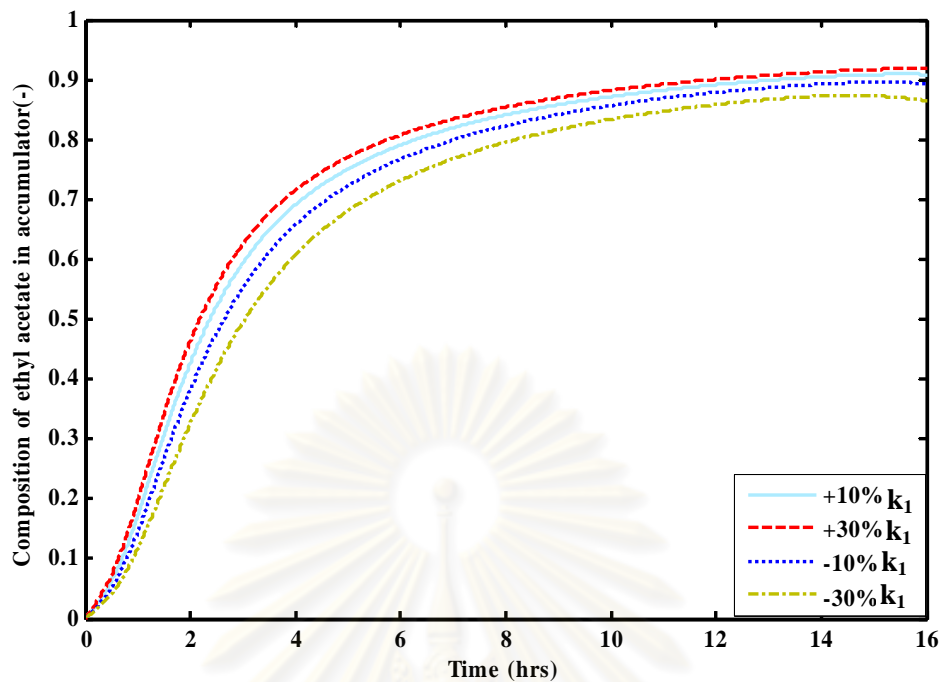


Figure 4.18 Concentration of ethyl acetate in accumulator when increased and decreased reaction rate constant (k_1)

After the sensitivity analysis of variables and the parameters are studied, it has been found that the reboiler heat duty and reflux ratio are more sensitive to the product purity than other variables. Thus, these variables are chosen to be decision variables in the study of the optimization problem.

The advantages of the sensitivity analysis cannot only give information regarding the selection of variables as the most effect on the process but also define the boundary conditions for reducing the CPU time for solution finding of the process.

4.2 Dynamic Optimization Study

The maximum product and the minimum heat duty problem by manipulating the reflux ratio and the reboiler heat duty to achieve 90% by mole of ethyl acetate of a batch reactive distillation by the constant reboiler heat duty operation is studied in the dynamic optimization section. The reflux ratio and the heat duty are chosen to apply

with many research. For example, Sorensen et al. (1996) studied a reactive batch distillation process to maximize profitability both zero cost function of cost raw material and fixed cost material or to minimize operating time. Manipulated variables for optimal control were the heat input to the reactor and the reflux ratio and Young Han Kim (1999) developed optimization problem for maximum product problem by manipulated reflux ratio. The outcome of the optimization for the example system indicated that more of the desired product with less operation time is necessary but, those papers show a distilled product with only 80% maximum by mole of the ethyl acetate. Thus, this work improves the product purity and save energy consumption for increasing profit of the process.

4.2.1 Problem formulation

Two optimization problems related to a batch reactive distillation operation: maximization the amount of the desired product in the problem 1 and maximization the amount of the desired product whereas minimization of the energy consumption in problem 2 are studied to determine an optimal reflux ratio profile and an optimal reboiler heat duty profile, which highly influence the purity and the amount of the desired product. The obtained optimal profiles have to satisfy the specified objective function and other desired process constraints.

The optimization problems are divided into two problems and four cases as follows:

- **Maximum desired product Problem (P1)**

$$J = H_a x_{a3} M_{W3}$$

In this problem, the objective function is to compute the optimal reboiler heat duty (case1) and reflux ratio (case 2) policy for maximizing the amount of the desired product (J) for a given fixed a batch time subject to bounds on the purity of the desired product, the reboiler heat duty and the reflux ratio.

Case 1 Reflux ratio is decision variable

In this case, the optimal reflux ratio profile is computed to obtain the maximum product by fixed batch time subject to boundaries on the reflux ratio. The case can be written mathematically as:

$$\text{Max}_{r_f} J$$

subject to:

Eqs. 3.1-3.21 (rigorous model with chemical reactions)

$$x_{a3}(t_f) \geq 0.9$$

$$0.9 \leq r_f \leq 1$$

$$Q_r = 7.2 * 10^4 \text{ kJ}$$

$$t_f = 16 \text{ hr.}$$

where J is the amount of the desired product at the given final batch time, H_a is the amount of product (ethyl acetate and water), x_{a3} is mole fraction of ethyl acetate, M_{w_3} is molecular weight of ethyl acetate, r_f is reflux ratio, Q_r is reboiler heat duty and t_f is final batch time.

Case 2 Reboiler heat duty is decision variable

The optimization of case 2 is to determine the optimal heat duty profile to achieve the maximum product subject to heat duty constraint. The formulation of this case are shown as:

$$\text{Max}_{Q_r} J$$

Subject to:

Eqs. 3.1-3.21 (rigorous model with chemical reactions)

$$x_{a3}(t_f) \geq 0.9$$

$$1 * 10^4 \leq Q_r \leq 20 * 10^4 \text{ kJ / hr}$$

$$r_f = 0.952$$

$$t_f = 16 \text{ hr.}$$

- **Maximum desired product Minimum Heat duty Problem (P2)**

In a batch reactive distillation process for problem 2, the desired product is produced the high amount while the heat energy is used the lowest possible. For this relation, the aim of dynamic optimization is maximizing the desired product (C_1J) whereas using minimizing the heat duty (C_2Q_r) in terms of the cost function also subject to the given the desired product purity, the reflux ratio and the reboiler heat duty constraints. In case 3, reboiler heat duty is selected as the decision variables and in case 4, the reflux ratio and reboiler heat duty are selected as the decision variables to be optimized for fixed batch time.

Case 3 Reboiler heat duty is decision variable

The objective of the case 3 is to calculate the heat duty profile to achieve the maximum desired product using the minimum heat duty by constraining a bound on the heat duty. The formulation can be formed as follows:

$$\text{Max}_{Q_r} C_1J - C_2Q_r$$

Subject to

Eqs. 3.1-3.21 (rigorous model with chemical reactions)

$$x_{a3}(t_f) \geq 0.9$$

$$r_f = 0.952$$

$$1 * 10^4 \leq Q_r \leq 20 * 10^4 \text{ kJ / hr}$$

$$t_f = 16 \text{ hr.}$$

Case 4 Reflux ratio and reboiler heat duty are decision variable

In the last case, the optimal heat duty and the optimal reflux ratio profile are computed in order to obtain the maximization amount of the desired product by saving heat energy consumption. The relation of this case is shown below:

$$\text{Max}_{r_f, Q_r} C_2 J - C_1 Q_r$$

Subject to

Eqs. 3.1-3.21 (rigorous model with chemical reactions)

$$x_{a3}(t_f) \geq 0.9$$

$$0.9 \leq r_f \leq 1$$

$$1 * 10^4 \leq Q_r \leq 20 * 10^4 \text{ kJ / hr}$$

$$t = 16 \text{ hr}$$

Q_r is reboiler heat duty (kJ). C_1 is price of ethyl acetate 729.5171 Baht/kg (taken from Your personalized laboratory scientific supply and chemical distributor, 2010). C_2 is energy cost 0.0039 Baht/kJ (taken from Europe's energy portal, 2010).

The aims of the dynamic optimization problem in all cases are to compute the optimal profile and to study the factors affecting the amount of desired product and energy consumption as differences of objective functions, number of intervals and differences of decision variables. The first set of simulation studies have investigated the case where theoretical optimal profiles are determined by off-line computation providing and perfect tracking of such a profile is assumed. This results in the optimal trajectory that can be achieved at the end of the batch run and serves as a reference to

be compared with the results obtained from the proposed strategy. The optimal control problems are solved using time intervals (see concept time interval in section 3.51). The switching time is fixed and the length of each intervals is specified by dividing the fixed batch time (t_f) with a number of time intervals. Therefore, the problems are to find only optimal profile in each subinterval then all of the results are analysed in term the key performance indicator (KPI).

4.2.2 Dynamic Optimization Results

The optimization results are divided into three parts. The first part studies the influenced of time intervals to the amount of the desired product. The second studies the influenced of objective function and a decision variables to the amount of the desired product and heat duty of operation. The last studies the profits sensitivity.

4.2.2.1 The different time intervals

Simulation results in case one and case two given here are based on problem 1, in which the objective function is to find the optimal reflux ratio profile (case 1) and heat duty of operation profile (case 2). The optimal control problems have been solved using time intervals with equal lengths varied at 1,2,4,8 and 16 intervals to discretize the profile. Thus, the problem is to seek the optimal reflux ratio and the optimal heat duty (decision variables) in each subinterval.

Case 1 Optimal reflux ratio

The result of case 1 shows the optimal reflux ratio profile of a maximum desired product by fixing the final batch time. The reflux ratio is bounded according to $0.9 \leq r_f \leq 1$ and the ethyl acetate purity constraint at the final time is bounded by $x_{a3}(t_f) \geq 0.9$.

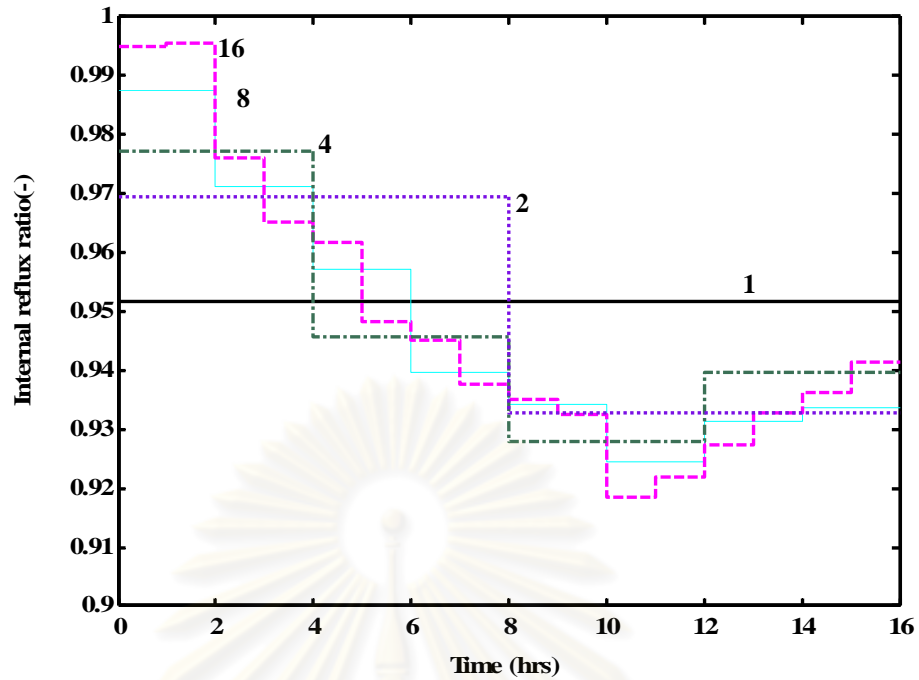


Figure 4.19 Optimal reflux ratio profile: 1 interval(1), 2 interval (2), 4 interval (4), 8 interval (8), 16 interval (16)

Simulation results with different time intervals of case 1 are reported in Table 4.4. Optimal control policy of reflux ratio for each sub interval is shown in Figure 4.20. As seen in Table 4.4, when one time interval is used, the amount of the desired product obtained at the final time ($t_f = 16$ hr.) is 139.9072 kg. The optimal reflux ratio set point is 0.9516. Whereas using time intervals = 16, the amount of the desired product achieved is 152.6412 kg. This reason was indicated that when the number of intervals increase, the amount of the desired product increases also because as the number of intervals enlarges, the approximated optimal profile with piecewise constant policy is closer to the actual optimal profile. Furthermore, when time interval is increased that the computational time to find optimal point increases.

Table 4.4 Summary of the optimal reflux ratio: off-line optimization

Intervals	The amount of desired product (kg.)
1	139.9072
2	141.6437
4	143.0312
8	146.6231
16	152.6412

Case 2 Optimal reboiler heat duty

The result presented here correspond to the case 1 where the objective is to maximize the amount of the desired product subject to a terminal constraint on heat duty $1 \times 10^4 \leq Q_r \leq 20 \times 10^4 \text{ kJ/hr}$, the ethyl acetate purity constraint more than 90% that is the same case 1. The optimization results are shown in optimal profile (Figure 4.20) and Table 4.5.

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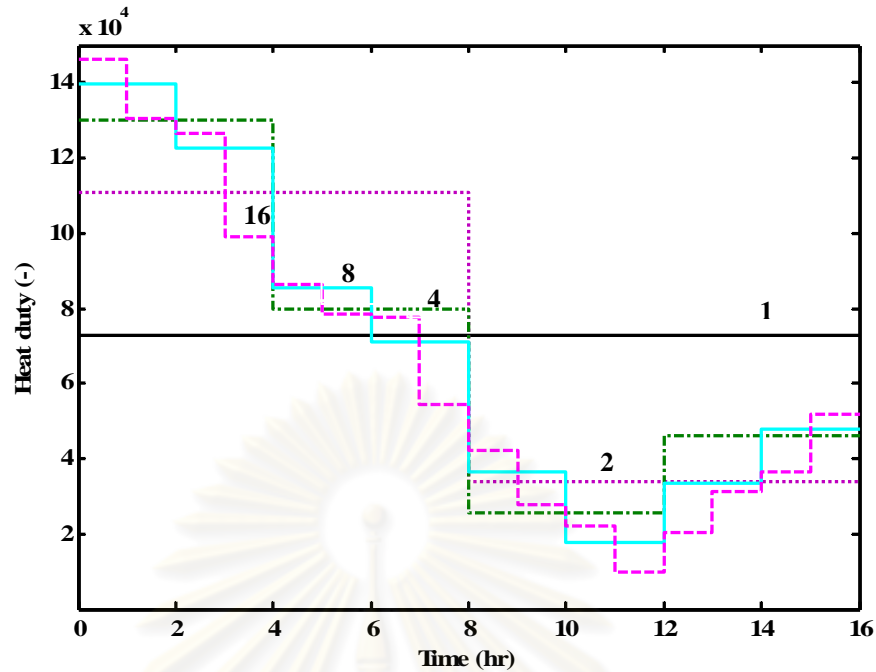


Figure 4.20: Optimal reboiler heat duty profile: 1 interval (1), 2 interval (2), 4 interval (4), 8 interval (8), 16 interval (16)

Optimal heat duty profile of operation is shown in Figure 4.21. Energy consumption through operation and the amount of the desired product are shown in the Table 4.5. For one time interval, the heat energy used is 1,167,728 kJ and the amount of the desired product obtained at the final time ($t_f = 16$ hr.) is 140.6893 kg. In the case 16 time intervals, the maximum of desired product is at 155.4798 kg. and the minimum heat duty is 1,040,631 kJ. When the time intervals are increased from 1 to 16, not only the amount of the desired product increases but also the energy consumed decreases.

While the time intervals are increased from 1 to 16 time intervals, the computation time of optimization increases. Therefore, The number of time intervals used must be carefully select to achieve maximum productd and with less energy consumption within feasible CPU time.

Table 4.5 Summary of the optimal heat duty: off-line optimization

Intervals	Sum heat duty (kJ)	The amount of desired product (ethyl acetate) kg.
1	1,167,728	140.6893
2	1,155,864	144.2919
4	1,139,724	146.7816
8	1,109,364	149.5647
16	1,040,631	155.4798

4.2.2.2 The difference of conditions

There are many factors affecting optimization problem that time intervals are one factor as indicated the previous section. In this section, the objective function and the decision variables are discussed to find the optimum answer. In testing, the time intervals are varied at 1,2,4,8 and 16 intervals then the simulation results of all case are compare in Table 4.6.

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Table 4.6 The results of dynamic optimization every case.

Intervals	Case	Sum energy consumption (kJ)	Amount of the desired product (kg)	xa	KPI (kJ/kg)
1	Maximum desired product (R_f)	1,152,000	139.9072	0.9000	8234.0294
	Maximum desired product (Q_r)	1,167,728	140.6893	0.9033	8300.0484
	Maximum desired product and Minimum heat (Q_r)	853,568	102.2207	0.9000	8350.2461
	Maximum desired product and Minimum heat (Q_r, R_f)	925,984	119.7517	0.9000	7732.5332
2	Maximum desired product (R_f)	1,152,000	141.6437	0.9000	8133.0832
	Maximum desired product (Q_r)	1,155,864	144.2919	0.9000	8010.5952
4	Maximum desired product (R_f)	1,152,000	143.0312	0.9012	8054.1868

Table 4.6 (Continued)

Intervals	Case	Sum energy consumption (kJ)	Amount of the desired product (kg)	$x_{a,3}$	KPI (kJ/kg)
4	Maximum desired product (Q_r)	1,139,724	146.7816	0.9071	7764.7607
8	Maximum desired product (R_f)	1,152,000	146.6231	0.9005	7856.8793
	Maximum desired product (Q_r)	1,109,364	149.5647	0.9056	7417.2850
	Maximum desired product and Minimum heat (Q_r)	811,800	107.3001	0.9025	7565.6966
	Maximum desired product and Minimum heat (Q_r, R_f)	888,984	132.8390	0.9102	6692.1913
16	Maximum desired product (R_f)	1,152,000	152.6412	0.9085	7547.1105
	Maximum desired product (Q_r)	1,040,632	155.4798	0.9138	6693.0367

Key Performance Indicator (KPI)

$$KPI = \frac{\text{Energy consumption (kJ)}}{\text{Product (kg)}}$$

The simulation results of all case (4 case of two problem) as shown in Table 4.6 can be analysed in many ways as follows:

1. Difference of the objective function

The optimization results of the maximum desired product (Q_r) in the case 2 is compared with the maximum desired product and the minimum heat duty (Q_r) in the case 3. For 1 and 8 time intervals, the case 2 obtains the amount of the desired product 140.6893 kg and KPI 8,300.0484 kJ/kg for 1 interval and obtains the amount of the desired product 149.5647 kg and KPI 7,417.2850 kJ/kg for 8 intervals whereas case 3 achieves the amount of the desired product 102.2207 kg and KPI 8,350.2461 kJ/kg for 1 interval and achieves the amount of the desired product 107.3001 kg and KPI 7,565.6966 kJ/kg for 8 interval. According to this simulation results, case 2 uses the energy consumption per the amount of the desired product less than case 3 to 0.60% for 1 interval and to 2.00% for 8 intervals. Moreover, the case 2 obtains the amount of the desired product more than the case 3 to 27.34% for 1 interval and to 28.25% for 8 intervals.

2. Difference of the decision variable

The maximum desired product and the minimum heat duty problem by manipulating heat duty (case 3) is compared with the maximum desired product and the minimum heat duty by manipulating reflux ratio and heat duty (case4). It has been found that the case 3 receives the amount of the desired product 102.2207 kg and KPI 8350.2461 kJ/kg for 1 interval and receives the amount of desired product 107.3001 kg and KPI 7565.6966 kJ/kg for 8 interval whereas the case 4 obtains the amount of the desired product 119.7517 kg and KPI 7732.5332 kJ/kg for 1 interval and obtains the

amount of the desired product 132.8390 kg and KPI 6692.1913 kJ/kg for 8 interval. According to this simulation results, case 4 dose not only uses energy consumption per the amount of the desired product less than case 3 to 7.39% for 1 interval and 11.54% for 8 intervals)but also obtains the amount of the desired product more than case 3 to 17.15% for 1 interval and 23.80% for 8 intervals.

The optimization results of every case are compared for finding the best answer in Table 4.6. It has been found that the maximum product and minimum heat duty by manipulating reflux ratio and heat duty (case 4) for 8 intervals used the minimum of energy consumption per the amount of the desired product (KPI) is 6692.1913 (heat duty decreased to 24.79% and product decreased to 19.93% when compared with case2 for 8 intervals) whereas the maximum product by manipulating heat duty (case2) for 16 intervals acheived the maximum the amount of the desired product is 155.4798 kg.

The performance of distillation operation not only receive the amount of the desired product but also consider energy consumption. Thus optimization should be selected objective function and decision variable with covered of quality and saving cost.

4.2.2.3 Profits

This part studies the effect of the difference time intervals to profit. In this study, 1 and 8 time intervals of each case is computed the profit per year for finding the maximum profit.

$$\begin{aligned} \text{Profit (Baht/yr)} &= \text{total product prices} - \text{total raw material cost} - \text{total energy cost} \\ &= C_1 J - (C_2 A - C_4 E) - C_3 Q_r \end{aligned}$$

Product prices = 729.5171 Baht/kg. Acetic acid cost =245.7320 Baht/kg. ethanol cost= 130.5451 (taken from Your personalized laboratory scientific supply and chemical distributor, 2010). Energy cost = 0.0039 Baht/kJ (taken from Europe's energy portal, 2010).

Table 4.7 Summary the profits of four cases with difference time intervals.

Intervals	Case	Sum energy consumption (kJ)	Amount of the desired product (kg)	Profit (Baht/Year)
1	1	1,152,000	139.9072	24,531,756
	2	1,167,728	140.6893	24,760,903
	3	853,568	102.2207	12,683,680
	4	925,984	119.7517	18,311,713
8	1	1,152,000	146.6231	34,464,912
	2	1,109,364	149.5647	35,512,897
	3	811,800	107.3001	22,212,610
	4	888,984	132.8390	30,447,584

From Table 4.7, it has been found that the profit increases when time intervals are increased from 1 to 8 intervals. One time interval of case 3 obtained the minimum profit is 32,059,275 Baht/Year whereas eight time intervals of case 2 obtained the maximum profit are 47,152,569 Baht/Year. When the different time intervals of the same case are compared the optimization result, it has been found that case 1, 2 and 3, the profit increase about 5-7% and in case 4, the profit increases to 11.57% or 4,361,269 Baht/Year.

4.2.2.4 Profit Sensitivity

The profit sensitivity is evaluated with respect to product prices, raw material cost and energy cost when the problem is formulate in term cost function. If it is formulated different from then the problem will depend on other factors. In study, product prices, raw material cost and energy cost are increased from 0% to +30% and decreased from 0% to -30% then profit sensitivity is calculated by using the optimization results in each case for 1 interval only (section 4.2.2.2). The profit sensitivity is shown as figure 4.21-4.24:

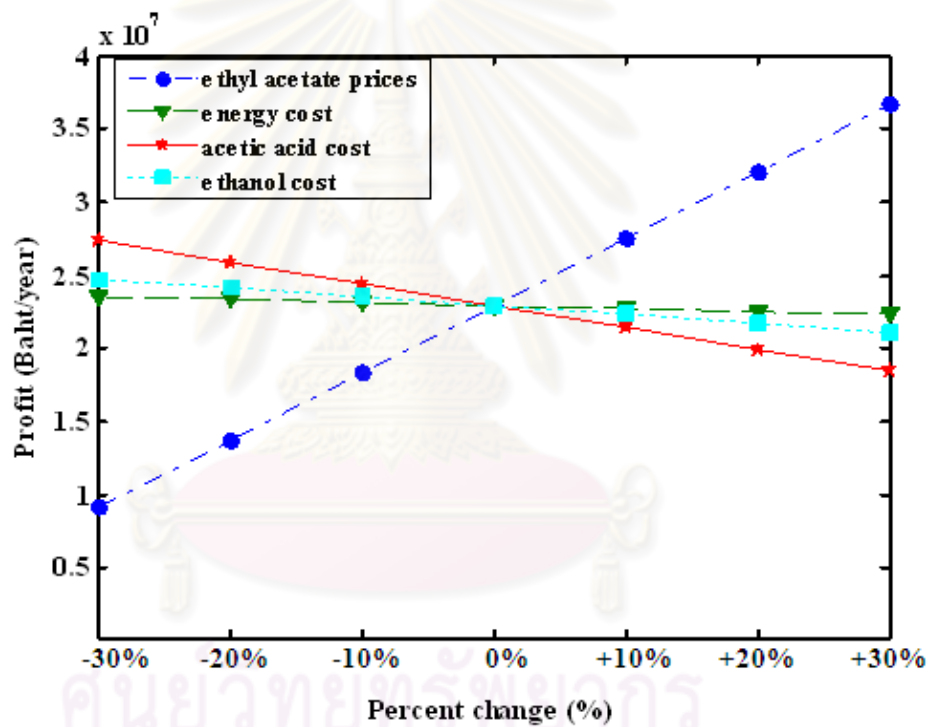


Figure 4.21 Sensitivity of profit case 1

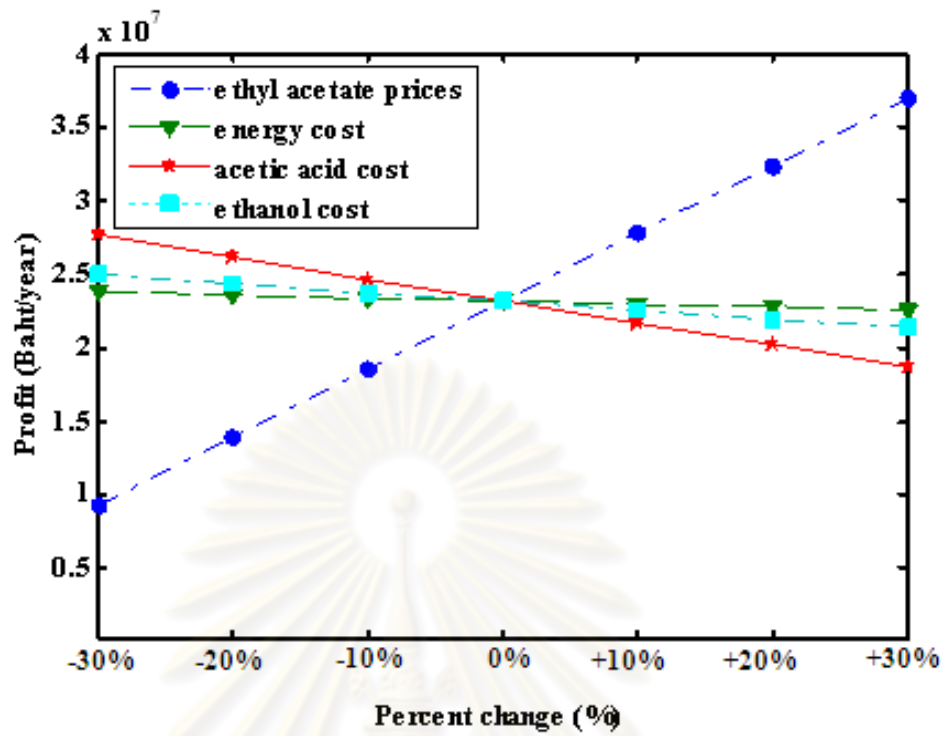


Figure 4.22 Sensitivity of profit case 2

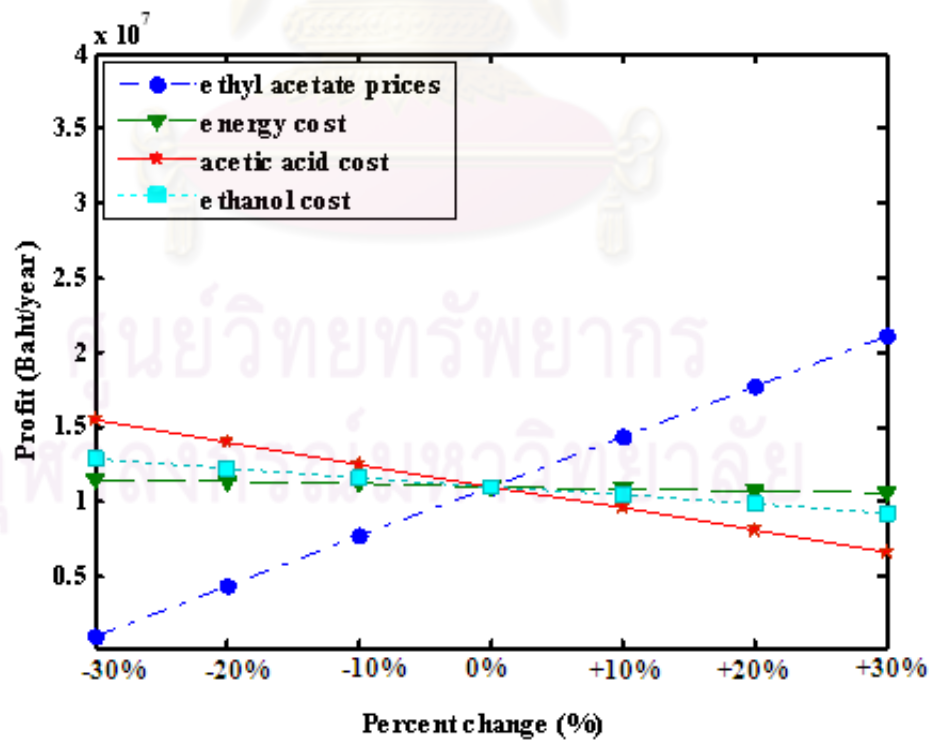


Figure 4.23 Sensitivity of profit case 3

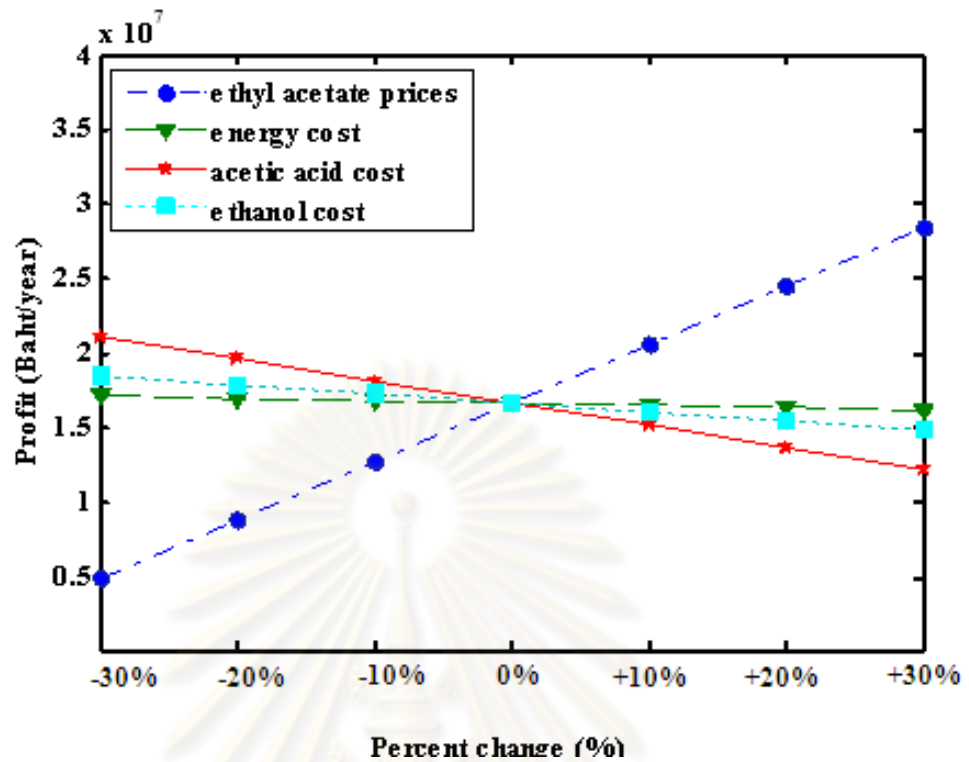


Figure 4.24 Sensitivity of profit case 4

The evaluated result of profit sensitivity has been found that for all case, the changed product price (ethyl acetate) affect on the most of profit rate which profit rate increases and decreased to 30% whereas energy cost affect on the least profit rate which profit rate increases and decrease 3% only.

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CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The dynamic optimization of a batch reactive distillation column that the reboiler heat duty and the reflux ratio are chosen to be the control variables, is studied in this work for reducing energy consumption. In the study, optimization problem is divided into 4 cases. First case finds the optimal reflux for the maximum product problem. Case two computes the optimal reflux and the optimal reboiler heat duty profile of the maximum product problem. Case three computes the optimal reboiler heat duty profile of the maximum product and minimum heat duty problem. In the last case, the optimal reflux and reboiler heat duty profile are computed for the maximum product and the minimum heat duty problem. The optimization results can be concluded as follows:

1. The number of time intervals are not only increased amount of product but also reduce the energy consumption because the number of intervals enlarges, the approximated optimal profile with piecewise constant policy is closer to the actual optimal profile.
2. Two decision variables give the amount of product more than one decision variable. Thus, two decision variables are preferable.
3. In terms of energy consumption, case four for 8 intervals can mostly save the energy consumption. In terms of amount of product, case two for 16 intervals obtains the maximum amount of product.
4. The profit increases when time intervals are increased from 1 to 8 intervals. Comparing all case, case two has the highest profits which is 47,152,569 bath/year.

Therefore, the number of time interval, the objective function and decision variables are considered with dynamic optimization problem for finding the optimal value in operation.

5.2 Recommendation

In general, the first step in developing system is a process simulation design based on the mathematical model. The researcher should test the mathematical model by openloop control to compared with the initial simulation results for checking the step calculation. When the results are the same then it can be further developed including optimization problem and controll system.

5.3 Development

1. Developed optimization problem should be studied about cost, fixed amout of product for enhance the efficeint of the column.
2. In the future, the optimization problem result of this research can be applied with controll system of a batch reactive distillation



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APPENDICES

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APPENDIX A

SUCCESSIVE QUADRATIC PROGRAMMING (SQP)

Successive quadratic programming (SQP) method solved a sequence of quadratic programming approximation to nonlinear programming problem. Quadratic Programs (QPs) have a quadratic objective function and linear constraints, and there exist efficient procedures for solving them.

- **Problem formulation with equality constraints**

To derive SQP, we again consider a general NLP

$$\begin{aligned} \text{Minimize : } & f(x) \\ \text{Subject to : } & g(x) = b \end{aligned} \tag{A.1}$$

The Langrangian function for this problem is

$$L(x, \lambda) = f(x) + \lambda^T (g(x) - b) \tag{A.2}$$

and the Kunh-Tucker Conditions (KTC) are

$$\nabla_x L = \nabla f(x) + \sum_{i=1}^m \lambda_i \nabla g_i(x) = 0 \tag{A.3}$$

and

$$g(x) = b \tag{A.4}$$

The equation (A.1)-(A.2) is a set of $(n+m)$ nonlinear equations in the n unknowns x and m unknown multipliers λ . Linearization of (A.2) – (A.3) with respect to x and λ

$$\nabla_x L - \nabla_x^2 L \Delta x + \nabla g^T \Delta \lambda = 0 \quad (\text{A.5})$$

$$g + \nabla g \Delta x = 0 \quad (\text{A.6})$$

For problem with only equality constraints, we could simply solve the linear equations (A.2)-(A.3). To accommodate both equalities and inequality, an alternative viewpoint is useful. Consider the quadratic programming problem

$$\begin{aligned} \text{minimize: } & \nabla L^T \Delta x + \frac{1}{2} \Delta x^T \nabla_x^2 L \Delta x \\ \text{Subject to: } & g + \nabla g \Delta x = 0 \end{aligned} \quad (\text{A.7})$$

If we call the Lagrange multipliers for (A.7) $\Delta \lambda$, the Lagrangian for the QP is

$$L_1(\Delta x, \Delta \lambda) = \nabla L^T \Delta x + \frac{1}{2} \Delta x^T \nabla_x^2 L \Delta x + \Delta \lambda^T (g + \nabla g \Delta x) \quad (\text{A.8})$$

- **Inclusion of the both equality and inequality constraints**

When the original problem has a mixture of equalities and inequalities, it can be transformed into a problem with equalities and simple bounds by adding slacks, so the problem has an objective function f , equalities (A.1) and bounds

$$l \leq x \leq u \quad (\text{A.9})$$

This system is the KTC for the QP in (A.7) with the additional bound constraints

$$l \leq \bar{x} + \Delta x \leq u \quad (\text{A.10})$$

Here the QP sub problem now has both equality constraints and must be solved by some iterative QP algorithm.

- **The approximate Hessian**

Solving a QP with a positive-definite Hessian is fairly easy. Several good algorithm all converge in finite number of iteration. However, the Hessian of the QP presented in (A.7) and (A.10) is $\nabla_x^2 L(\bar{x}, \bar{\lambda})$ is an optimal point. In addition, to compute $(\bar{x}, \bar{\lambda})$ is an optimal point. In addition, to compute $\nabla_x^2 L$ by positive-definite quasi-Newton approximate B, which is updated using only values of L and $\nabla_x L$. Most SQP algorithms use Powell's modification of Broyden–Fletcher–Goldfarb–Shanno (BFGS) update. Hence the QP subproblem becomes $QP(\bar{x}, B)$

$$\begin{aligned} \text{minimize : } & \nabla L^T \Delta x + \frac{1}{2} \Delta x^T B \Delta x \\ \text{Subject to: } & \nabla g \nabla x = -g, \quad I \leq \bar{x} + \Delta x \leq u \end{aligned} \quad (\text{A.11})$$

- **The SQP line search**

To arrive at a reliable algorithm, one more difficulty must be over come. Newton and quasi-Newton method may not converge if a step of 1.0 is used at each step. Both trust region and line search versions of SQP have been developed that converge reliability. A widely used line search strategy is to use the L_1 exact penalty function ($P(x, w)$). In a line search SQP algorithm, $P(x, w)$ is used only to determine the step size along the direction determined by the QP subproblem $QP(\bar{x}, B)$. The L_1 exact penalty function for the NLP problem is

$$P(x, w) = f(x) + \sum_{i=1}^m w_i |g_i(x) - b_i| \quad (\text{A.12})$$

where a separate penalty weight w_i is used for each constraint. The SQP line search chooses a positive step size α to find an approximate minimum of

$$r(\alpha) = P(x + \alpha\Delta x, w) \quad (\text{A.13})$$

A typical line search algorithm, which uses the derivative of $r(\alpha)$ evaluated at $\alpha = 0$ denote by $r'(0)$, is

1. $\alpha \leftarrow 1$
2. if $r(\alpha) < r(0) - 0.1\alpha r'(0)$ (A.14)

stop and return the current α value

3. Let α_1 be the unique minimum of the convex quadratic function that passes through $r(0)$, $r'(0)$ and $r(\alpha)$. Take the new estimate of α as

$$\alpha \leftarrow \max(0.1\alpha, \alpha_1) \quad (\text{A.15})$$

4. Go to step 2.

- **SQP algorithm**

Base on this line search and the QP subproblem $QP(\bar{x}, B)$

1. Initialize: $B^0 \leftarrow I, x^0 \leftarrow x, k \leftarrow 0$
2. Solved the QP subproblem $QP(\bar{x}, B)$, yielding a solution Δx^k and Langrange multiplier estimates λ^k
3. Update the penalty weights in penalty function
4. Apply the line search algorithm, yielding a positive step size α^k
5. $x^{k+1} = x^k + \alpha^k \Delta x^k, \lambda^{k+1} = \lambda^k$

6. Evaluated all problem function and their gradients at new point. Update matrix B^k

7. Replace k by $k+1$, and go to step 2

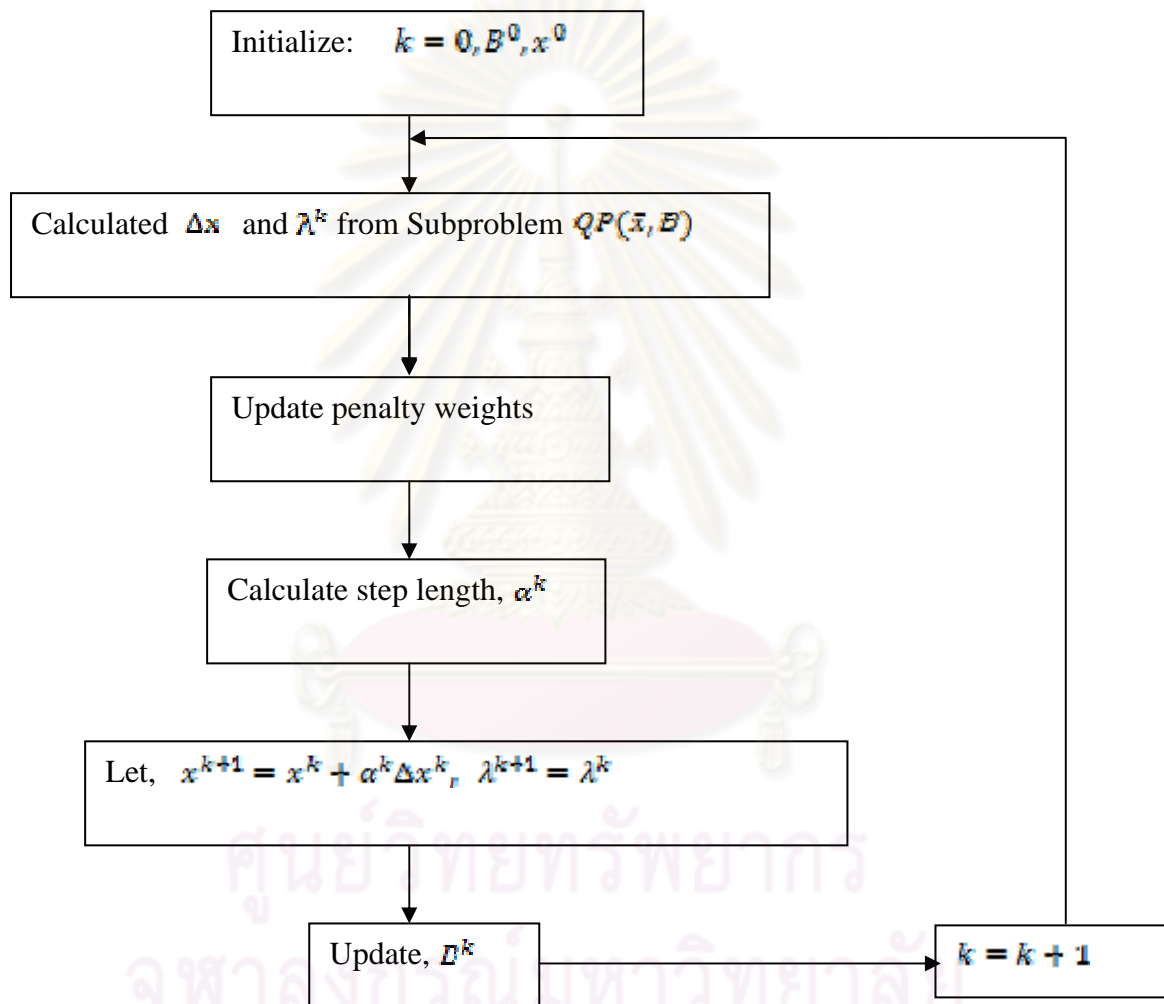


Figure A.1 Flowchart of SQP algorithm (Edgar (1983))

APPENDIX B

GEAR METHOD

Gear method is solver in ode15s. It is presented for solving nonlinear dynamics differential equations by Wang and Wen (2006).

For an ordinary differential equation with initial values

$$\begin{cases} \dot{x}(t) = f(x) \\ x(t_0) = x_0 \end{cases} \quad (\text{B.1})$$

Euler method can be obtained by differentiating equation (B.1), namely substituting the forward differentiation form $x(t+h) - x(t)/h$ into $\dot{x}(t)$ then

$$x(t+h) = x(t) + hf[t, x(t)] \quad (\text{B.2})$$

Gear method can improve the precision formula (B.2) by selecting more accurate numerical integration algorithm. For equation (B.1), given $t_m = t_0 + ih$, $x_i = x(t_i)$, $f_i = f[t_i, x(t_i)]$ then the three data series are expressed by

$$t_m, t_{m-1}, t_{m-2}, \dots, t_{m-k} \quad (\text{B.3})$$

$$x_m, x_{m-1}, x_{m-2}, \dots, x_{m-k} \quad (\text{B.4})$$

$$f_m, f_{m-1}, f_{m-2}, \dots, f_{m-k} \quad (\text{B.5})$$

Gear method using equation (B.3) and (B.4) to form a Lagrange interpolation polynomials $q_{m,k}(t)$ in terms of k power of $x(t)$, if $x(t)$ can be differentiate $k+1$ times in success at interval $[t_0, T]$ and the rest term is $s_{m,k}(t)$, then

$$\begin{aligned}
 x(t) &= q_{m,k}(t) + s_{m,k}(t) \\
 &= \sum_{i=0}^k \left(\prod_{\substack{j=0 \\ j \neq i}}^k \frac{t - t_{m-j}}{t_{m-i} - t_{m-j}} \right) x_{m-i} + \frac{x^{k+1}(\xi)}{(k+1)!} \prod_{j=0}^k (t - t_{m-j})
 \end{aligned} \tag{B.6}$$

Substituting equation (B.6) into (B.1), then timing h in both sides, $t = t_m$, then

$$hq'_{m,k}(t_m) + hs'_{m,k}(t_m) = hf[t_m, x(t_m)] \tag{B.7}$$

Neglecting the rest term and substituting x_i into $x(t_i)$ when $(i = m - k, m - k + 1, \dots, m)$, then

$$\sum_{i=0}^k \tilde{c}_{k,i} x_{m-i} = hf_m \tag{B.8}$$

where

$$\tilde{c}_{k,i} = h \left(\prod_{\substack{j=0 \\ j \neq i}}^k \frac{t - t_{m-j}}{t_{m-i} - t_{m-j}} \right)_{t=t_m} = \begin{cases} \sum_{j=1}^k \frac{1}{j}, & i = 0, \\ (-1)^i \frac{1}{i} \binom{k}{i}, & i > 0. \end{cases}$$

For calculation, equation (B.8) can be rewritten as

$$x_m = \sum_{i=0}^k c_{k,i} x_{m-i} + hg_k f_m \tag{B.9}$$

$$c_{k,i} = \frac{\tilde{c}_{k,i}}{\tilde{c}_{k,0}}, \quad g_k = \frac{1}{\tilde{c}_{k,0}}$$

Equation (B.9) is known as k step algorithm of GEAR method.

APPENDIX C

Data for Reactive Batch Distillation system

Table C.1 Component density data

Density calculation is taken from Balasubramhanya and Doyle (2000)

$$\text{Density}(g/cc) = A_d B_d^{-(1-T_r)^{2/7}}$$

Components	A_d	B_d	$T_c (K)$	MW
Acetic acid	0.3512	0.200	594.4	60
Ethanol	0.2903	0.276	516.2	46
Ethylacetate	0.3084	0.252	523.2	88
Water	0.3471	0.274	647.3	18

Table C.2 Heat capacity

Heat capacity is taken from Carl Yaw, 1999

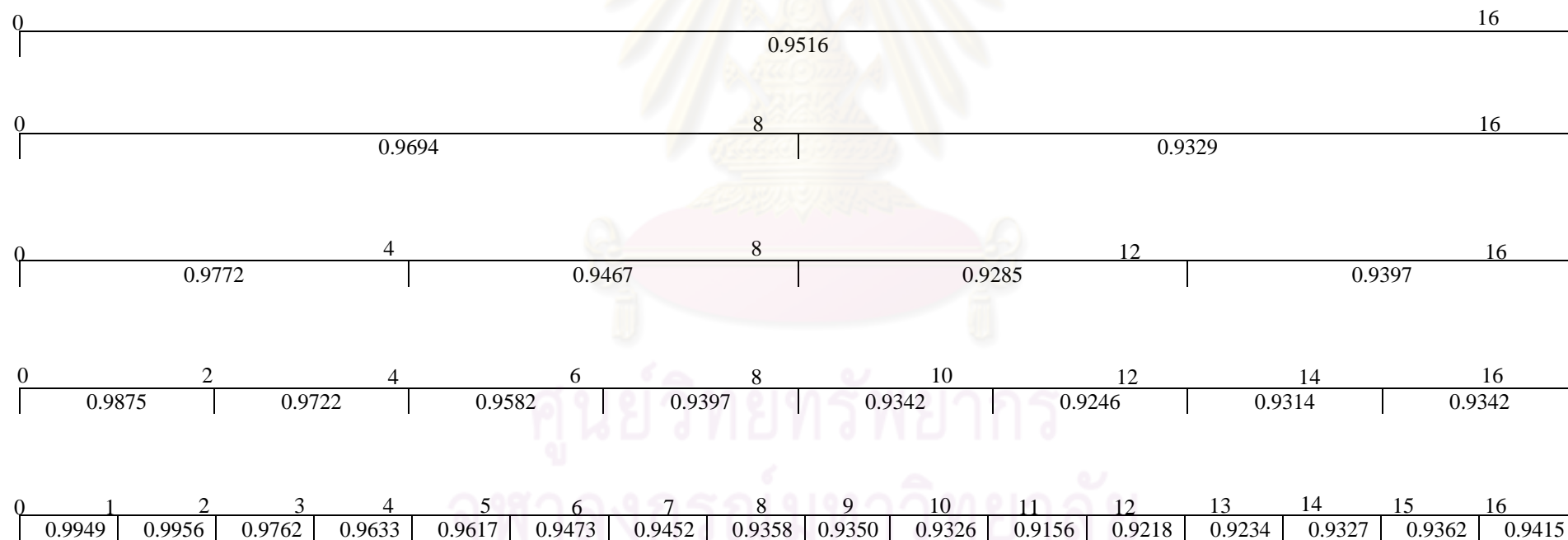
$$C_{pL} = a + bT + cT^2 + dT^3 + eT^4 / T(K)$$

Component	a	b	c	d	e
Acetic acid	14.6934	0.22987e-1	-0.102199e-4	0.2589e-8	-0.8044e-12
Ethanol	14.0480	0.51531e-1	-0.215340e-4	-0.4607e-8	0.1893e-11
Ethylacetate	24.9801	0.33297e-1	-0.731006e-6	-0.1247e-8	0.4824e-11
Water	7.9857	0.46331e-3	-0.140280e-5	-0.6578e-9	0.9895e-13

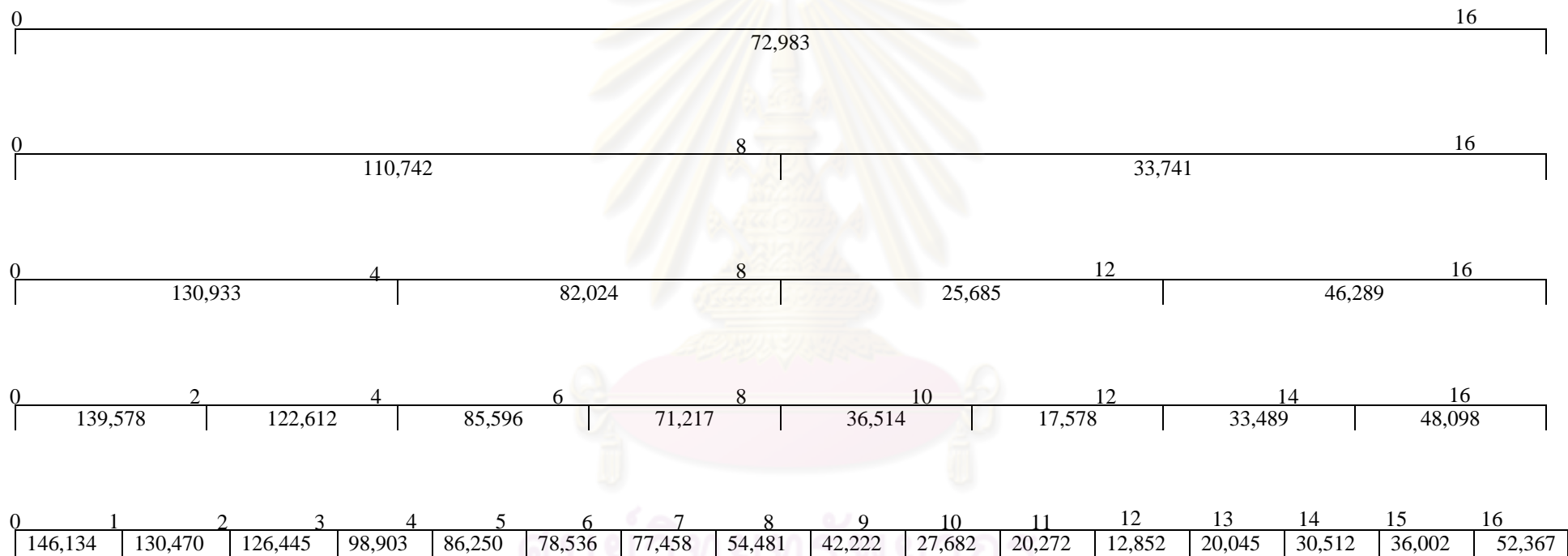
APPENDIX D

OPTIMIZATION RESULTS

Case 1 Reflux ratio is decision variable

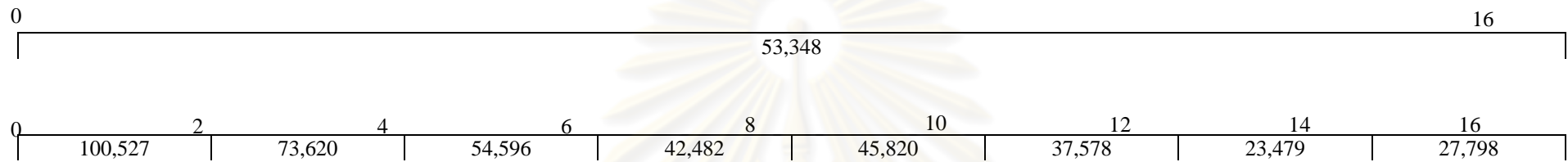


Case 2 Reboiler heat duty is decision variable

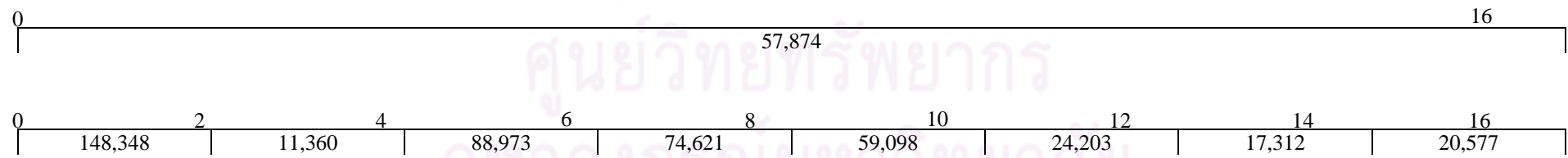
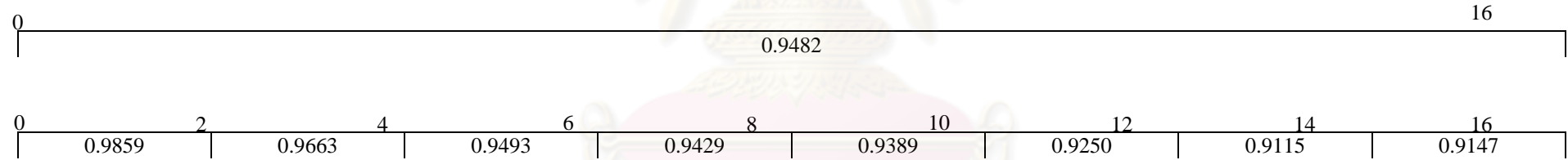


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Case 3 Reboiler heat duty is decision variable



Case 4 Reflux ratio and reboiler heat duty are decision variable



VITA

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