

หอกลับแบบมีปฏิกริยาแบบกะสำหรับเอทิลอะซิเตด : การเลียนแบบเชิงพลวัต  
และการตรวจสอบความถูกต้องด้วยการทดลอง



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## สถาบันวิทยบริการ จุฬาลงกรณ์มหาวิทยาลัย

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต

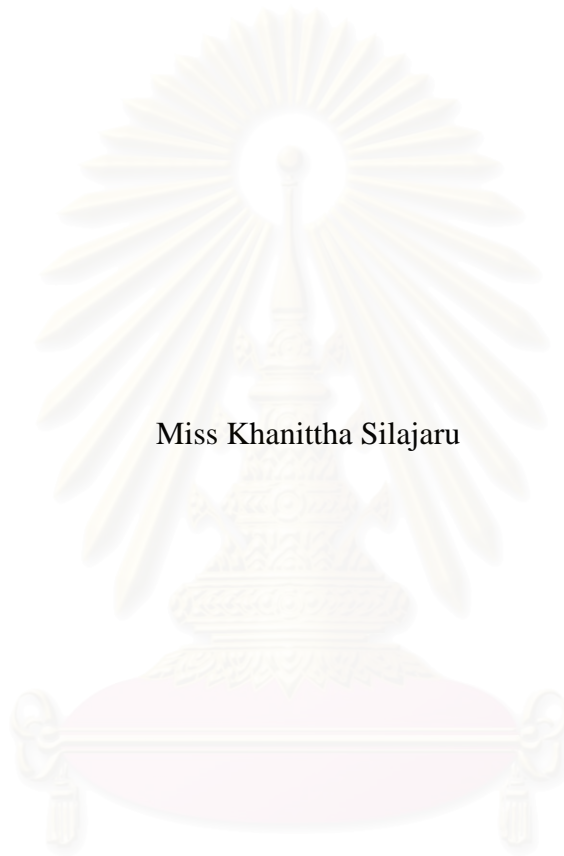
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REACTIVE BATCH DISTILLATION OF ETHYL ACETATE  
: DYNAMIC SIMULATION AND EXPERIMENTAL VALIDATION



Miss Khanittha Silajaru

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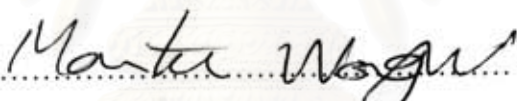
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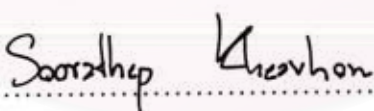
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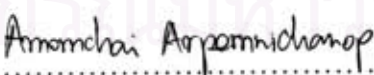
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ชนิษฐา ศิลาจารุ : หอกลิ้นแบบมีปฏิกิริยาแบบกะสำหรับเอทิลอะซิเตด : การเลียนแบบเชิงพลวัตและการตรวจสอบความถูกต้องด้วยการทดลอง. (REACTIVE BATCH DISTILLATION OF ETHYL ACETATE : DYNAMIC SIMULATION AND EXPERIMENTAL VALIDATION) อ. ที่ปริกษาวิทยานิพนธ์หลัก : อ. ดร. สุรเทพ เขียวหอม, 70 หน้า.

หอกลิ้นแบบมีปฏิกิริยาเป็นหน่วยปฏิบัติการแบบหลายหน้าที่ ซึ่งรวมเครื่องปฏิกรณ์และหอกลิ้นไว้ในหน่วยเดียว ปฏิกิริยาเอสเทอร์รีฟิเคชันของกรดไขมันถูกนำไปใช้กับกระบวนการกลั่นแบบมีปฏิกิริยามากขึ้นเนื่องจากการใช้กระบวนการนี้กระทบต่อสมดุลปฏิกิริยาเคมี ในงานวิจัยนี้ได้สร้างแบบจำลองทางคณิตศาสตร์แบบไม่สมดุลของหอกลิ้นแบบมีปฏิกิริยาแบบกะสำหรับการสกัดเอทิลอะซิเตด และแสดงแบบจำลองในระบบสมการพีชคณิตและสมการอนุพันธ์แบบจำลองที่พัฒนาขึ้นจะใช้ในการหารายละเอียดทางพลวัตของหอ ผลการเลียนแบบกระบวนการให้ค่าพลวัตขององค์ประกอบต่างๆในหม้อต้มซ้ำและสายการกลั่น ความบริสุทธิ์ของเอทิลอะซิเตดในสายการกลั่นสะสมและการเปลี่ยนแปลงของสารตั้งต้น ผลที่ได้จากการเลียนแบบกระบวนการนี้จะนำไปเปรียบเทียบกับผลที่ได้จากการทดลอง และผลการเปรียบเทียบแสดงให้เห็นถึงความสอดคล้องกันดี แบบจำลองที่พัฒนาขึ้นจะใช้ในการสร้างปัญหาออปติไมเซชันแบบพลวัตเพื่อที่จะใช้หาแนวทางการดำเนินการที่ดีที่สุด และรูปโครงสร้างอัตราการผลิต

## สถาบันวิทยบริการ จุฬาลงกรณ์มหาวิทยาลัย

ภาควิชา.....วิศวกรรมเคมี.....  
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KHANITTHA SILAJARU : REACTIVE BATCH DISTILLATION OF ETHYL  
ACETATE : DYNAMIC SIMULATION AND EXPERIMENTAL  
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Reactive distillation is a multi-functional unit operation combining chemical reactor and distillation column in a single unit. Fatty acid esterification is increasingly realized as a reactive distillation (RD) process because of its formation being affected by the chemical equilibrium. In this work, a detailed mathematical dynamic rate-based model of reactive batch distillation column is formulated for ethyl acetate synthesis and presented as a system of differential and algebraic equations (DAEs). The developed model is then solved to obtain the detailed column dynamics. The simulation results provide the dynamics of reboiler and distillate compositions, ethyl acetate purity in the accumulated distillate and conversion of the reactants. These simulation results are compared with experimental data, and it indicates a very good agreement. The developed model is then applied to formulate dynamic optimization problem in order to derive the optimum operating policy, reflux profile.

สถาบันวิทยบริการ  
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## NOMENCLATURES

$a$	effective specific area of the packing	$[\text{m}^{-1}]$
$c$	number of components	$[-]$
$C_t$	total molar concentration	$[\text{mol}/\text{m}^3]$
$D$	distillate rate	$[\text{mol}/\text{s}]$
$D_{AB}$	mass diffusivity of $A$ diffusing through liquid solvent $B$	$[\text{cm}^2/\text{s}]$
$D_T$	diameter of the column	$[\text{m}]$
$E$	energy holdup	$[\text{J}]$
$h$	heat transfer coefficients	$[\text{W}/\text{m}^2\text{K}]$
$h_t$	total liquid holdup	$[-]$
$H$	enthalpy	$[\text{J}/\text{mol}]$
$H_{\text{VAP}}$	enthalpy of vaporization	$[\text{kJ}/\text{mol}]$
$\bar{H}$	partial enthalpy	$[\text{J}/\text{mol}]$
$k$	mass transfer coefficient matrix	$[\text{m}/\text{s}]$
$K$	vapor-liquid equilibrium constant	$[-]$
$l$	height of a segment	$[\text{m}]$
$L$	liquid flowrate	$[\text{mol}/\text{s}]$
$n_{\text{liq}}$	viscosity of liquid	$[\text{cP}]$
$n_{\text{gas}}$	viscosity of gas	$[\mu\text{P}]$
$N$	number of stages (segments) in the column, including condenser and reboiler	$[-]$
$N^m$	mass flux	$[\text{mol}/\text{m}^2\text{s}]$
$M$	molar holdup	$[\text{mol}]$

$M_B$	molecular weight of the solvent	[g/mol]
$P$	vapor pressure	[mm/Hg]
$Q$	heat loss	[J/s]
$R$	reaction rate	[mol/kg]
$t$	time	[s]
$T$	temperature	[K]
$T_c$	reduce temperature	[K]
$V$	vapor flowrate	[mol/s]
$V_A$	molecular volumes at normal boiling points	[cm <sup>3</sup> /g mol]
$W$	catalyst weight	[kg]
$x$	liquid mole fraction	[-]
$y$	vapor mole fraction	[-]

### GREEK LETTERS

$\varepsilon$	void fraction of the packing	[-]
$\pi$	3.1415926	[-]
$\rho$	density	[g/ml]
$\Phi_B$	association" parameter for solvent $B$	[-]
$\mu_B$	viscosity of the solution	[cP]
$v_i$	molecular diffusion volumes of component $i$	[-]

### SUBSCRIPTS

$i$	component index	[-]
$j$	segment (stage) index	[-]
$t$	total	[-]



**SUPERSCRIPTS**

<i>I</i>	interface	[-]
<i>L</i>	liquid phase	[-]
<i>V</i>	vapor phase	[-]
<i>m</i>	mass transfer	[-]

**ACRONYM**

RD	Reactive distillation	[-]
RBD	Reactive batch distillation	[-]
DAEs	Differential and algebraic equations	[-]
EtAc	Ethyl acetate	[-]
EtOH	Ethanol	[-]
HAc	Acetic acid	[-]
W	Water	[-]

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# CHAPTER I

## INTRODUCTION

In chemical process industries, chemical reaction and purification of the desired products by distillation are usually carried out sequentially. In many cases, the performance of this classic chemical process structure can be significantly improved by integration of reaction and distillation in a single multifunctional process unit. This integration concept is called 'reactive distillation' (RD). Thus, reactive distillation combines a chemical reactor and a distillation column in a single unit operation. By performing reaction and separation simultaneously, chemical equilibrium can be shifted towards maximum conversion. Economic benefits also result from direct heat integration and reduction of equipment costs. Particularly, in case of exothermic reactions, the heat of reaction can be used to provide the heat of vaporization and in turn reduce the reboiler heat duty required to perform distillation.

The concept of reactive distillation is not new. It was first implemented in esterification process in late 1920. Several factors make these systems suitable for reactive distillation. First, mixtures of organic acids, esters, alcohols and water have a strong tendency to form azeotropes. In esterification process, it is likely that several binary azeotropes are formed. Moreover, ternary and higher azeotropes may also be possible. Thus, the separation of the desired product from the reaction mixture is usually an expensive process involving many distillation columns. Second, esterification reactions occur at moderate temperatures in the liquid phase, under conditions that are convenient for distillation. Third, the reactions are limited by reaction equilibrium. Reactive distillation provides an incentive for removing the products to improve the performance. Finally, because of the presence of azeotropes, it is usually possible to exploit changes in the volatility order in the distillation column and maintain high concentrations of the reagents in the reactive section.

Although reactive distillation has achieved to favor, but sometimes this unit operation is not suitable for operational. Particularly chemical, food and pharmaceutical industries where small amounts of production and flexibility are needed. Therefore, batch reactor is used combine with batch distillation column. This unit operation is called 'Reactive batch distillation (RBD)'. The synergistic effect of this combination has the potential to increase conversion, improve selectivity, significantly reduce capital investment and provide additional flexibility. Due to all these inherent advantages, RBD technology is gaining wide acceptance in chemical processes such as etherification, nitration, esterification, transesterifications, polycondensations, acylations, halogenations, etc.

However, dynamic modeling of reactive distillation processes has recently achieved considerable attention, but most authors restrict themselves to continuous process with homogeneous reactions in liquid phase. Models for the description of reactive batch distillation are rarely found in literature. Different assumptions have been made in order to limit the complexity of the model equations. Without exception, mass transfer resistances have either been neglected or considered by efficiencies according to the simplifications of the equilibrium stage model (Cuille and Reklaitis, 1986; Albet, Le Lann, Joulia and Koehret, 1991). The model complexity with respect to mass transfer phenomena can be increased by the application of rate-based approaches or nonequilibrium stage models (Taylor and Krishna, 1993) based on the two-film theory.

In this work, we focus on the development of the model of a packed reactive batch distillation column for the production of ethyl acetate using rate-based models. Pilot plant batch experiments are carried out to validate the model. The results of simulation are compared with the results obtained from actual experiments.

## **1.1 Research Objective**

The objectives of this research are:

1. Develop a mathematical model of packed reactive batch distillation column operated under warm up state using rate-based model for ethyl acetate production

2. To investigate the operating condition to obtain optimum operating profiles; i.e. reflux ratio and batch time.

3. Compare the results of simulation with the results obtained from actual experiments.

## 1.2 Scopes of Research

The scopes of this research are presented as following:

1. Packed reactive batch distillation column operated under warm up state is studied. The assumptions are:

- Each phase is perfectly mixed in each segment.
- Vapor-liquid equilibrium is only assumed at interface.
- At the liquid-catalyst interface, pseudo-homogeneous reaction is assumed.

Thus, reaction and diffusion inside the catalyst are not considered.

- The finite flux mass transfer coefficients are assumed to be same as the low flux mass transfer coefficients.

- The heat transfer coefficients are assumed to be constant for all segments.
- The condenser and the reboiler are treated as equilibrium stages.

2. The simulation of packed reactive batch distillation column using inhouse program.

3. Compare the results of simulation with the results obtained from actual experiments.

## 1.3 Contributions of Research

The contribution of this research are as following:

1. Mathematical model of packed reactive batch distillation column operated under warm up state.

2. To obtain optimum operating condition of packed reactive batch distillation for ethyl acetate production.

## 1.4 Research Procedures

1. The first step, we investigate the reactive batch distillation column and ethyl acetate production.
2. Various literatures related to the operation of reactive batch distillation and its development, are studied.
3. Develop the mathematical model of a reactive batch distillation and simulate using inhouse program.
4. To perform experiment of ethyl acetate production by using stirred batch reaction pilot unit with distillation column and corrected data.
5. Verify and test the developed model with experimental data.
6. Study the effects of operation conditions of packed reactive batch distillation to conversion of distillate and batch time.
7. Finally, we conclude our research and write thesis.

## 1.5 Research Framework

This thesis is organized as follows: First, the literature reviews related to the simulation of reactive batch distillation are presented in Chapter II. Second, the theories of the ethyl acetate production, reactive batch distillation column, optimization of batch distillation are explained in Chapter III. Third, the simulations, experimental and the results of the reactive batch distillation are presented in Chapter IV. Finally, the conclusions and the recommendations for future work are given in Chapter V.

## CHAPTER II

### LITERATURE REVIEW

#### 2.1 Dynamic Simulation of Reactive Distillation

Cuille and Reklaitis (1986) considered the simulation of RBD with reaction occurring on the plates, in the condenser and in the reboiler. The model was posed as a system of differential and algebraic equations (DAEs) and a stiff solution method was employed for integration. 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. However, the main purpose of the study was to present numerical solution techniques.

Alejski and Duprat (1996) developed a dynamic equilibrium model for tray reactive distillation column. Vapor holdup was ignored and different levels of simplification were tested against dynamic experiments for the production of ethyl acetate. It was found that the model which contains hydraulic description of trays was the most accurate.

Bollyn and Wright (1998) presented the development of a complex fine chemical process involving simultaneous reaction and fractionation. They used the synthesis of the ethyl ester of pentanoic acid involves the substitution of allyl alcohol for ethanol on triethyl orthoacetate as case study and used data from automated reactor experiments to determine reaction kinetics. Then they used data of the kinetics in a comprehensive simulation of the reactive distillation for scale-up and to establish safe, optimum production conditions. The results are all the stated process requirements were met and selectivity for the desired product was raised to >98% under production conditions.

Rahul et al. (2006) presented a detailed mathematical dynamic model of reactive batch distillation column for ethyl acetate synthesis and presented in terms of differential and algebraic equations (DAEs). These DAEs are solved using fourth order Runge-Kutta method in MATLAB to obtain the detailed column dynamics. The simulation results provide the dynamics of reboiler and distillate compositions, reboiler temperature, ethyl acetate purity in the accumulated distillate and conversion of the reactants. These results are analyzed to derive the optimum operating policy, i.e., reflux ratio and batch time. They was found optimum operating reflux ratio to be around 0.875 with a batch time of 8.3 hours for a given product purity at 50% of ethyl acetate.

## **2.2 Rate-based Model**

Kreul et al. (1996) developed a dynamic rate-based model for a packed reactive distillation column for the production of methyl acetate. All the important dynamic changes except the vapor holdup were considered in the model. It was found that high-index problems may arise if the pressure drop is not related to vapor and liquid flowrates. The dynamic rate-based model was implemented into the ABACUSS large-scale equation-based modeling environment. Dynamic experiments were carried out and the results were compared to the simulation results. It was shown that the model is able to describe the complex operation within the error margins of the experiment over the process time.

Baur et al. (2001) proposed a dynamic rate-based cell model for reactive distillation tray columns. Both the liquid and vapor phases were divided into a number of contacting cells and the Maxwell–Stefan equations were used to describe mass transfer. Liquid holdup, vapor holdup, and energy holdup were all included in the model. A reactive distillation tray column for the production of ethylene glycol was used to carry out dynamic simulations. It was concluded that for proper description of the reactive distillation tray column dynamics, the nonequilibrium cell model is essential.

Schneider et al. (2001) studied reactive batch distillation for the methyl acetate system, using a two-film dynamic rate-based model. The developed model has been

applied to a semi-batch process performed in a packed column with a new catalytic packing. For the model validation, several experiments have been carried out in a pilot column, equipped with an online NIR-spectrometer and temperature measuring points for the analysis of dynamic temperature and concentration profiles. For the investigated operation range, the simulation results are in good agreement with the experimental data. It was pointed out that model reduction without significant loss of accuracy was necessary for the dynamic rate-based model to be used in model-based control.

Jianjun et al. (2003) developed and compared a dynamic rate-based with a dynamic equilibrium models for a packed reactive distillation column for the production of tert-amyl methyl ether (TAME). The two types of models, consisting of differential algebraic equations, were implemented in gPROMS and dynamic simulations were carried out to study the dynamic behavior of reactive distillation of the TAME system. The results is the dynamic rate-based model is much more complicated than the equilibrium model, and simplification of the rate-based model is necessary.

Markus et al. (2005) described the modeling framework and process simulator PROFILER developed within the European research project *Intelligent Column Internals for Reactive Separations* (INTINT). The application is illustrated by two heterogeneously catalysed esterification processes: the synthesis of ethyl acetate from ethanol and acetic acid via reactive distillation and the synthesis of octyl hexanoate from octanol and hexanoic acid via reactive stripping. For both processes, the simulation results are satisfactory agreement with the experimental data.



# CHAPTER III

## THEORY

### 3.1 Synthesis of Ethyl Acetate via Esterification process

Ethyl acetate (EtAc), also known as ethyl ethanoate or ethyl ester. It is a colourless liquid and a fruity odour. Generally, It is slightly soluble in water and soluble in most organic solvents, such as alcohol, acetone, ether and chloroform. It finds use as a solvent in a wide range of applications, across many industries, including:

**Surface coating and thinners:** Ethyl acetate is one of the most popular solvents and finds wide use in the manufacture of nitrocellulose lacquers, varnishes and thinners. It exhibits high dilution ratios with both aromatic and aliphatic diluents and is the least toxic of industrial organic solvents.

**Pharmaceuticals:** Ethyl acetate is an important component in extractants for the concentration and purification of antibiotics. It is also used as an intermediate in the manufacture of various drugs.

**Flavors and essences:** Ethyl acetate finds extensive use in the preparation of synthetic fruit essences, flavors and perfumes.

**Flexible packaging:** Substantial quantities of ethyl acetate are used in the manufacture of flexible packaging and in the manufacture of polyester films and BOPP films. It is also used in the treatment of aluminium foils.

**Miscellaneous:** Ethyl acetate is used in the manufacture of adhesives, cleaning fluids, inks, nail-polish removers and silk, coated papers, explosives, artificial leather, photographic films & plates.

### 3.1.1 Reaction Kinetics

The production of ethyl acetate by esterification of acetic acid (HAc) with ethanol (EtOH) in the presence of an acid catalyst either homogeneous or heterogeneous generally follows the elementary reaction



(Acetic acid)      (Ethanol)                      (Ethyl acetate)      (Water)

This is an exothermic reversible reaction. Generally this reaction is catalyzed by sulfuric acid, para toluene sulphonic acid or ion exchange resins. The kinetic model for this chemical reaction system is adopted from that described by Alejski and Duprat (1996). The model consists of two sets of parameters: one is for the reaction with sulfuric acid as a homogeneous catalyst and the other is for the reaction without a catalyst. The kinetic equations in the model are:

With sulfuric acid as homogeneous catalyst:

$$r = k_1 C_{\text{HAc}} C_{\text{EtOH}} - \frac{k_1}{K_C} C_{\text{EtAc}} C_W \quad (3.2)$$

$$k_1 = (4.195C_k + 0.08815) \exp(-6500.1/T) \quad (3.3)$$

$$K_C = 7.558 - 0.012T \quad (3.4)$$

where  $k_1$  is the forward reaction rate constant (in  $\text{m}^3/\text{gmol.s}$ ),  $T$  is the temperature (in K) and  $C_k$  is the catalyst concentration (in vol%), and all of other concentrations in Eqs. (3.2)-(3.4) are in  $\text{mol}/\text{m}^3$ .

Without catalyst:

$$r = k_1 C_{\text{HAc}} C_{\text{EtOH}} - k_2 C_{\text{EtAc}} C_W \quad (3.5)$$

$$k_1 = 0.485 \exp(-59,744/RT) \quad (3.6)$$

$$k_2 = 0.123 \exp(-59,744/RT) \quad (3.7)$$

where  $R$  is the gas constant (in  $\text{J}/(\text{gmol.K})$ ).

### 3.1.2 Thermodynamic Properties

Thermodynamic properties of four components involved with the esterification of ethyl acetate as shown in Table 3.1-3.3

**Table 3.1** Molecular weight of pure components

Pure components	Molecular weight (g mol <sup>-1</sup> )
Acetic acid	60.05
Ethanol	46.07
Ethyl acetate	88.11
Water	18.02

**Table 3.2** Liquid density at 20°C of pure components

Pure components	Liquid density (kg/m <sup>3</sup> )
Acetic acid	1049.10
Ethanol	789.20
Ethyl acetate	900.60
Water	998.20

**Table 3.3** Normal boiling point (°C) of pure components

Pure components	Normal boiling point (°C)
Acetic acid	118.10
Ethanol	78.40
Ethyl acetate	77.10
Water	100.00

The reaction mixture exhibits azeotropism due to the formation of EtOH-EtAc, EtOH-H<sub>2</sub>O, and EtOH-EtAc-H<sub>2</sub>O which are homogeneous azeotropes and also one heterogeneous azeotrope of EtAc-H<sub>2</sub>O.

**Table 3.4** Azeotropic data for ethyl acetate esterification system (Tang et al.,2005).

System	Azeotropic composition (mole fraction)	Azeotropic temperature (°C)
Ethanol/Ethyl Acetate/Water	(0.1126, 0.5789, 0.3085)	70.23
Ethyl Acetate/Water	(0.6885, 0.3115)	70.83
Ethanol/Ethyl Acetate	(0.4620, 0.5380)	71.81
Ethanol /Water	(0.9037, 0.00963)	78.17

The vapor-liquid equilibrium model as shown in Eq. (3.8)-(3.12).

$$K_1 = (2.25 \times 10^{-2})T - 7.812 ; T > 347.6K \quad (3.8)$$

$$K_1 = 0.001 ; T \leq 347.6K \quad (3.9)$$

$$\log K_2 = -2.3 \times 10^3 / T + 6.588 \quad (3.10)$$

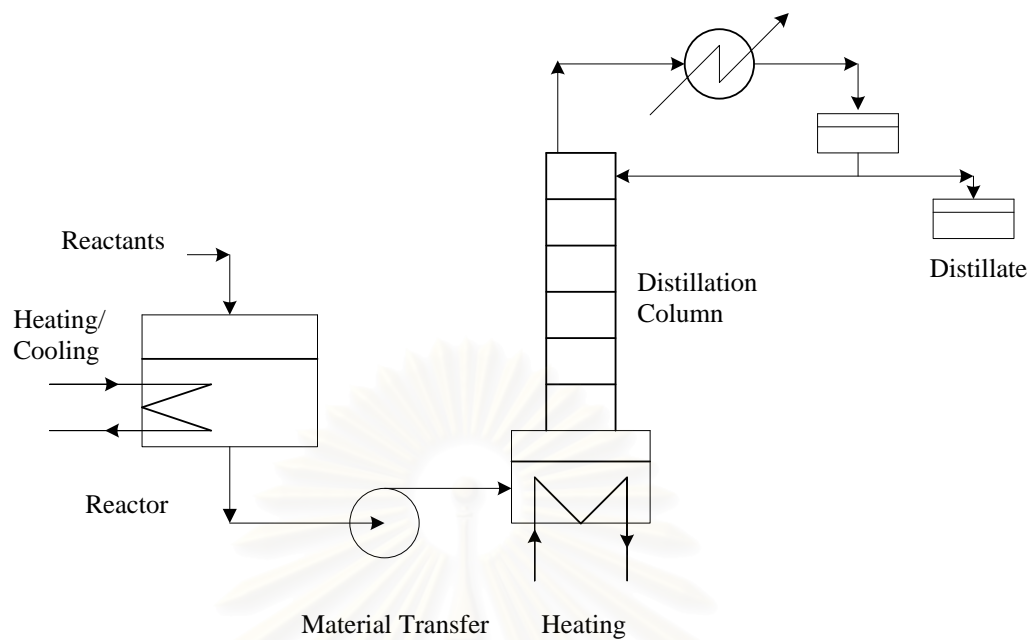
$$\log K_3 = -2.3 \times 10^3 / T + 6.742 \quad (3.11)$$

$$\log K_4 = -2.3 \times 10^3 / T + 6.484 \quad (3.12)$$

### 3.2 Reactive Batch Distillation Column

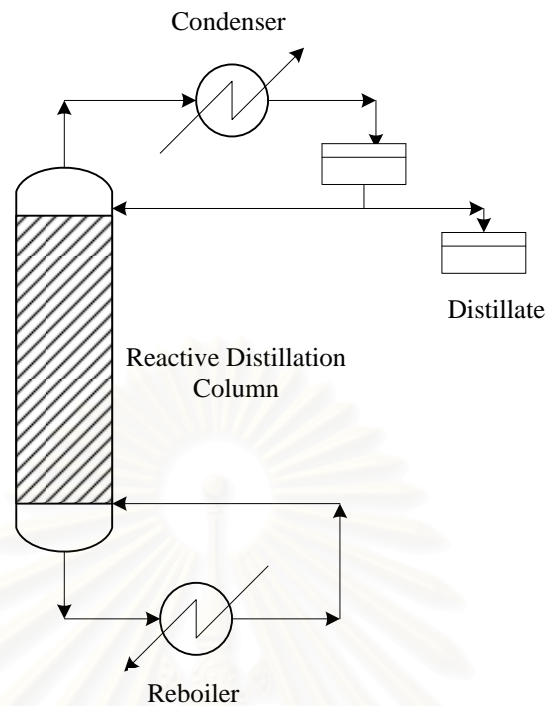
Reactive Distillation processes combine the benefit of traditional unit operations with a substantial process in reducing capital and operating costs and environmental impact (Taylor and Krishna, 2000).

Traditionally, as in many chemical industries, reaction and separation take place separately (Figure 3.1) in a batch reactor followed by a batch distillation column. Therefore, the distillation of desired species cannot influence the conversion of reactants in the reactor.



**Figure 3.1** Traditional Batch Reaction-Distillation System.

However, conventional batch distillation with chemical reaction (reaction and separation taking place in the same vessel and hence referred to as Batch Reactive Distillation or Reactive Batch Distillation (Figure 3.2)) is particularly suitable when one of the reaction products has a lower boiling 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 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 by reaction alone. Therefore, in both cases higher amount of distillate (proportional to the increase in conversion of the reactant) with desired purity is expected than by distillation alone (as in traditional approach).



**Figure 3.2** Batch Reactive Distillation System.

### 3.2.1 Advantages of Reactive Batch Distillation Column

Carrying out reaction and distillation in the same piece of equipment offers several advantages compared to conventional reactor-separator sequences:

a) Shifting of equilibrium. Removing one or more products from the reaction phase causes the equilibrium to be reestablished at a higher conversion. If the relative volatilities are favorable it may be possible to maintain the reagents in the column and draw off only the products. Even if only one product can be separated from the reaction phase, the increase in conversion still gives a benefit in reduced recycle costs.

b) Reduction in plant cost. Simplification or elimination of the separation system can lead to significant capital savings.

c) Heat integration benefits. If the reaction is exothermic, the heat of reaction can be used to provide heat of vaporization and reduce the reboiler duty. Other heat integration benefits can be obtained through use of intermediate condenser, reboilers and pump-arounds.

d) Avoidance of azeotropes. Reactive distillation is particularly advantageous when the reactor product is mixture of species that can form several azeotropes with each other. In such cases a conventional separation scheme would require many distillation columns and use of entrainers to break the azeotropes. Instead, careful choice of reactive distillation conditions can allow the azeotropes to be “reacted away in a single vessel. Azeotropic behavior can also be exploited to maintain high concentrations of the reagents in the reaction zone of the column, or to separate close-boiling mixtures of reagent and products.

e) Improved selectivity. Removing one of the products from the reaction mixture or maintaining a low concentration of one of the reagents can lead to reduction of the rates of side reactions and hence improved selectivity for the desired products.

f) Multifunctional reactor designs. In some case several catalyst zones can be included in the same reactive distillation column, allowing more than one reaction function. This is particularly useful when processing an impure feed.

### **3.2.2 Disadvantages of Reactive Batch Distillation Column**

The applications of reactive distillation technology in industrial scale is somewhat limited by several constraints, for examples,

a) Volatility constraints. The reagents and products must have suitable volatility to maintain high concentrations of the reagents and low concentrations of products in the reaction zone.

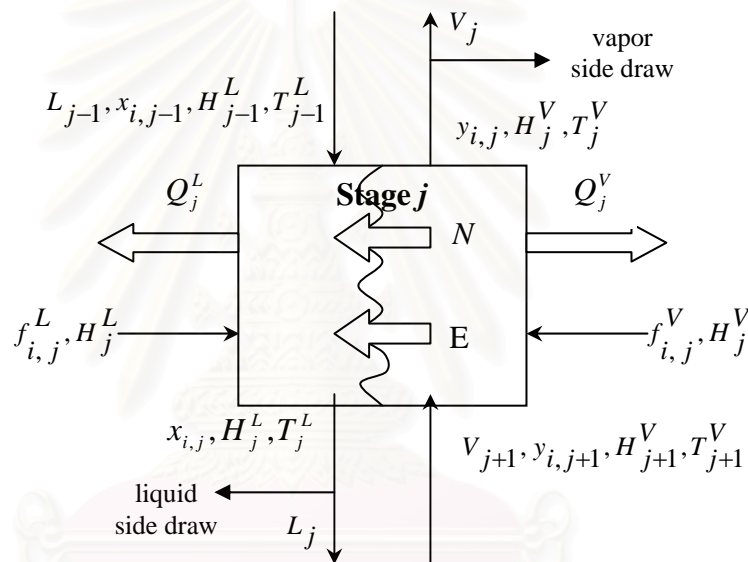
b) Residence time requirement. If the residence time for the reaction is long, a large column size and large tray hold-ups will be needed and it may be more economic to use a reactor-separator arrangement.

c) Plant scale. It is difficult to design reactive distillation processes for very large flow rates because of liquid distribution problems, etc.

d) Process conditions. In some processes the optimum conditions of temperature and pressure for distillation may be far from optimal for reaction and vice versa.

### 3.3 Nonequilibrium Model

A schematic illustration of a nonequilibrium stage is provided in Figure 3.3. Vapor from the stage below is brought into contact with liquid from the stage above and allowed to exchange mass and energy across their common interface represented in diagram by the wavy line. Provision is made for vapor and liquid feed streams. Sidestream drawoffs of vapor and/or liquid may also be accounted for if necessary. The entire column is taken to consist of a sequence of such stages. Stages are numbered starting at the top with the condenser, if required, being stage number 1.



**Figure 3.3** The schematic diagram of a nonequilibrium stage.

The nonequilibrium stage in Figure 3.3 may represent either a single tray or a section of packed column. For packed columns each model stage represents a section of packing and the height of that section must be specified in advance. Shorter section heights mean more stages are needed to represent a specific total height, therefore, more calculations and longer computation times. Smaller stages mean more accurate results. It is not always easy to know in advance how many stages should be used in any given situation. To some extent, experience plays a role in choosing an appropriate height of packing for each model stage.



### 3.4. Molecular Diffusion in Fluids

Molecular diffusion is concerned with the movement of individual molecules through a substance by virtue of their thermal energy. The kinetic theory of gases provides a means of visualizing what occurs, and indeed it was the success of this theory in quantitatively describing the diffusional phenomena which led to its rapid acceptance. In the case of a simplified kinetic theory, a molecule is imaged to travel in a straight line at a uniform velocity changes both in magnitude and direction. The average distance the molecule travels between collisions is its mean free path, and the average velocity is dependent upon the temperature. The molecule thus travels a highly zigzag path, the net distance in one direction which it moves in a given time, the rate of diffusion, being only a small fraction of the length of its actual path. For this reason the diffusion rate is very slow, although we can expect it to increase with decreasing pressure, which reduces the number of collisions, and with increased temperature, which increases the molecular velocity. The phenomenon of molecular diffusion ultimately leads to a completely uniform concentration of substances throughout a solution which may initially have been nonuniform.

#### 3.4.1. Diffusivity of Gases

The diffusivity, or diffusion coefficient,  $D$  is a property of the system dependent upon temperature, pressure and nature of the components. An advanced kinetic theory predicts that in binary mixtures there will be only a small effect of composition. The dimensions of diffusivity can be established from its definition, Eq.(3.13), and length<sup>2</sup>/time. Most of the values for  $D$  reported in the literature are expressed as cm<sup>2</sup>/s; the SI dimensions are m<sup>2</sup>/s.

$$J_A = -D_{AB} \frac{\partial c_A}{\partial z} = -cD_{AB} \frac{\partial x_A}{\partial z} \quad (3.13)$$

Fuller et al. give a large collection of data for many gas pairs and also compare various method of prediction. The following equation is recommended

$$D_{AB} = \frac{CT^{1.75}[(1/M_A) + (1/M_B)]^{1/2}}{P[(v_A)^{1/3} + (v_B)^{1/3}]^2} \quad (3.14)$$

where  $T$  is in kelvin (K),  $P$  is in pascals (Pa),  $M_1$  and  $M_2$  in grams per moles (g/mole) and  $C = 1.013 \times 10^{-2}$ ,  $D_{AB}$  will be in square meters per second ( $\text{m}^2/\text{s}$ ). The term  $v_A$  and  $v_B$  are molecular diffusion volumes and are calculated by summing the atomic contributions in Table 3.5.

**Table 3.5** Diffusion Volumes in Fuller-Schettler-Giddings Correlation Parameters From Fuller et.al (1969).

Atomic and Molecular Diffusion Volume Increments					
C	15.9	Cl		21.0	
H	2.31	S		22.9	
O	6.11	Aromatic ring		-18.3	
N	4.54	Heterocyclic ring		-18.3	
Diffusion Volumes for Some Simple Molecules					
He	2.67	N <sub>2</sub>	18.5	NH <sub>3</sub>	20.7
Ar	16.2	O <sub>2</sub>	16.3	H <sub>2</sub> O	13.1
Kr	24.5	Air	19.7	SF <sub>6</sub>	71.3
Xe	32.7	CO	18.0	Cl <sub>2</sub>	38.4
H <sub>2</sub>	6.12	CO <sub>2</sub>	26.7	Br <sub>2</sub>	69.0
D <sub>2</sub>	6.84	N <sub>2</sub> O	35.9	SO <sub>2</sub>	41.8

### 3.4.2. Diffusivity of Liquids

Diffusion in liquids is important in many separation operations, notably liquid-liquid extraction, gas absorption and distillation. There are two prominent theories for the prediction of approximate diffusivities in liquids. In the Eyring theory the molecules of a liquid are pictured as forming a quasi-crystalline lattice and the analysis is performed more or less as it was for diffusion in solid. In the hydrodynamical theory the diffusivity is first related to the force which acts on a sphere moving in a continuum. This force can be evaluated in terms of Stokes' law,

and the resulting expression is called the Stokes Einstein equation. The results of both theories can be put into the form

$$\frac{D_{AB}\mu_B}{T} = F(V) \quad (3.15)$$

in which  $F(V)$  represents a function which depends on the molecular volume  $V$  of the mixture. For the Stokes-Einstein equation the right-hand side of Eq. (3.15) is simply inversely proportional to the radius of the diffusing molecule  $A$ .

Equation (3.15) has been used by Wilke and later by Wilke and Chang as a basis of a method for the correlation of liquid diffusivities. Their relation is the following dimensional equation:

$$\frac{D_{AB}\mu_B}{T} = \frac{7.4 \times 10^{-8} (\Phi_B M_B)^{1/2}}{V_A^{0.6}} \quad (3.16)$$

where  $D_{AB}$  is the mass diffusivity of  $A$  diffusing through liquid solvent  $B$ , in  $\text{cm}^2/\text{s}$ ;  $\mu_B$  is the viscosity of the solution, in centipoises;  $T$  is absolute temperature, in  $\text{K}$ ;  $M_B$  is the molecular weight of the solvent;  $V_A$  is the molar volume of solute at normal boiling point, in  $\text{cm}^3/\text{g mole}$ ;  $\Phi_B$  is the "association" parameter for solvent  $B$ .

Molecular volumes at normal boiling points,  $V_A$ , for some commonly encountered compounds, are tabulated in Table 3.6. For other compounds, the atomic volumes of each element present are added together as per the molecular formula. Table 3.7 lists the contributions for each of the constituent atoms. When certain ring structures are involved corrections must be made to account for the specific ring configuration; following corrections are recommended:

for three-membered ring, as ethylene oxide	deduct 6
for four- membered ring, as cyclobutane	deduct 8.5
for five- membered ring, as furan	deduct 11.5
for pyridine	deduct 15
for benzene ring	deduct 15
for naphthalene ring	deduct 30
for anthracene ring	deduct 47.5

**Table 3.6** Molecular Volumes at Normal Boiling Point for Some Commonly Encountered Compounds

Compound	Molecular volume, cm <sup>3</sup> /g mol	Compound	Molecular volume, cm <sup>3</sup> /g mol
Hydrogen, H <sub>2</sub>	14.3	Nitric oxide, NO	23.6
Oxygen, O <sub>2</sub>	25.6	Nitrous oxide, N <sub>2</sub> O	36.4
Nitrogen, N <sub>2</sub>	31.2	Ammonia, NH <sub>3</sub>	25.8
Air	29.9	Water, H <sub>2</sub> O	18.9
Carbon monoxide, CO	30.7	Hydrogen sulfide, H <sub>2</sub> S	32.9
Carbon dioxide, CO <sub>2</sub>	34.0	Bromine, Br <sub>2</sub>	53.2
Carbonyl sulfide, COS	51.4	Chlorine, Cl <sub>2</sub>	48.4
Sulfur dioxide, SO <sub>2</sub>	44.8	Iodine, I <sub>2</sub>	71.5

**Table 3.7** Atomic Volumes for Complex Molecular Volumes for Simple Substances

Element	Atomic volume, in cm <sup>3</sup> /g mol	Element	Atomic volume, in cm <sup>3</sup> /g mol
Bromine	27.0	Oxygen, except as noted below	7.4
Carbon	14.8	Oxygen, in methyl esters	9.1
Chlorine	21.6	Oxygen, in methyl ethers	9.9
Hydrogen	3.7	Oxygen, in higher ethers and other esters	11.0
Iodine	37.0	Oxygen in acids	12.0
Nitrogen, double bond	15.6	Sulfer	25.6
Nitrogen, in primary amines	10.5		
Nitrogen, in secondary amines	12.0		

Recommended values of the association parameter,  $\Phi_B$ , are given in Table 3.8 for a few common solvents.

**Table 3.8** The association parameter

Solvent	$\Phi_B$
water	2.26
methanol	1.9
ethanol	1.5
benzene, ether, heptane, and other unassociated solvents	1.0

## 3.5 Dynamic Optimization

### 3.5.1 Optimization

Typical chemical engineering problems (such as process design or plant operation) have many, and possibly an infinite number of solutions. The term of optimization is freely used to describe the complete spectrum of techniques from the basic multiple run approach of trial and error to highly complex numerical strategies. This assortment stems from the fact that optimization is not idyllic in the real world but there are a lot of issues that require a practical approach. However, the potential benefit is huge and hence it is the next logical step after developing a model. So to avoid the numerous pitfalls it must not be flippantly treated or downsized in complexity.

#### 3.5.1.1 Essential Features of Optimization Problems

Every optimization problem will have:

1. At least one *Objective Function* to be optimized (e.g. profit function, cost function, etc.) often called the *economic model*.
2. One or more *Equality Constraints* (e.g. model equations)
3. One or more *Inequality Constraints* (e.g. lower and upper bounds of operating variables, such as temperature in a reactor, reflux ratio in a distillation column)

A set of variables that satisfy the items 2 and 3 precisely will provide a feasible solution of the optimization problem.

A set of variables that satisfy the items 2 and 3 and also provide an optimal value for the function in item 1 will provide an *optimal solution* of the optimization problem.

Two types of optimization problems are often encountered:

(a) *Linear Optimization*: Objective function, constraints are linear.

(b) *Non-linear Optimization*: Objective function, constraints are non-linear or combination of linear and non-linear systems.

### 3.5.2 Dynamic Optimization of Batch Distillation

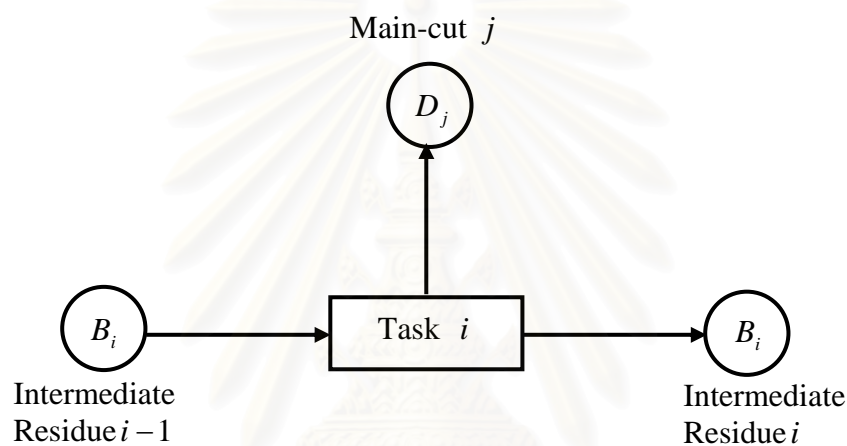
Batch distillation is inherently a dynamic process and thus results to optimal control or dynamic optimization problems (unless batch distillation task is carried out in a continuous distillation column).

The optimal control of a process can be defined as a control sequence in time, which when applied to the process over a specified control interval, will cause it to operate in some optimal manner. The criterion for optimality is defined in terms of an objective function and constraints and the process is characterised by a dynamic model. The optimality criterion in batch distillation may have a number of forms, maximizing a profit function, maximizing the amount of product, minimizing the batch time, etc. subject to any constraints on the system. The most common constraints in batch distillation are on the purity of the product at the end of the process or at some intermediate point in time. The most common control variable of the process is the reflux ratio for a conventional column and reboil ratio for an inverted column and both an MVC column.

The optimal operation of a batch column depends of course on the objectives one wishes to achieve at the end of the process. Depending on the objective function and any associated constraints, a variety of dynamic optimization problems were defined in the past for conventional batch distillation column. Brief formulations of these optimization problems are presented in the following subsections. Situations in which each formulation can be applied are discussed.

All the formulations are presented with reference to batch operation schematically represented by a STN. Figure 3.4 shows a single distillation task  $i$

producing a main-cut  $j$  ( $D_j, x_D^j$ ) and a bottom residue product ( $B_i, x_B^i$ ) from an initial charge ( $B_{i-1}, x_B^{i-1}$ ) charged to the reboiler at the beginning of the task ( $t_0^i$ ). The batch time for the operation is given by  $t_C^i = t_F^i - t_0^i$ , where  $t_F^i$  is the end time of distillation task  $i$ . Note that if  $t_0^i = 0$ , ( $B_{i-1}, x_B^{i-1}$ ) because ( $B_0, x_{B0}^0$ ) and  $t_C^i$  becomes equal to  $t_F^i$ . The batch time, here, is simply the required to complete a distillation task. It excludes any charging, cleaning and transfer time before or at the end of the cut. For simplicity, we drop the use of superscript  $i$  in the following sections.



**Figure 3.4** State Task Network for Batch Distillation.

In general, the optimization problem to optimize the operation of a CBD column can be stated as follows:

*given:* the column configuration, the feed mixture, vapor boilup rate a separation task in terms of product purity (+recovery or amount of product or operation time or none)

*determine:* optimal reflux ratio which governs the operation

*so as to:* minimize the operation time or maximize the amount of product or maximize the profit

*subject to:* equality and inequality constraints (e.g. model equations)

Mathematically it can be represented as:

Minimise (or Maximise)  $J$   
 $u(t)$

subject to Equality Constraints (Model)  
 Inequality Constraints

where  $u(t)$  denotes all the optimization variable (e.g. controls (reflux ratio) and its switching times and or the final time). Inequality constraints refer to simple bounds on  $u(t)$  and final time constraints to the amount and/or purity of top or bottom product.



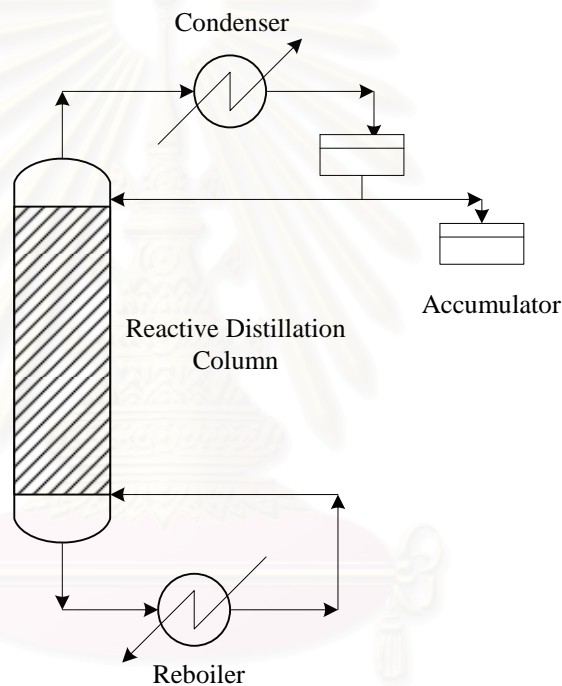
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## CHAPTER IV

### REACTIVE BATCH DISTILLATION COLUMN

This chapter describes the simulation and the experimental of reactive batch distillation column in ethyl acetate production. The reactive batch distillation column (RBD) consists of a reboiler, column, and condenser as shown in Figure 4.1.



**Figure 4.1** The schematic diagram of Reactive Batch Distillation Column.

#### 4.1 Simulation

The simulation of this work is study in the case of reactive batch distillation which is packed column. The details of the simulation are discussed below.

##### 4.1.1 Mathematical Model

The mathematical model for the packed reactive batch distillation column is developed based on the following assumptions:

1. Each phase is perfectly mixed in each segment.
2. Vapor-liquid equilibrium is only assumed at interface.
3. At the liquid-catalyst interface, pseudo-homogeneous reaction is assumed.

Thus, reaction and diffusion inside the catalyst are not considered.

4. The finite flux mass transfer coefficients are assumed to be same as the low flux mass transfer coefficients.
5. The heat transfer coefficients are assumed to be constant for all segments.
6. The condenser and the reboiler are treated as equilibrium stages is performed.

Derivation of a basic mathematical model consists essentially of mass and energy balances around three section of column as show in Figure 4.1, namely, the condenser (denoted by suffix 1), the column is divided the segment (denoted by suffix j) and the reboiler (denoted by suffix N).

#### Equations for the total condenser:

Molar component balances:

$$\frac{dM_{i,1}^L}{dt} = V_2 y_{i,2} - (L_1 + D)x_{i,1} \quad (4.1)$$

Total energy balance:

$$\frac{dE_1^L}{dt} = V_2 H_2^V - (L_1 + D)H_1^L - Q_1 \quad (4.2)$$

Summation:

$$\sum_{i=1}^c x_{i,1} - 1 = 0 \quad (4.3)$$

#### Equations for the reboiler:

Molar component balances:

$$\frac{dM_{i,N}^L}{dt} = L_{N-1}x_{i,N-1} - V_N y_{i,N} \quad (4.4)$$

Total energy balance:

$$\frac{dE_N^L}{dt} = L_{N-1}H_{N-1}^L - V_N H_N^V \quad (4.5)$$

Summation:

$$\sum_{i=1}^c x_{i,N} - 1 = 0 \quad (4.6)$$

$$\sum_{i=1}^c y_{i,N} - 1 = 0 \quad (4.7)$$

Vapor-liquid equilibrium:

$$y_{i,N} - K_{i,N} x_{i,N} = 0 \quad (4.8)$$

**Equations for the  $j$ th segment:**

Molar component balances of the liquid phase:

$$\frac{dM_{i,j}^L}{dt} = L_{j-1} x_{i,j-1} - L_j x_{i,j} + \frac{\pi}{4} D_T^2 l_j a_j N_{i,j}^m + W_j R_{i,j} \quad (4.9)$$

Molar component balances of the vapor phase:

$$\frac{dM_{i,j}^V}{dt} = V_{j+1} y_{i,j+1} - V_j y_{i,j} - \frac{\pi}{4} D_T^2 l_j a_j N_{i,j}^m \quad (4.10)$$

Energy balances of the liquid phase:

$$\frac{dE_j^L}{dt} = L_{j-1} H_{j-1}^L - L_j H_j^L - Q_j + \frac{\pi}{4} D_T^2 l_j a_j \left( h_j^L (T_j^L - T_j^L) + \sum_{i=1}^c N_{i,j}^m \overline{H_{i,j}^L} \right) \quad (4.11)$$

Energy balances of the vapor phase:

$$\frac{dE_j^V}{dt} = V_{j+1} H_{j+1}^V - V_j H_j^V - \frac{\pi}{4} D_T^2 l_j a_j \left( h_j^V (T_j^V - T_j^L) + \sum_{i=1}^c N_{i,j}^m \overline{H_{i,j}^V} \right) \quad (4.12)$$

Energy balance at the vapor-liquid interface:

$$h_j^V (T_j^V - T_j^L) + \sum_{i=1}^c N_{i,j}^m \overline{H_{i,j}^V} = h_j^L (T_j^L - T_j^L) + \sum_{i=1}^c N_{i,j}^m \overline{H_{i,j}^L} \quad (4.13)$$

Summation:

$$\sum_{i=1}^c x_{i,j} - 1 = 0 \quad (4.14)$$

$$\sum_{i=1}^c y_{i,j} - 1 = 0 \quad (4.15)$$

$$\sum_{i=1}^c x_{i,j}^I - 1 = 0 \quad (4.16)$$

$$\sum_{i=1}^c y_{i,j}^I - 1 = 0 \quad (4.17)$$

Vapor-liquid equilibrium at the vapor-liquid interface:

$$y_{i,j}^I - K_{i,j} x_{i,j}^I = 0 \quad (4.18)$$

Mass transfer fluxes:

$$N_j^m = C_{ij}^V k^V (y_j - y_j^I) + y_j \sum_{i=1}^c N_{i,j}^m \quad (4.19)$$

$$N_j^m = C_{ij}^L k^L (x_j^I - x_j) + x_j \sum_{i=1}^c N_{i,j}^m \quad (4.20)$$

Definition of the holdups:

$$M_{i,j}^L = \frac{\pi}{4} D_T^2 l_j h_{ij}^L C_{ij}^L x_{i,j} \quad (4.21)$$

$$M_{i,j}^V = \frac{\pi}{4} D_T^2 l_j (\varepsilon_j - h_{ij}^L) C_{ij}^V y_{i,j} \quad (4.22)$$

$$E_j^L = \frac{\pi}{4} D_T^2 l_j h_{ij}^L C_{ij}^L H_j \quad (4.23)$$

$$E_j^V = \frac{\pi}{4} D_T^2 l_j (\varepsilon_j - h_{ij}^L) C_{ij}^V H_j \quad (4.24)$$

where  $M$  is molar holdup (mol),  $E$  is energy holdup (J),  $V$  is vapor flowrate (mol/s),  $D$  is distillate rate (mol/s),  $L$  is liquid flowrate (mol/s),  $H$  is enthalpy (J/mol),  $Q$  is heat loss (J/s),  $K$  is vapor-liquid equilibrium constant,  $D_T$  is diameter of the column (m),  $l$  is height of a segment (m),  $a$  is effective specific area of the packing ( $\text{m}^{-2}$ ),  $N^m$  is mass flux ( $\text{mol}/\text{m}^2\text{s}$ ),  $R$  is reaction rate (mol/kg),  $h$  is heat transfer coefficients ( $\text{W}/\text{m}^2\text{K}$ ),  $T$  is temperature (K),  $C_t$  is total molar concentration ( $\text{mol}/\text{m}^3$ ),  $c$  is number of components,  $\bar{H}$  is partial enthalpy (J/mol),  $\varepsilon$  is void fraction of the packing,  $x$  is liquid mole fraction and  $y$  is vapor mole fraction.

#### 4.1.2 Operating Conditions

The operating conditions and parameter values for the case simulation are given in Table 4.1.

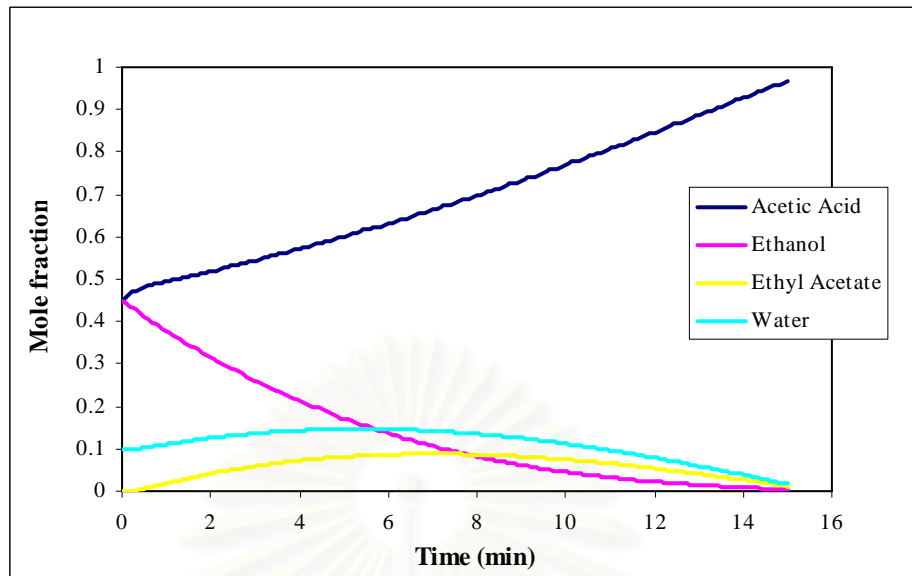
**Table 4.1** The operating conditions and parameter values

Number of ideal separation stages (including reboiler and condenser)	12
Total fresh feed	50 mol
Feed composition (acetic acid, ethanol, ethyl acetate, water) in mole fraction	0.45, 0.45, 0.0, 0.1
Condenser holdup	1 mol
Each segment holdup	0.083 mol
Column pressure	1.013 bar
Diameter of the column	0.07 m
Height of a stage (segment)	0.05 m
Effective specific area of the packing	1047 m <sup>-1</sup>
Void fraction	0.6

The kinetic model for chemical reaction of this work is adopted from Alejski and Duprat (1996), which describe following as Eq.(3.2)-(3.4) in chapter 3. The vapor-liquid equilibrium as shown in Eq.(3.8)-(3.12) in chapter 3, which is adopted from Mujtaba and Macchietto (1997) to calculate vapor-liquid equilibrium for ethyl acetate system. The mass diffusion of vapor phase and liquid phase was calculated following as Eq.(3.14) and Eq.(3.16) in chapter 3. The approach of Taylor and Krishna (1993) was followed to calculate the mass transfer coefficient matrices  $k^L$ ,  $k^V$ .

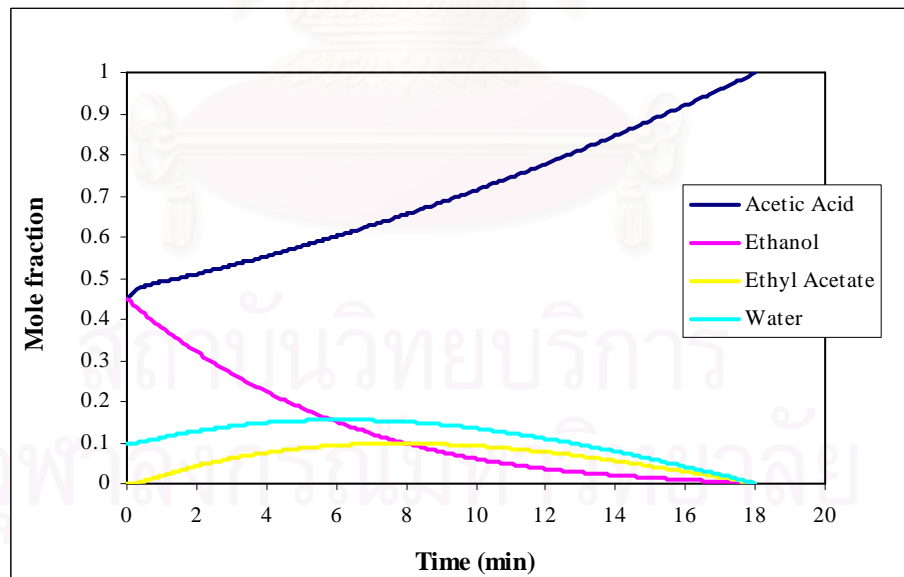
### 4.1.3 Simulation Results

Reactive batch distillation column for the production of ethyl acetate was used to carry out simulation with rate-based model in this work. The dynamic simulation was carried out for several reflux ratios ranging from 0.80 to 0.975. For each of the different but constant reflux ratio, optimal operating conditions were derived. The reboiler composition is plotted in Figure 4.2-4.9



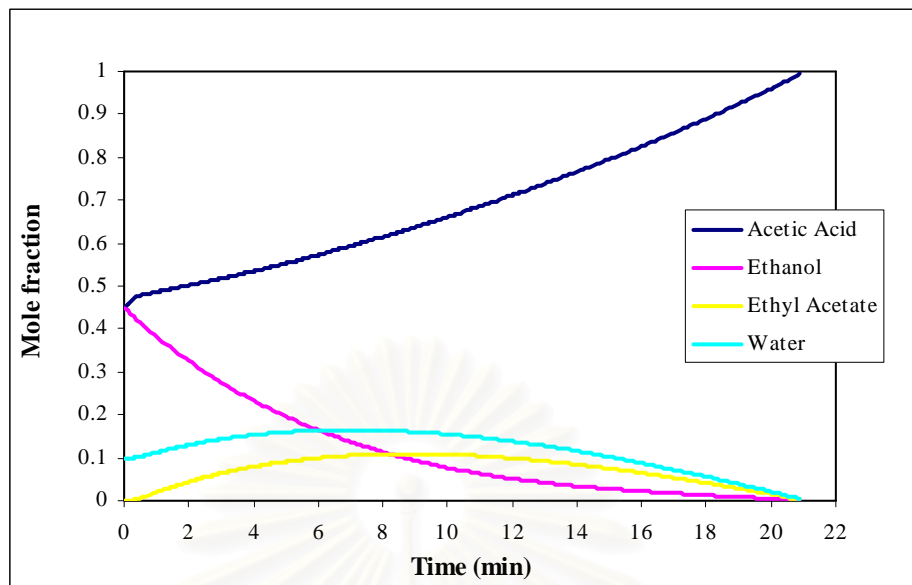
**Figure 4.2** Dynamic of reboiler composition at reflux ratio of 0.80.

Figure 4.2 shows that the mole fraction of acetic acid increase, when operating times increase, while the mole fraction of ethanol decrease, when operating times increase and at 15 min remain only acetic acid in the reboiler.



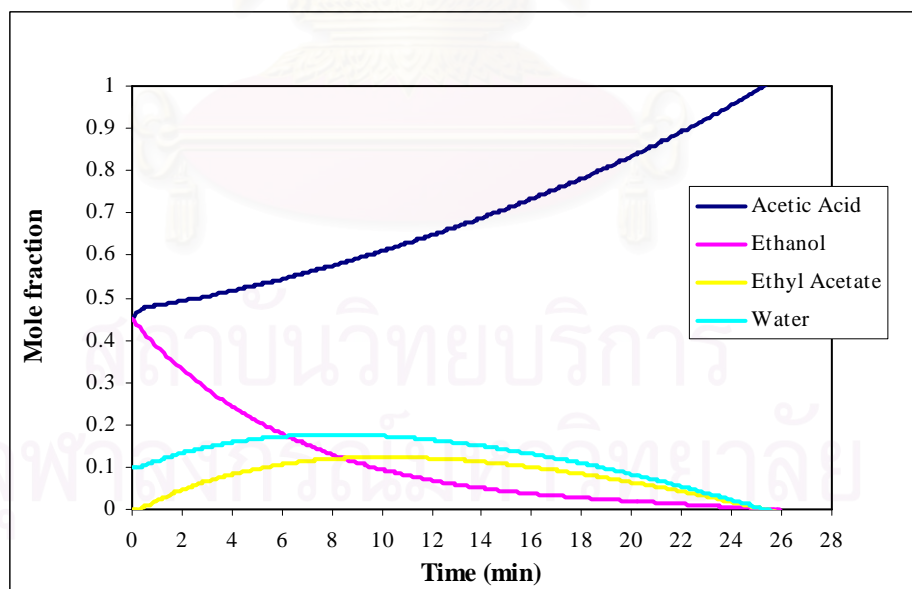
**Figure 4.3** Dynamic of reboiler composition at reflux ratio of 0.825.

Figure 4.3 shows that the mole fraction of acetic acid increase, when operating time increase, while the mole fraction of ethanol decrease, when operating time increase and at 18 min remain only acetic acid in the reboiler.



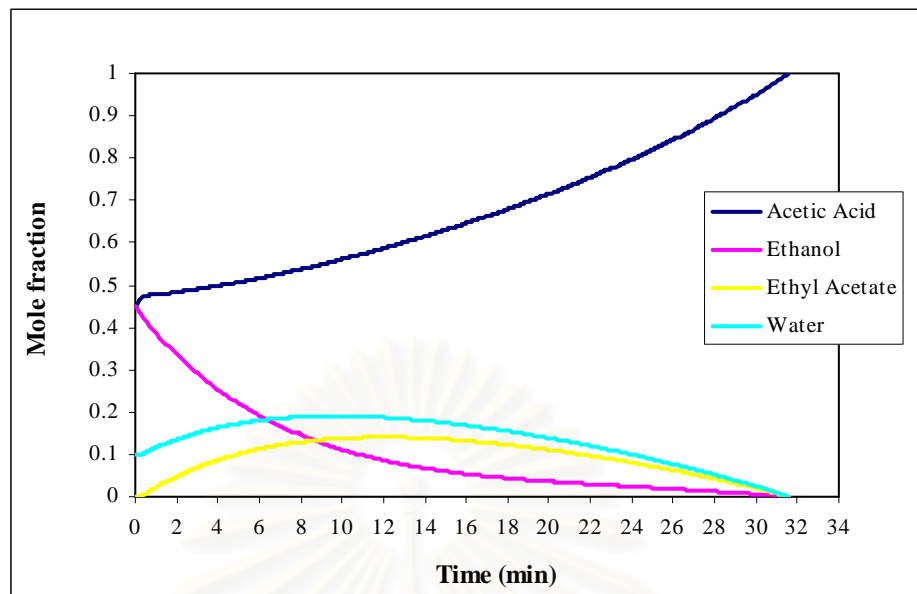
**Figure 4.4** Dynamic of reboiler composition at reflux ratio of 0.85.

Figure 4.4 shows that the mole fraction of acetic acid increase, when operating time increase, while the mole fraction of ethanol decrease, when operating time increase and at 21 min remain only acetic acid in the reboiler.



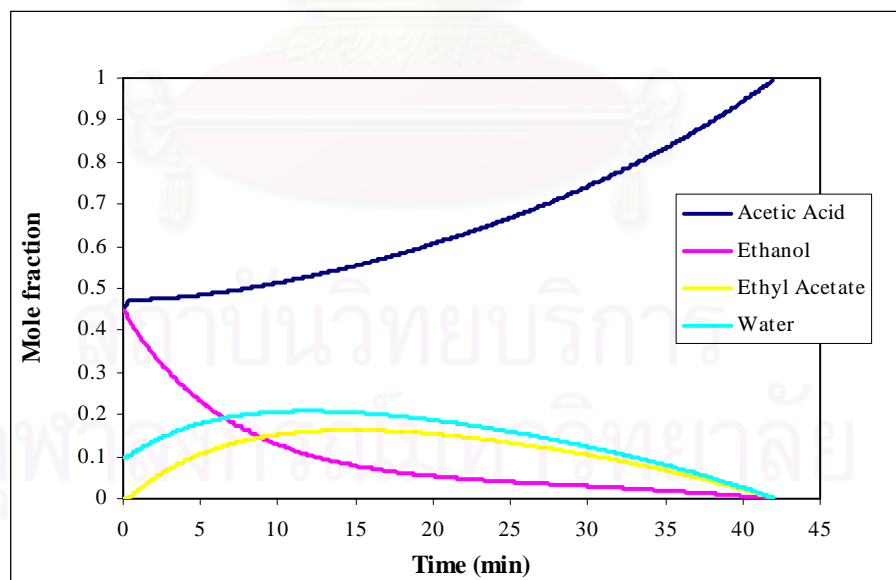
**Figure 4.5** Dynamic of reboiler composition at reflux ratio of 0.875.

Figure 4.5 shows that the mole fraction of acetic acid increase, when operating time increase, while the mole fraction of ethanol decrease, when operating time increase and at 25 min remain only acetic acid in the reboiler.



**Figure 4.6** Dynamic of reboiler composition at reflux ratio of 0.90.

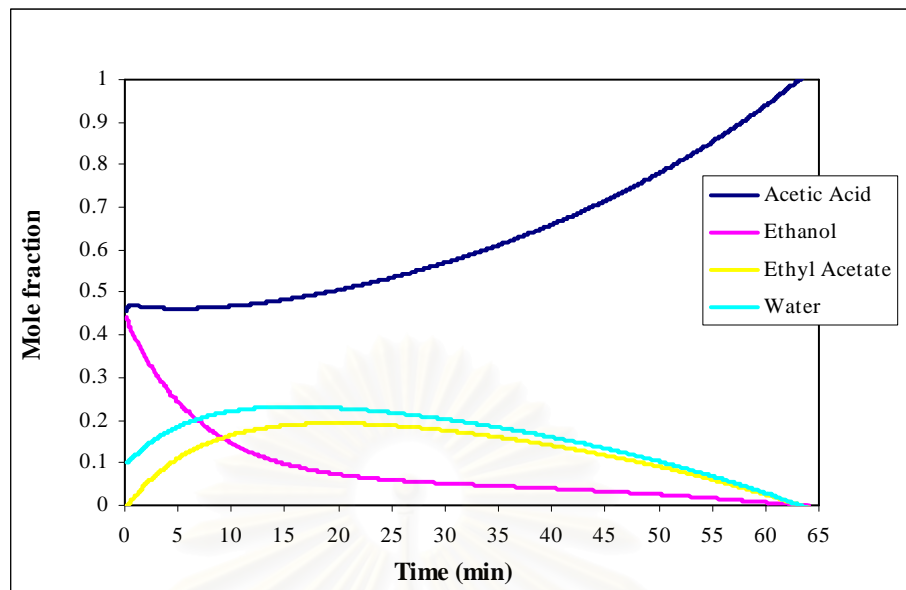
Figure 4.6 shows that the mole fraction of acetic acid increase, when operating time increase, while the mole fraction of ethanol decrease, when operating time increase and at 31 min remain only acetic acid in the reboiler.



**Figure 4.7** Dynamic of reboiler composition at reflux ratio of 0.925.

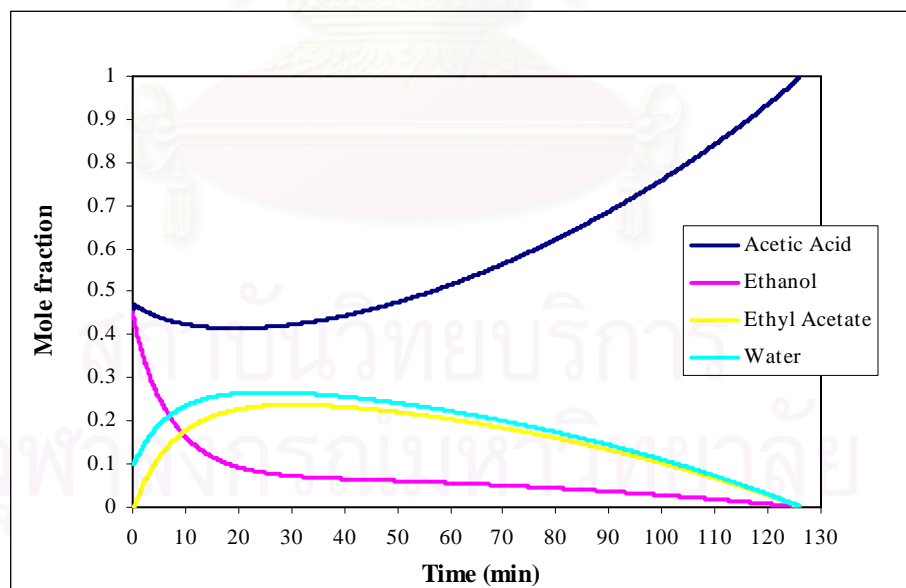
Figure 4.7 shows that the mole fraction of acetic acid increase, when operating time increase, while the mole fraction of ethanol decrease, when operating time increase and at 41 min remain only acetic acid in the reboiler.





**Figure 4.8** Dynamic of reboiler composition at reflux ratio of 0.95.

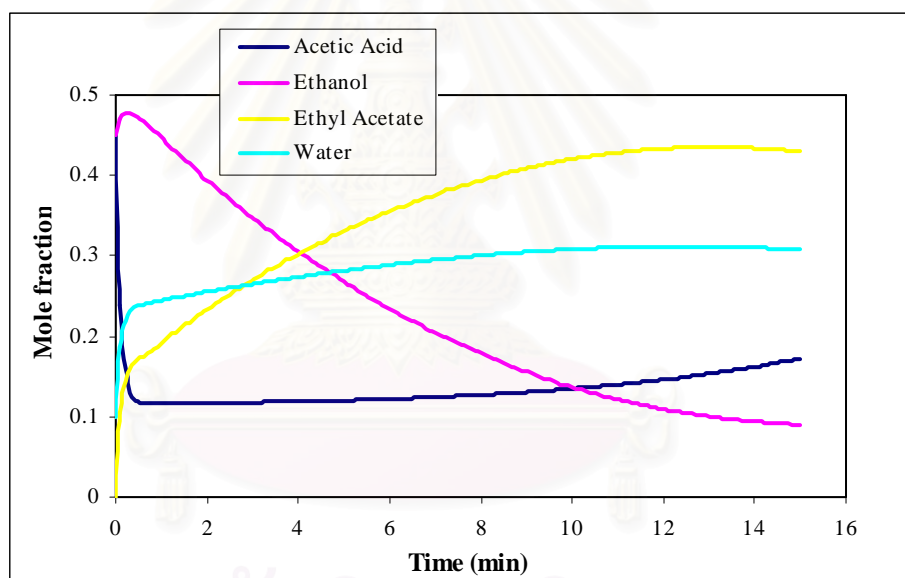
Figure 4.8 shows that the mole fraction of acetic acid increase, when operating time increase, while the mole fraction of ethanol decrease, when operating time increase and at 63 min remain only acetic acid in the reboiler.



**Figure 4.9** Dynamic of reboiler composition at reflux ratio of 0.975.

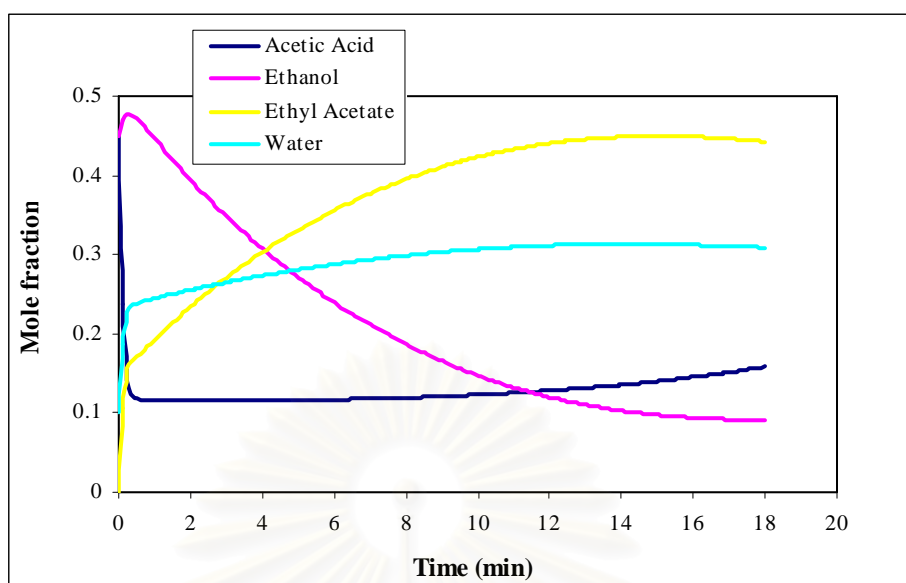
Figure 4.9 shows that the mole fraction of acetic acid increase, when operating time increase, while the mole fraction of ethanol decrease, when operating time increase and at 125 min remain only acetic acid in the reboiler.

Figure 4.2-4.9 show that the dynamic of reboiler in ranging 0.80-0.975 of reflux ratio has behaviour in the same direction. These figures show that the mole fraction of EtAc in reboiler rises from zero, reaches a maximum value and then gradually falls to zero. This rise in mole fraction is due to the high rate of reaction initially, then the rate of EtAc production by reaction becomes less than the rate of separation by distillation and therefore there is a fall in the mole fraction of EtAc. Acetic acid concentration increases with time. This behaviour is due to acetic acid's highest boiling point in the reaction mixture, which retains it in the lower sections of the column to carry out the reaction more efficiently. The corresponding distillate composition is shown in Figure 4.10-4.17 for several reflux ratios ranging from 0.80 to 0.975.



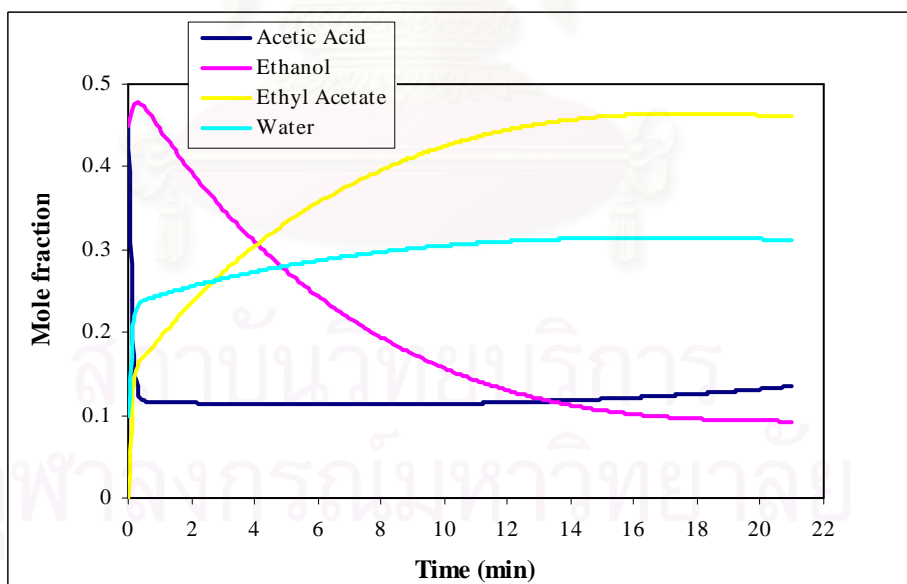
**Figure 4.10** Dynamic of distillate composition at reflux ratio of 0.80.

The result of simulation at the reflux ratio of 0.80 shows that the distillate has a maximum mole fraction of ethyl acetate of 0.433 in product can be obtained in the range of operating time 12-14 min.



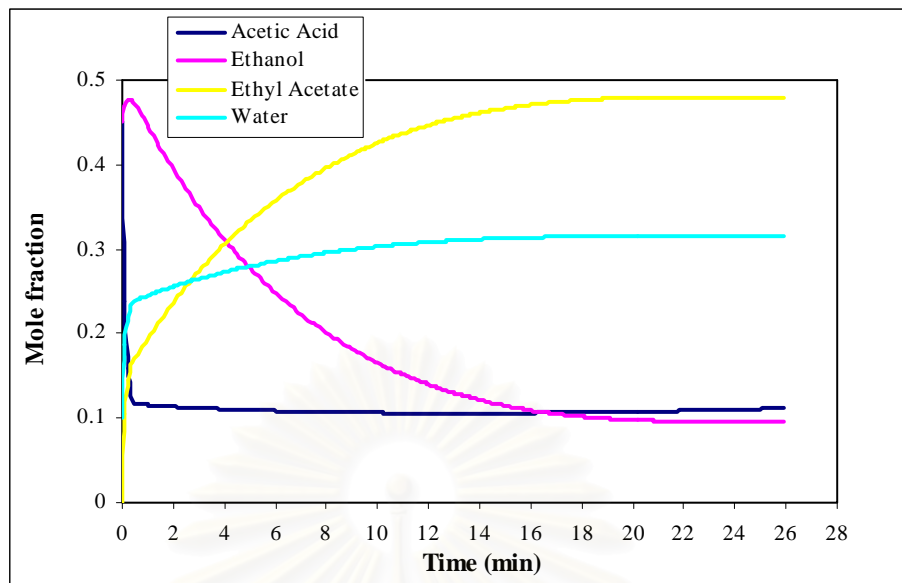
**Figure 4.11** Dynamic of distillate composition at reflux ratio of 0.825.

The result of simulation at the reflux ratio of 0.825 shows that the distillate has a maximum mole fraction of ethyl acetate of 0.45 in product can be obtained in the range of operating time 14-18 min.



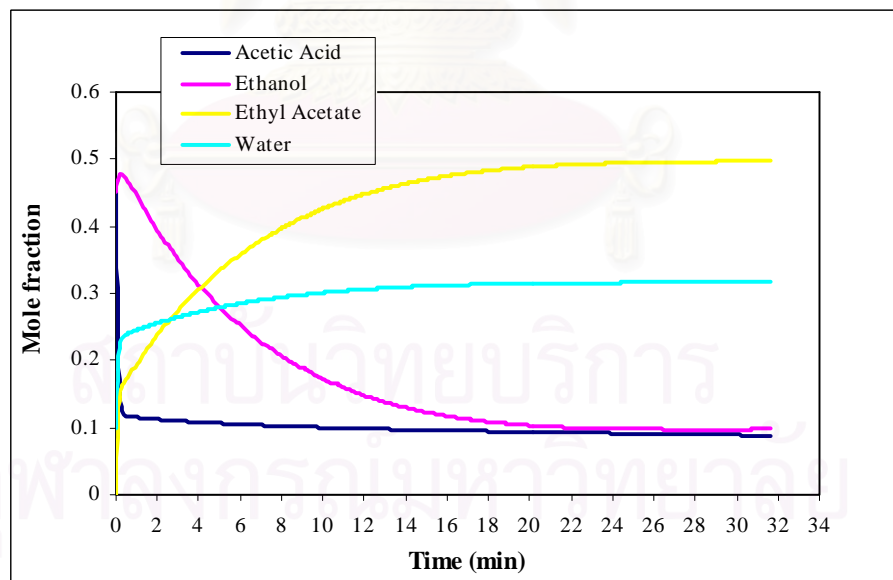
**Figure 4.12** Dynamic of distillate composition at reflux ratio of 0.85.

The result of simulation at the reflux ratio of 0.85 shows that the distillate has a maximum mole fraction of ethyl acetate of 0.464 in product can be obtained in the range of operating time 16-21 min.



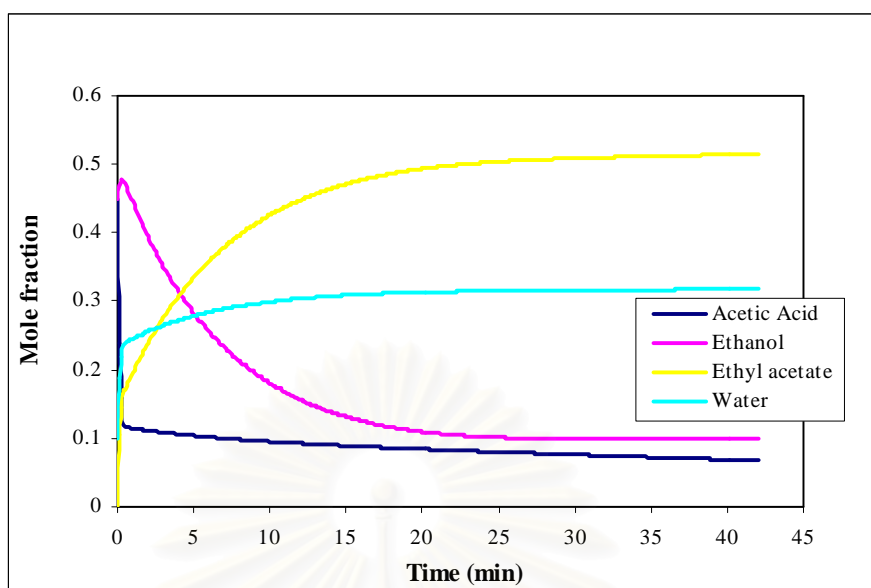
**Figure 4.13** Dynamic of distillate composition at reflux ratio of 0.875.

The result of simulation at the reflux ratio of 0.875 shows that the distillate has a maximum mole fraction of ethyl acetate of 0.48 in product can be obtained in the range of operating time 17-26 min.



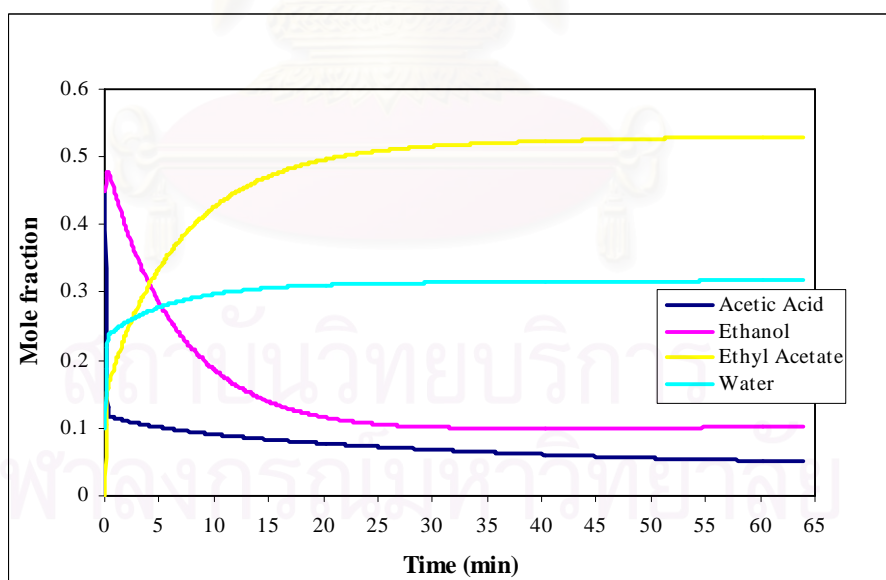
**Figure 4.14** Dynamic of distillate composition at reflux ratio of 0.90.

The result of simulation at the reflux ratio of 0.90 shows that the distillate has a maximum mole fraction of ethyl acetate of 0.496 in product can be obtained in the range of operating time 25-32 min.



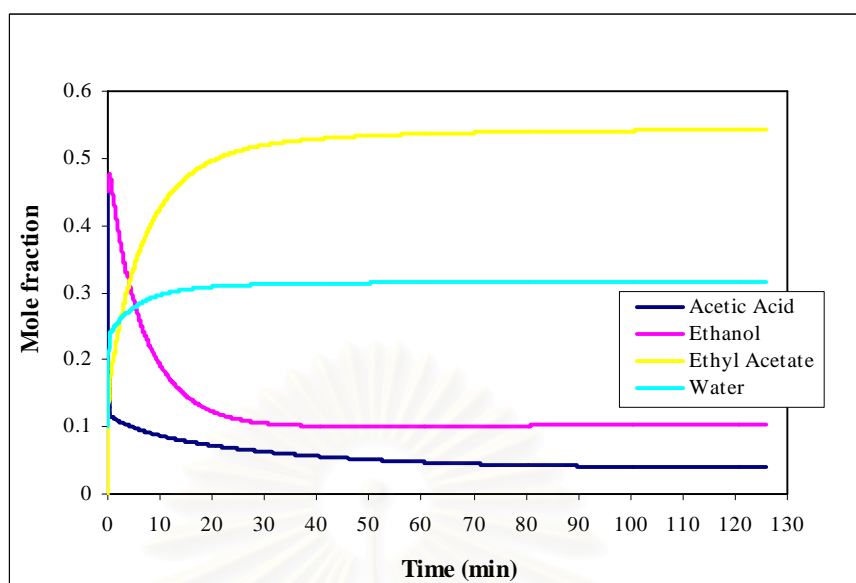
**Figure 4.15** Dynamic of distillate composition at reflux ratio of 0.925.

The result of simulation at the reflux ratio of 0.925 shows that the distillate has a maximum mole fraction of ethyl acetate of 0.51 in product can be obtained in the range of operating time 27-40 min.



**Figure 4.16** Dynamic of distillate composition at reflux ratio of 0.95.

The result of simulation at the reflux ratio of 0.95 shows that the distillate has a maximum mole fraction of ethyl acetate of 0.524 in product can be obtained in the range of operating time 35-60 min.



**Figure 4.17** Dynamic of distillate composition at reflux ratio of 0.975.

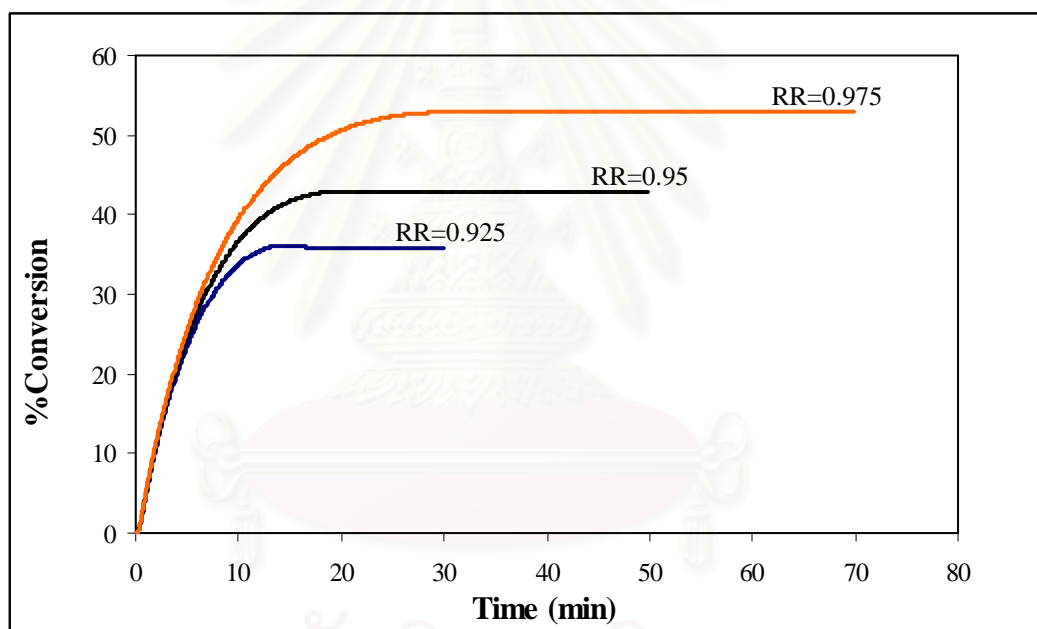
The result of simulation at the reflux ratio of 0.975 shows that the distillate has a maximum mole fraction of ethyl acetate of 0.535 in product can be obtained in the range of operating time 60-120 min.

Figure 4.10-4.17 show that the dynamic of distillate in ranging 0.80-0.975 of reflux ratio has behaviour in the same direction. These figure show that the mole fraction of EtAc in distillate rises from zero, reaches a maximum value, and then constant. This rise in mole fraction due to EtAc is product, which is removed continuously, therefore occur forward reaction. The mole fraction of EtOH in distillate increases rapidly in minute, then it decreases until constant.

The mole fraction of distillate and batch time of reflux ratio in range 0.80-0.975 from Figure 4.10-4.17 are compared in Table 4.2. The results show that reflux ratio at 0.975, the mole fraction of ethyl acetate is maximum value and batch time is maximum too, due to this reflux ratio has return substances into column much more than other reflux ratio, therefore reactant is used to occur reaction increase, the mole fraction of ethyl acetate at condenser is increase.

**Table 4.2** Effect of reflux ratio on EtAc production

Reflux Ratio	Mole fraction of distillate				Batch Time (min)
	Acetic Acid	Ethanol	Ethyl Acetate	Water	
0.80	0.146	0.109	0.433	0.312	12-14
0.825	0.14	0.097	0.45	0.313	14-18
0.85	0.125	0.097	0.464	0.314	16-21
0.875	0.109	0.096	0.48	0.315	17-26
0.90	0.09	0.097	0.496	0.317	25-32
0.925	0.075	0.099	0.51	0.316	27-40
0.95	0.06	0.1	0.524	0.316	35-60
0.975	0.05	0.1	0.535	0.315	60-120

**Figure 4.18** Effect of reflux ratio on conversion.

The percent conversion of the reactants for three different reflux ratios is shown in Figure 4.18, indicating that the conversion first rises rapidly due to high rate of reaction, however as ethanol is consumed at fast rate due to the reaction and separation both, the rate of rise of percent conversion becomes less and eventually the conversion becomes constant after 30 minutes for optimum reflux ratio of 0.975.

## 4.2 Experimental

The production of ethyl acetate by esterification between acetic acid and ethanol is studied in this work. The reactant, experimental apparatus, procedure and results is described below.

### 4.2.1 Reagents of Ethyl Acetate Production

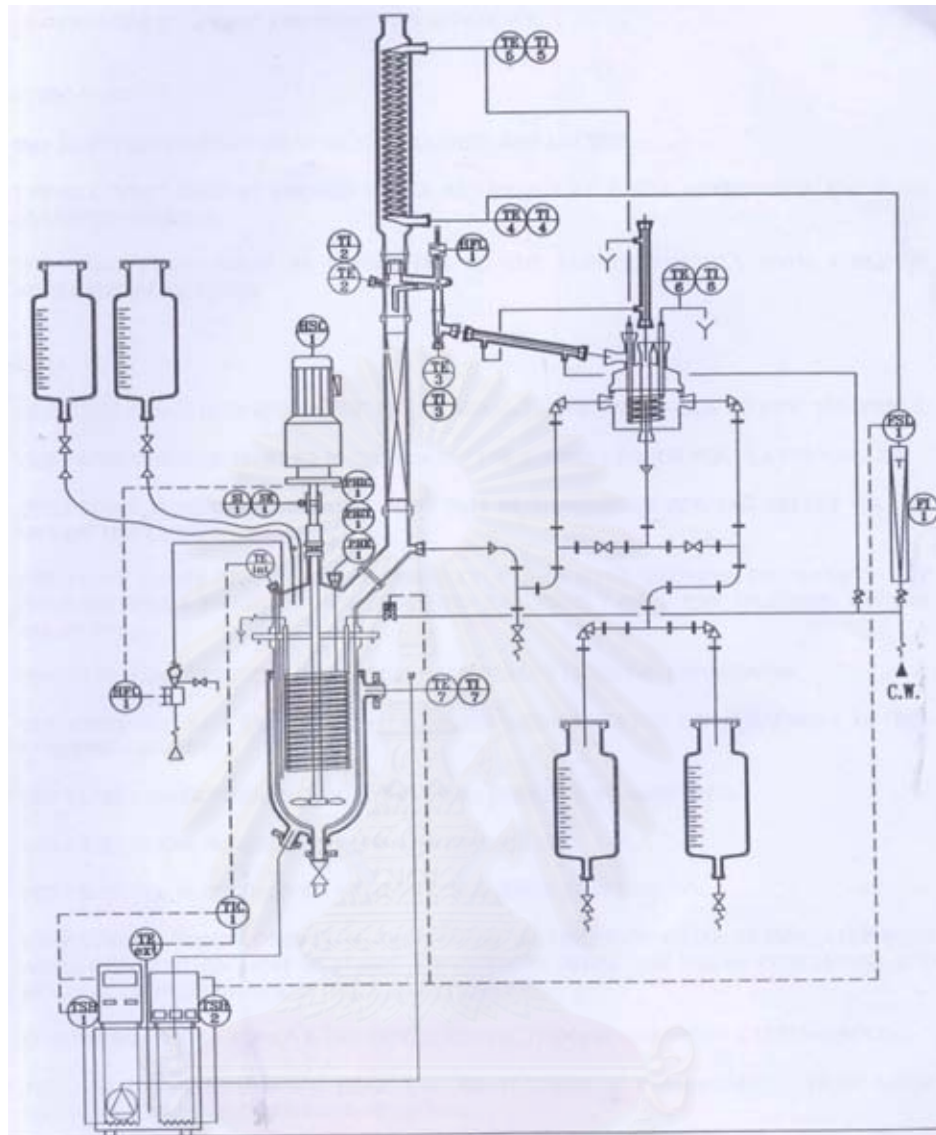
1. Acetic acid solution in water (about 75% mass concentration).
2. Sulphuric acid (about 95% mass concentration).
3. Ethanol

### 4.2.2 Experimental Apparatus

The pilot plant reactive batch distillation column configuration is shown in Figure 4.19 for the production of ethyl acetate. The Stirred batch reaction pilot unit with distillation column is used test in this work. This system consists of two feed flasks, one reactor with integral jacket, one packed column in borosilicate glass in one element of 50 cm. which within is packed with RASCHIG rings and one vertical condenser which has exchange area 0.3 m<sup>2</sup>. Dynamic experiments will be carried out the on this column to validate the dynamic models developed.

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**Figure 4.19** Configuration of the stirred batch reaction pilot unit with distillation column.

### 4.2.3 Procedure of Ethyl Acetate Production

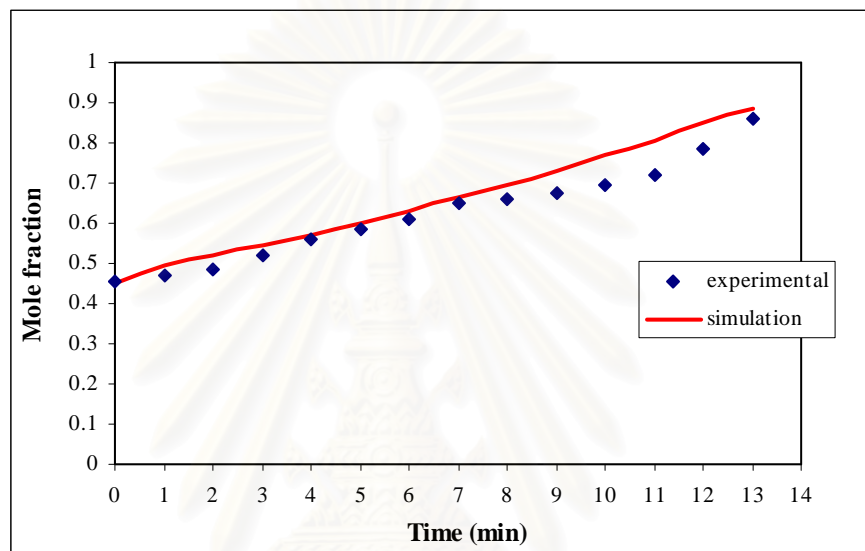
The reagents are poured into weighed tanks.

- Take a sample of each reagent and determine their mass concentration exactly,
- Weigh every reagent exactly,
- Introduce the sulphuric acid into acetic acid tank,
- Mix the two acids in the tank,
- Take a sample in the acid tank and determine the acid concentration,

- Fill the reactor with the mixture of acids,
- Weigh the empty acid tank and determine the exact quantity of reagents poured,
- Start the stirrer,
- Introduce the whole quantity of alcohol into the reactor,
- Take a sample of the reaction mixture and determine the acid concentration,
- Heat the reactor to 100 °C,
- Record the temperature versus time and record the parameters at reflux beginning,
- Wait for two hours at total reflux distillation,
- Start distilling the azeotrope (reflux rate = 2),
- Modify the reflux rate during the distillation so as to obtain a constant temperature at the head of the column,
- Take samples and determine the concentrations of:
  - The distillate (refractive index),
  - The reaction products (acid determination),
- When the distillation is finished (no more azeotrope at the head of the column), stop heating,
- Cool the reaction products,
- Weigh another free tank,
- Drain the reactants into this tank when their temperature has cooled down to room temperature,
- Weigh the drained reactant,
- Determine the mass of the reaction product,
- Take a sample of reaction product and determine its acid concentration,
- Determine the volumic mass of the reactant,
- Weight another free tank,
- Drain the distillate into this tank,
- Weight the drained distillate,
- Determine the mass of the distillate,
- Take a sample of the distillate and determine its refractive index,
- Determine the volumic mass of distillate
- Determine the concentration of distillate.

### 4.3 Comparison the results of simulation with experimental

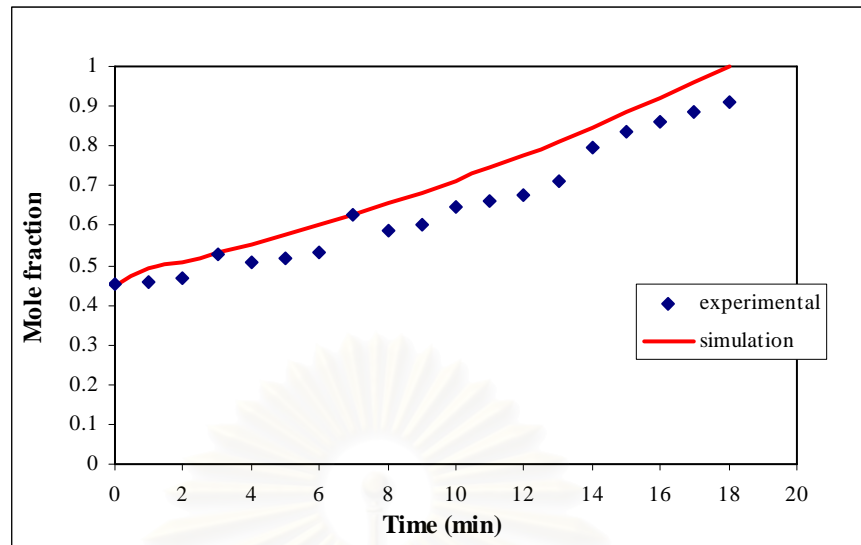
The comparison of acetic acid concentration in reboiler and ethanol concentration at condenser is considered in this section. The results of the simulation of acetic acid concentration in reboiler versus experimental data are shown in Figure 4.20-4.27.



**Figure 4.20** The mole fraction of acetic acid in the reboiler at reflux ratio 0.8.

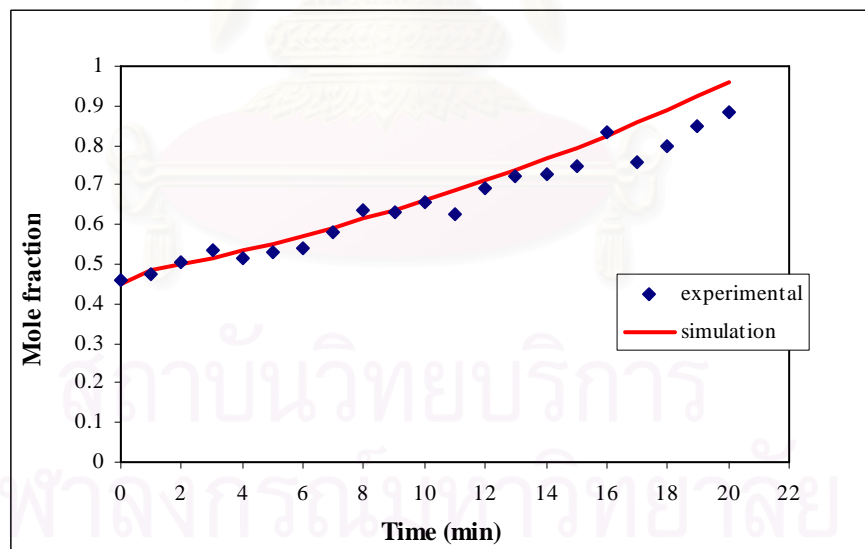
Figure 4.20 shows that the mole fraction of acetic acid in the reboiler increase when operating times increase, which the results from experimental agreement with the simulation.

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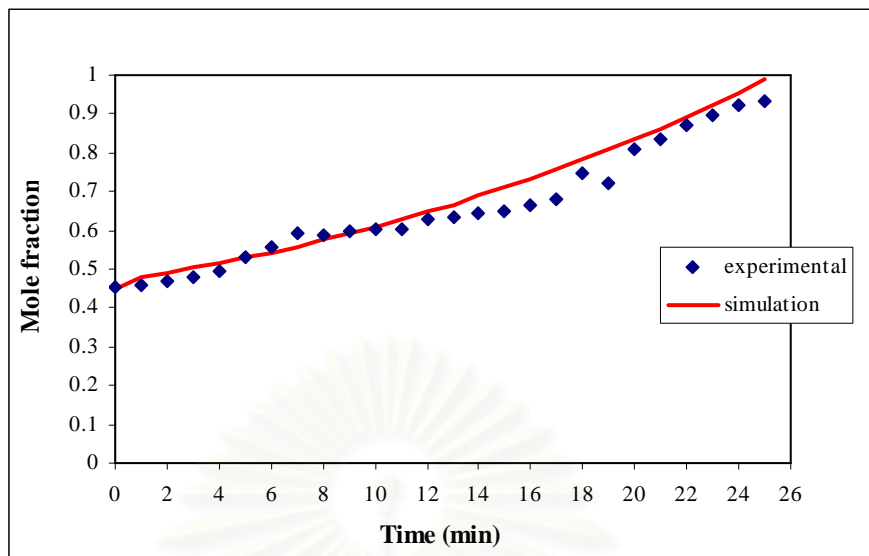
**Figure 4.21** The mole fraction of acetic acid in the reboiler at reflux ratio 0.825.

Figure 4.21 shows that the mole fraction of acetic acid in the reboiler increase when operating times increase, which the results from experimental agreement with the simulation.



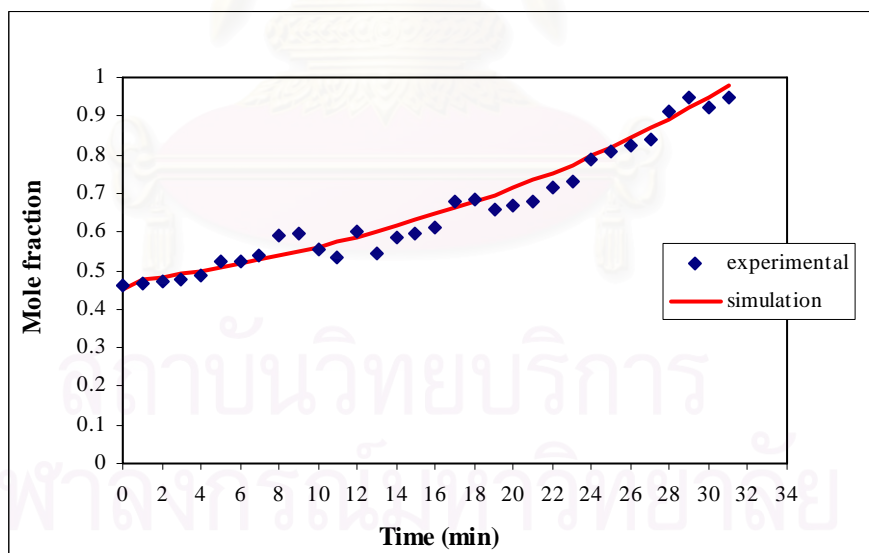
**Figure 4.22** The mole fraction of acetic acid in the reboiler at reflux ratio 0.85.

Figure 4.22 shows that the mole fraction of acetic acid in the reboiler increase when operating times increase, which the results from experimental agreement with the simulation.



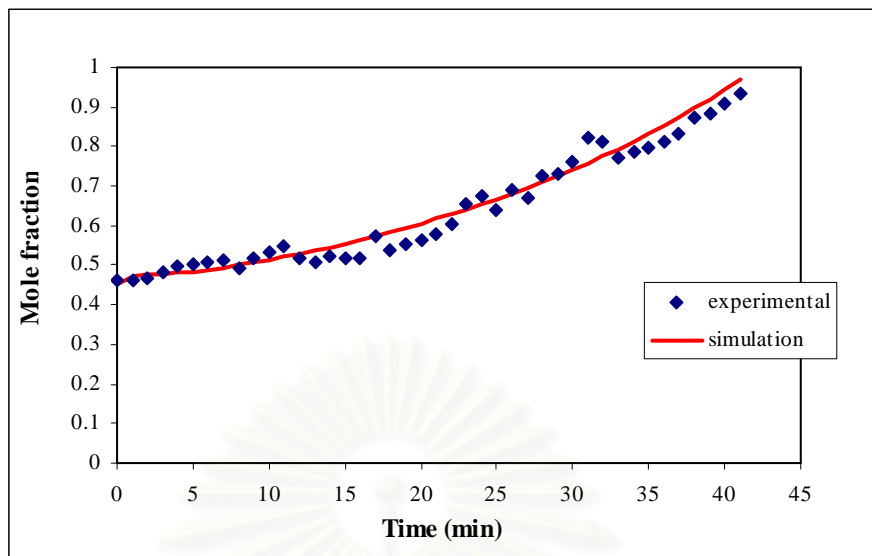
**Figure 4.23** The mole fraction of acetic acid in the reboiler at reflux ratio 0.875.

Figure 4.23 shows that the mole fraction of acetic acid in the reboiler increase when operating times increase, which the results from experimental agreement with the simulation.



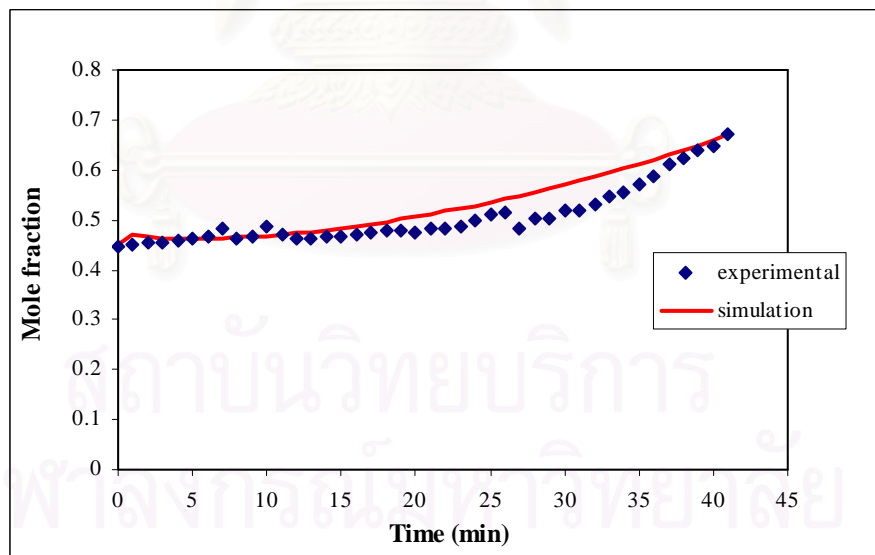
**Figure 4.24** The mole fraction of acetic acid in the reboiler at reflux ratio 0.90.

Figure 4.24 shows that the mole fraction of acetic acid in the reboiler increase when operating times increase, which the results from experimental agreement with the simulation.



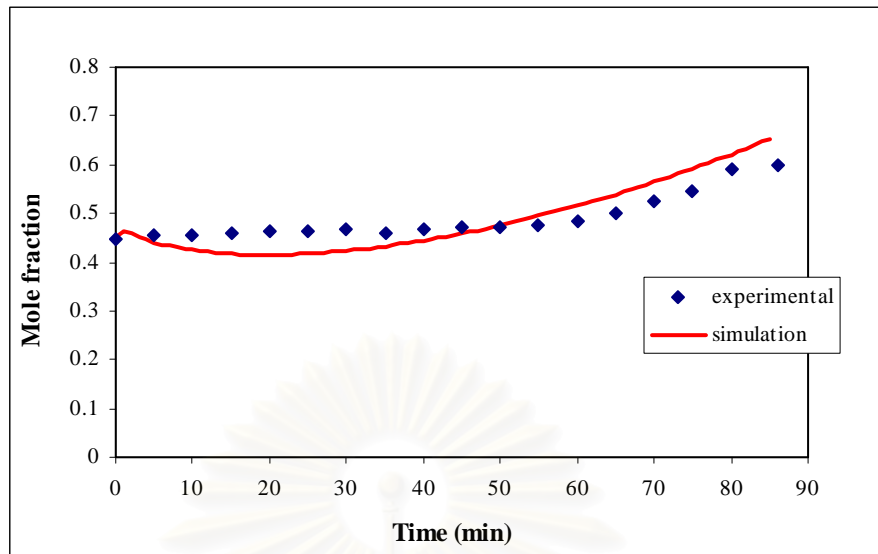
**Figure 4.25** The mole fraction of acetic acid in the reboiler at reflux ratio 0.925.

Figure 4.25 shows that the mole fraction of acetic acid in the reboiler increase when operating times increase, which the results from experimental agreement with the simulation.



**Figure 4.26** The mole fraction of acetic acid in the reboiler at reflux ratio 0.95.

Figure 4.26 shows that the mole fraction of acetic acid in the reboiler increase when operating times increase, which the results from experimental agreement with the simulation.

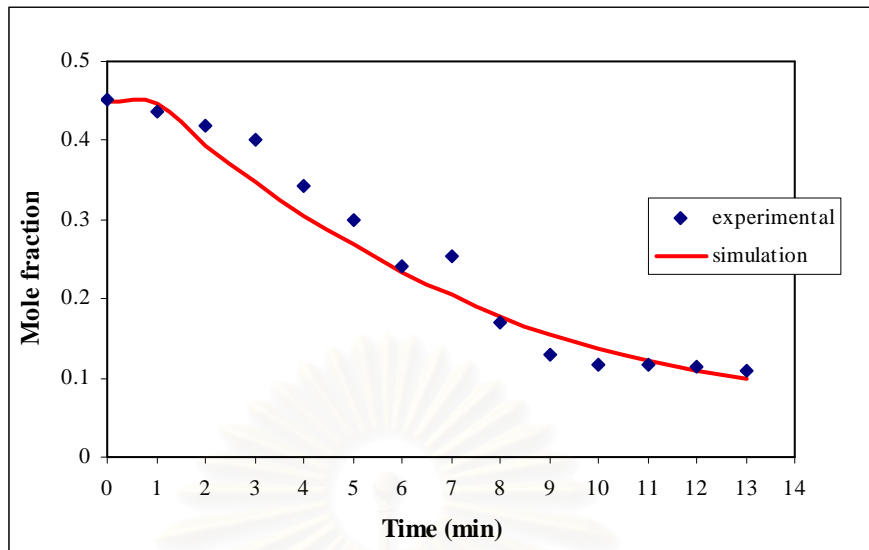


**Figure 4.27** The mole fraction of acetic acid in the reboiler at reflux ratio 0.975.

Figure 4.27 shows that the mole fraction of acetic acid in the reboiler increase when operating times increase, which the results from experimental agreement with the simulation.

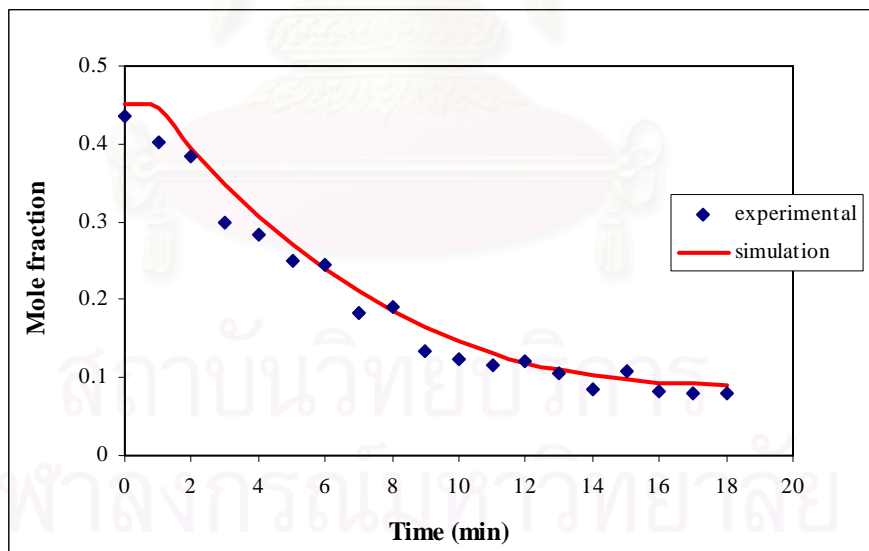
The conversion of acetic acid over time in reboiler demonstrated in Figure 4.20-4.27 show agreement between experimental data and simulation results. The concentration of acetic acid in the reboiler increases, when the operating time increases, due to acetic acid's highest boiling pointing the reaction mixture, therefore concentration of acetic acid still remain in the range of separated by distillation in the lower section.

The results of the simulation of ethanol concentration in distillate versus experimental data are shown in Figure 4.28-4.35. The reflux ratio ranging from 0.80-0.975 are considered.



**Figure 4.28** The mole fraction of ethanol in distillate at reflux ratio 0.80.

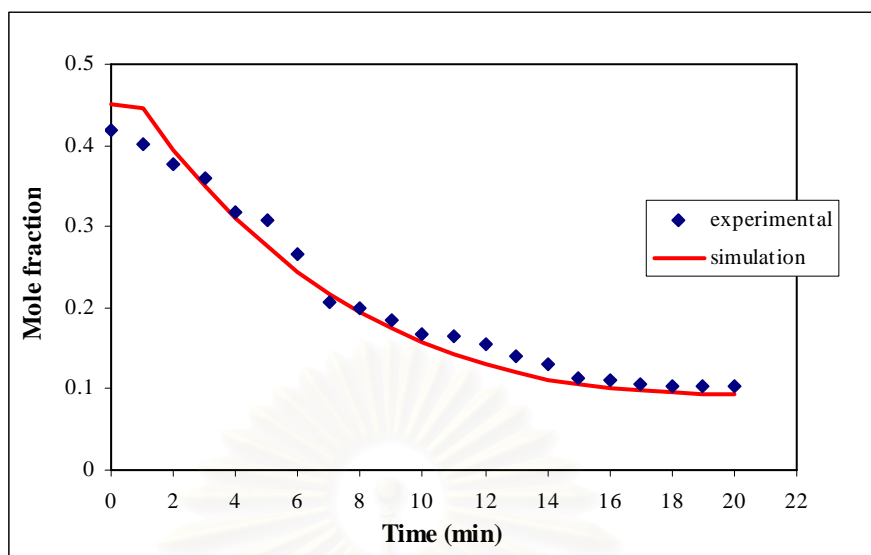
Figure 4.28 shows that the mole fraction of ethanol in distillate decrease when operating times increase, which the results from experimental agreement with the simulation.



**Figure 4.29** The mole fraction of ethanol in distillate at reflux ratio 0.825.

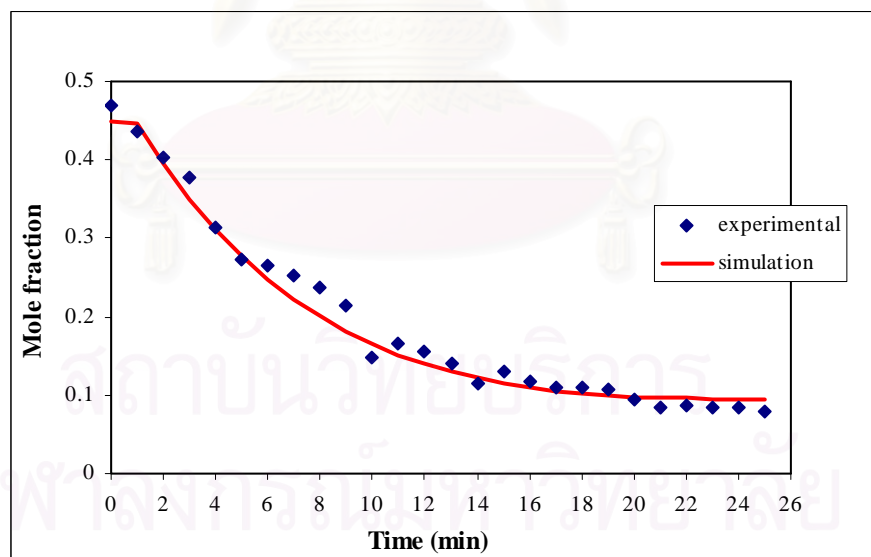
Figure 4.29 shows that the mole fraction of ethanol in distillate decrease when operating times increase, which the results from experimental agreement with the simulation.





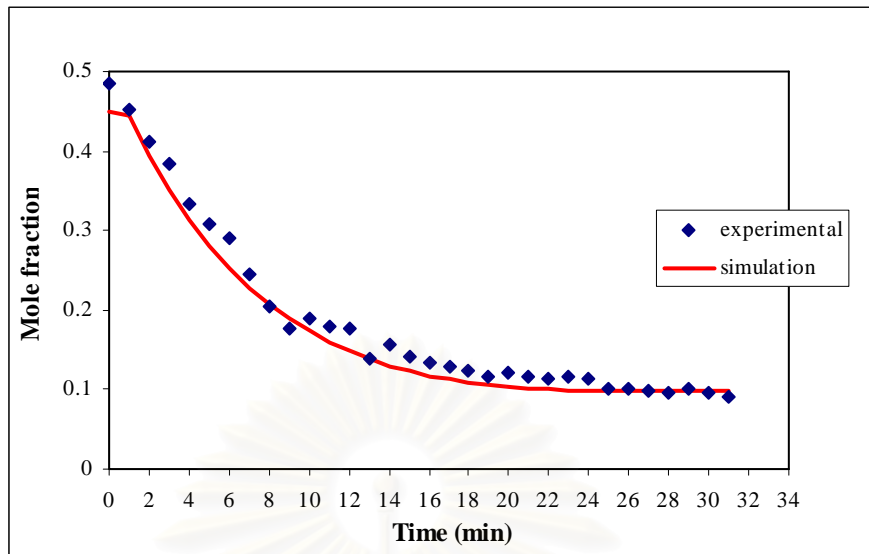
**Figure 4.30** The mole fraction of ethanol in distillate at reflux ratio 0.85.

Figure 4.30 shows that the mole fraction of ethanol in distillate decrease when operating times increase, which the results from experimental agreement with the simulation.



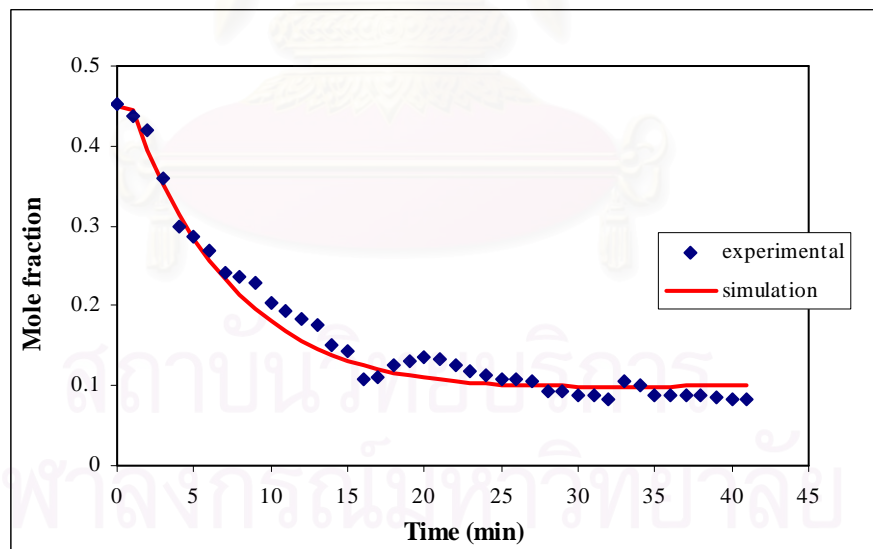
**Figure 4.31** The mole fraction of ethanol in distillate at reflux ratio 0.875.

Figure 4.31 shows that the mole fraction of ethanol in distillate decrease when operating times increase, which the results from experimental agreement with the simulation.



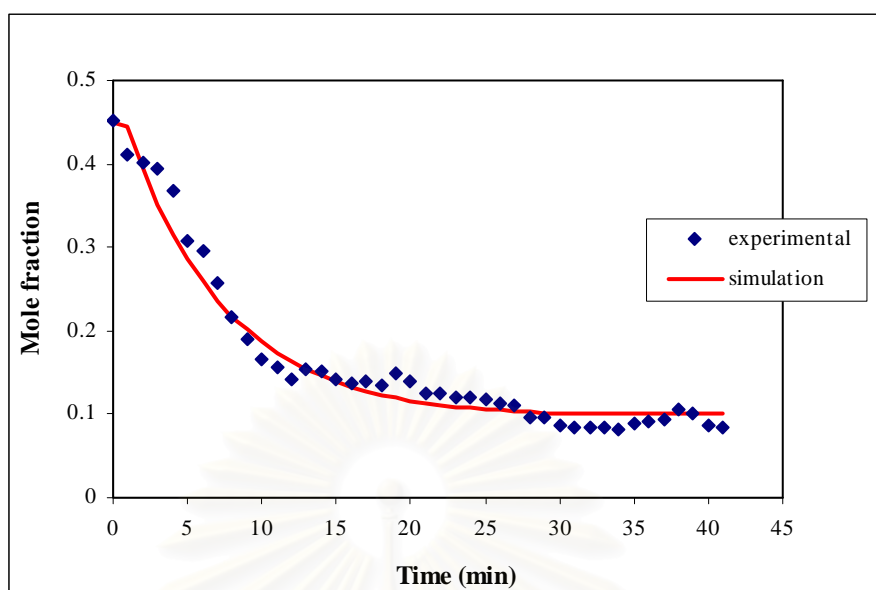
**Figure 4.32** The mole fraction of ethanol in distillate at reflux ratio 0.90.

Figure 4.32 shows that the mole fraction of ethanol in distillate decrease when operating times increase, which the results from experimental agreement with the simulation.



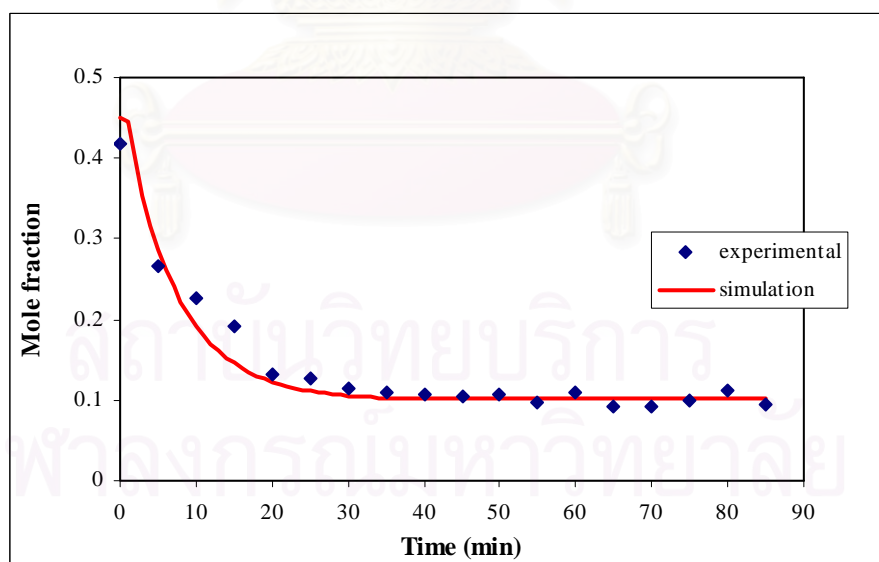
**Figure 4.33** The mole fraction of ethanol in distillate at reflux ratio 0.925.

Figure 4.33 shows that the mole fraction of ethanol in distillate decrease when operating times increase, which the results from experimental agreement with the simulation.



**Figure 4.34** The mole fraction of ethanol in distillate at reflux ratio 0.95.

Figure 4.34 shows that the mole fraction of ethanol in distillate decrease when operating times increase, which the results from experimental agreement with the simulation.



**Figure 4.35** The mole fraction of ethanol in distillate at reflux ratio 0.975.

Figure 4.35 shows that the mole fraction of ethanol in distillate decrease when operating times increase, which the results from experimental agreement with the simulation.

The conversion of ethanol over time in distillate demonstrated in Figure 4.28-4.35 show agreement between experimental data and simulation results. The concentration of ethanol in the distillate decreases, when the operating time increases, due to ethanol is reactant of reaction and occur change to product, therefore mole fraction of ethanol decrease when versus with operating time.

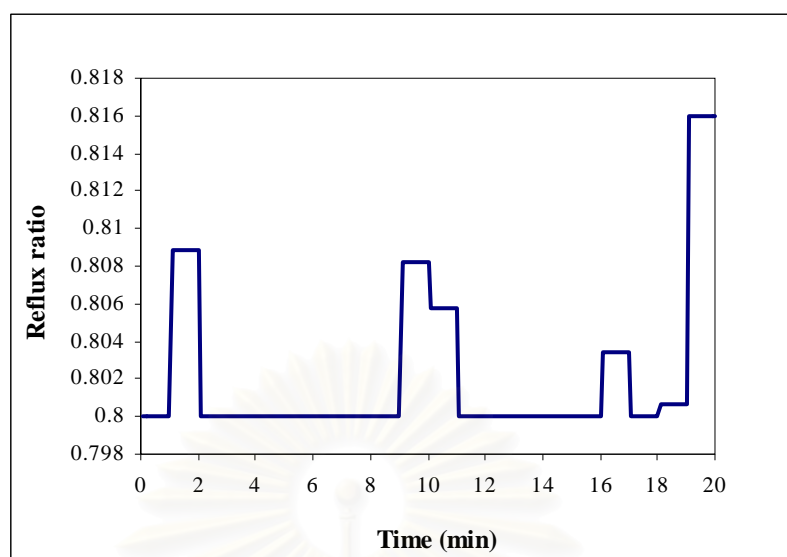
## 4.4 Optimization

We considered an optimization problem which maximizes the amount of distillate product for a given time of operation  $t_F^*$ . This type of operation is often useful when a fixed period is assigned to a particular batch unit for a particular job. Mathematically the optimization problem can be written as:

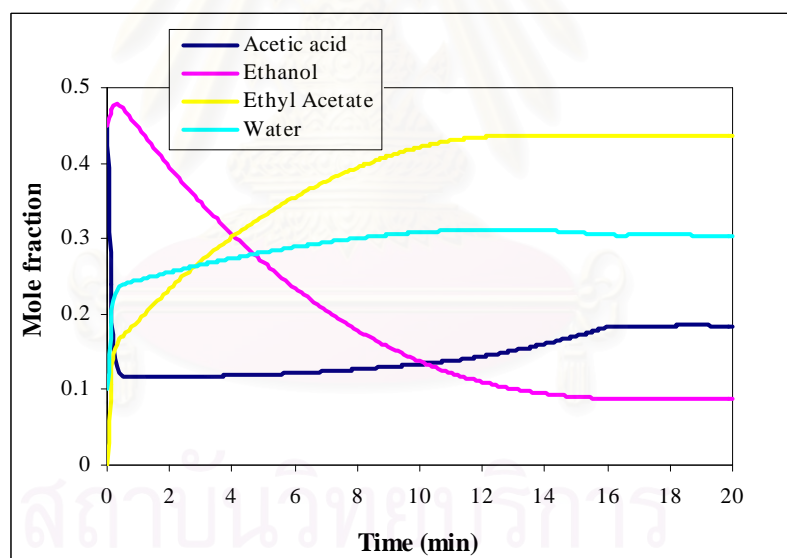
$$\begin{array}{ll}
 \text{Max} & J = D \\
 r(t) & \\
 \text{s.t.} & \text{Model Equations} \quad (\text{equality constraints}) \\
 & x_D \geq x_D^* \quad (\text{inequality constraints}) \\
 & t = t_F^* \\
 & \text{Linear bounds on reflux ratio (inequality constraints)}
 \end{array}$$

where  $D$ ,  $x_D$  are the amount of distillate and its composition at the final time  $t_F$ ,  $x_D^*$  are the specified amount of distillate product and its purity.  $r(t)$  is the reflux ratio profile which is optimized.

The input data are same as in Table 4.1 and batch time is fixed at 20 min. The lower and upper bounds on the reflux ratio are 0.8 and 1.0. The maximum amount of distillate obtain from the optimization are 39.5699 mol and composition of ethyl acetate at the final time is 0.436, however the average composition obtained in the accumulated distillate is only 0.373. The reflux ratio profile is presented in Figure 4.36. This figure shows that reflux ratio change in range of 0.8-0.816, which the maximum amount of product occur.



**Figure 4.36** Reflux ratio profile from optimization of the reactive batch distillation column.

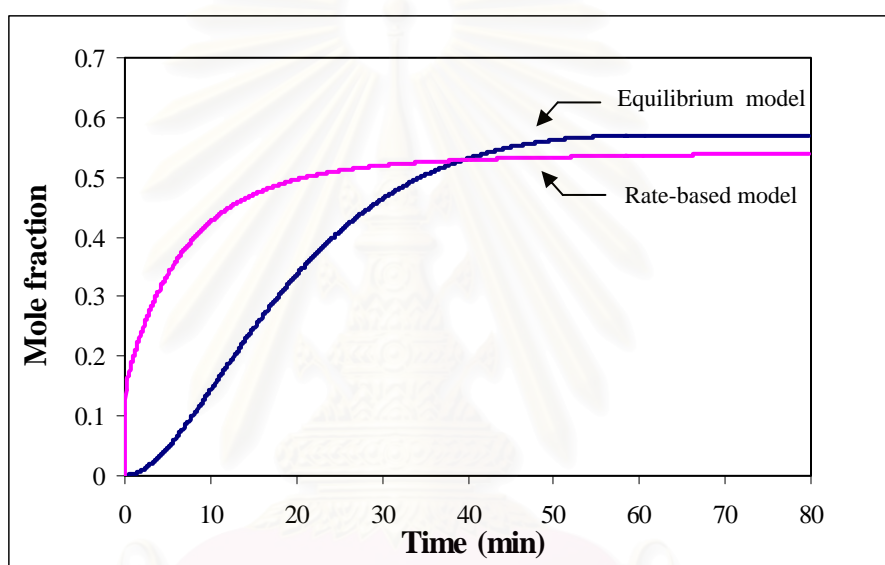


**Figure 4.37** Composition profile from optimization of the reactive batch distillation column.

The composition profile is presented in Figure 4.37. Mole fraction of ethyl acetate increase rapidly in first time, then it is constant in range 12-20 min., while ethanol and acetic acid are decrease due to are reactants of ethyl acetate synthesis, thus amount of reactants are withdrawn into column, mole fraction of acetic acid and ethanol in distillate as decrease.

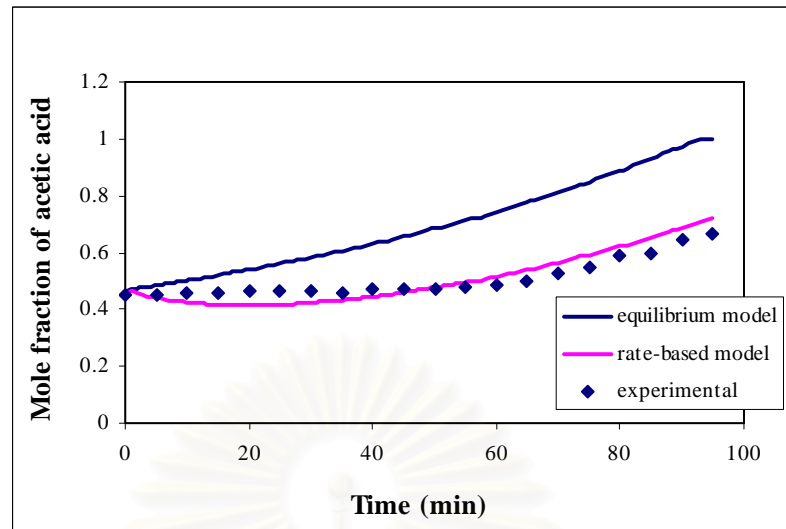
## 4.5 Comparison of the Equilibrium and Rate-based Models

In this section, we compare the dynamic rate-based model with the equilibrium model. The equilibrium model used in this study follows the conventional approach for a reactive batch distillation which assumes physical and mechanical equilibria (Mujtaba and Macchietto,1997). The nonequilibrium model is described in section 4.1 of this chapter. The data defining the column configuration, feed composition, column holdup etc. are given in Table 4.1.



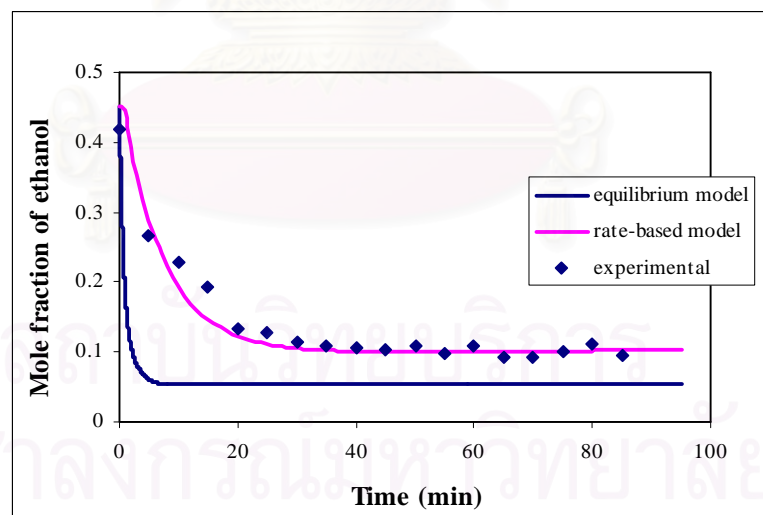
**Figure 4.38** Comparison of ethyl acetate profiles between the equilibrium model and the rate-based model of reflux ratio 0.975.

The results from the comparison of dynamic response of the EtAc purity between equilibrium and rate-based models are shown in Figure 4.38. The purity of EtAc from calculation of rate-based model see also at times 0-20 minutes, the purity of EtAc increase rapidly and then, the purity of EtAc is constant at mole fraction 0.535, while the calculation from equilibrium model see also the purity of EtAc increase slowly when operating time increase and maximum mole fraction of 0.565. Figure 4.39-4.40 is the comparison of acetic acid profiles between the equilibrium model and the rate-based model in the reboiler and ethanol profiles between the equilibrium model and the rate-based model in the distillate of reflux ratio 0.975.



**Figure 4.39** Comparison of acetic acid profiles between the equilibrium model and the rate-based model in the reboiler.

The results from Figure 4.39 show that, the remain of acetic acid in the reboiler, the equilibrium model is much more than the rate-based model, which the rate-based model show agreement with the experimental data.



**Figure 4.40** Comparison of ethanol profiles between the equilibrium model and the rate-based model in the distillate.

The results from Figure 4.40 show that, the ethanol in the distillate increase, when operating time increase, while the rate-based model show agreement with the experimental data.

# CHAPTER V

## CONCLUSIONS AND RECOMMENDATIONS

### 5.1 Conclusions

In this work, the reactive batch distillation has been studied. The dynamic simulation of this distillation is implemented to find optimal reflux ratio for the maximum purity of ethyl acetate in distillate. The optimal reflux ratio of the simulation is 0.975 and purity of ethyl acetate is 53.5%. The mole fraction of ethyl acetate in the distillate increases with an increasing of reflux ratio. Due to the fact that high reflux ratio increases reaction time. The reflux ratio is another factor which governs the distillation performance. Even though the increase suppresses the forward reaction rate in the column, it can enhance the purity of the light key component in the distillate.

In the part of comparison of the results of simulation and the experimental is proved to validate the mathematical model for this simulation. It is found that, the results of simulation shows agreement with the results of experimental. Therefore, the mathematical model is used in this work can be described the operational of the reactive batch distillation column.

Dynamic rate-based and equilibrium models are used to the simulation of ethyl acetate synthesis of reactive batch distillation column. In comparison of mole fraction, the predictions from the equilibrium and rate-based models are similar. However, the rate-based model is much more complicated than the equilibrium model, and is also more difficult to converge.

### 5.2 Recommendations

Some recommendations for future work are given below. In this research, the simulation of reactive batch distillation column should change the range of reflux



ratio is more than the range of 0.8-0.975 and vary other parameter to find profiles of that parameters. The experimental should test more than three times for change one reflux ratio and should use other instrument for analysis of sample in distillation column. In the part of optimization, should optimize to find minimum operating cost or maximum purity of ethyl acetate for this process.



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## REFERENCES

- Albet, J.M., Le Lann, J.M., Joulia, X., and Koehret, B., Rigorous simulation of multicomponent multisequence batch reactive distillation. Computers-Oriented Process Engineering 75 (1991): 75-80.
- Alejski, K., and Duprat, F., Dynamic simulation of the multicomponent reactive distillation. Chemical Engineering Science 51 (1996): 4237-4252.
- Baur, R., Taylor, R., and Krishna, R., Dynamic behaviour of reactive distillation tray columns described with a nonequilibrium cell model Chemical Engineering Science 56 (2001): 1721-1729.
- Baur, R., Taylor, R., and Krishna, R., Dynamic behaviour of reactive distillation columns described by a nonequilibrium stage model. Chemical Engineering Science 56 (2001): 2085-2102.
- Bollyn, M.P., and Wright, A.R., Development of a process model for a batch reactive distillation - a case study. Computers and Chemical Engineering 22 (1998): S87-S94.
- Cuille, P.E., and Reklaitis, G.V., Dynamic simulation of multicomponent batch rectification with chemical reactions. Computers and Chemical Engineering 10 (1986): 389-398.
- Hiwale, R.S., Bhate, N.V., Mahajan, Y.S., and Mahajani, S.M., Industrial applications of reactive distillation: recent trends. International Journal of Chemical Reactor Engineering 2 (2007): R1.
- Jianjun, P., Edgar, T.F., and Eldridge, R.B., Dynamic rate-based and equilibrium models for a packed reactive distillation column. Chemical Engineering Science 58 (2003): 2671-2680.
- Jianjun, P., Lextrait, S., Edgar, T.F., and Eldridge, R.B., A comparison of steady-state equilibrium and rate-based models for packed reactive distillation columns. Industrial & Engineering Chemistry Research 41 (2002): 2735-2744.
- Kloker, M., Kenig, E.Y., Hoffmann, A., Kreis, P., and Gorak, A., Rate-based modeling and simulation of reactive separations in gas/vapour-liquid systems. Chemical Engineering and Processing 44 (2005): 617-629.

- Kreul, L., Gorak, A., Dittrich, C., and Barton, P., Dynamic catalytic distillation: Advanced simulation and experimental validation. Computers and Chemical Engineering 22 (1996): S371-S378.
- Mujtaba, I.M., Batch distillation design and operation. London: Imperial College Press, 2003.
- Mujtaba, I.M., and Macchietto, S., Efficient optimization of batch distillation with chemical reaction using polynomial curve fitting techniques. Industrial & Engineering Chemistry Research 36 (1997): 2287-2295.
- Rahul, P., Kailash, S., Vishnu, P., and Moses, O.T., Dynamic simulation of reactive batch distillation column for ethyl acetate synthesis. Chemical Product and Process Modeling 2 (2007): 1-18.
- Richard, M.F., and Ronald, W.R., Elementary principles of chemical processes. New York: Wiley, 3<sup>rd</sup> edn. 2000.
- Schneider, R., Noeres, C., Kreul, L.U., and Gorak, A., Dynamic modeling and simulation of reactive batch distillation. Computers and Chemical Engineering 25 (2001): 169-176.
- Simandl, J., and Svrcek, W.Y., Extension of the simultaneous solution and inside-outside algorithms to distillation with chemical reactions. Computers and Chemical Engineering 15 (1991): 337-348.
- Smith, J.M., Abbott, M.M., and Van Ness H.C., Introduction to chemical engineering thermodynamics. Boston: McGraw-Hill, 6<sup>th</sup> edn. 2001.
- Taylor, R., and Krishna, R., Multicomponent mass transfer. New York: Wiley, 1993.



## **APPENDICES**

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## APPENDIX A

### PARAMETERS FOR SIMULATION

#### 1. Antoine Equation

$$\text{Vapor pressure (mmHg)} : \log_{10}(P) = A_p - \frac{B_p}{T(^{\circ}\text{C}) + C_p} \quad (\text{A.1})$$

**Table A.1** Parameter for calculation Antoine Equation

Components	Antoine's constants		
	$A_p$	$B_p$	$C_p$
Acetic acid	7.38782	1533.313	222.309
Ethanol	8.11220	1592.864	226.184
Ethyl acetate	7.09808	1238.710	217.000
Water	7.96681	1668.210	228.000

#### 2. Density

$$\text{Density (g/ml)} : \rho_i = A_d B_d^{-(1-T/T_c)^n} \quad (\text{A.2})$$

**Table A.2** Parameter for calculation density

Components	$A_d$	$B_d$	$n$	$T_c$
Acetic acid	0.35182	0.26954	0.26843	592.71
Ethanol	0.26570	0.26395	0.23670	516.25
Ethyl acetate	0.30654	0.25856	0.2780	523.30
Water	0.34710	0.2740	0.28571	647.13

## 3. Vapor Enthalpy

$$\text{Vapor Enthalpy (kJ/kg)} : H_v = a + bT + cT^2 + dT^3 + eT^4 + fT^5 \quad (\text{A.3})$$

**Table A.3** Parameter for calculation Vapor Enthalpy

Components	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>
Acetic acid	0.0	8.06502E-02	2.12358E-03	9.736780E-07	2.06162E-10	0.0
Ethanol	0.0	0.19577	2.32519E-03	-6.07458E-07	7.45539E-12	0.0
Ethyl acetate	0.0	8.21701E-02	2.31235E-03	-7.91971E-07	8.10602E-11	0.0
Water	5.7296	1.9145	-3.9574E-04	8.76206E-07	-4.95055E-10	1.03846E-13

## 4. Enthalpy of Vaporization

$$\text{Enthalpy of Vaporization (kJ/mol)} : H_{VAP} = A_e \left(1 - T/T_c\right)^{n_e} \quad (\text{A.4})$$

**Table A.4** Parameter for calculation Enthalpy of Vaporization

Components	<i>A<sub>e</sub></i>	<i>T<sub>c</sub></i>	<i>n<sub>e</sub></i>
Acetic acid	11.575	592.71	-0.65
Ethanol	43.122	516.25	0.079
Ethyl acetate	49.346	523.30	0.385
Water	52.053	647.13	0.321

## 5. Viscosity of Liquid

$$\text{Viscosity of Liquid (cP)} : \log_{10}(n_{liq}) = A_{vl} + B_{vl}/T + C_{vl}T + D_{vl}T^2 \quad (\text{A.5})$$

**Table A.5** Parameter for calculation Viscosity of Liquid

Components	$A_{vl}$	$B_{vl}$	$C_{vl}$	$D_{vl}$
Acetic acid	-3.8937	7.8482E+02	6.665E-03	-7.5606E-06
Ethanol	-6.4406	1.1176E+03	1.3721E-02	-1.5465E-05
Ethyl acetate	-3.6861	5.5228E+02	8.0018E-03	1.0439E-05
Water	-10.2158	1.7925E+03	1.7730E-02	-1.2631E-05

## 6. Viscosity of Gas

$$\text{Viscosity of Gas } (\mu\text{P}) : n_{gas} = A_{vg} + B_{vg}T + C_{vg}T^2 \quad (\text{A.6})$$

**Table A.6** Parameter for calculation Viscosity of Gas

Components	$A_{vg}$	$B_{vg}$	$C_{vg}$
Acetic acid	-28.660	2.3510E-01	2.2087E-04
Ethanol	1.499	3.0741E-01	-4.4479E-05
Ethyl acetate	-9.259	3.0725E-01	-7.1069E-05
Water	-36.826	4.2900E-01	-1.6200E-05

## APPENDIX B

### EXPRIMENTAL DATA

The experimental is tested by the stirred batch reaction pilot unit with distillation column. In each experiment takes a sample of the distillate to measure refractive index and determine concentration of ethanol, in part of reboiler take a sample in the reboiler to measure conductivity and determine concentration of remain acetic acid.

**Table B.1** The Conductivity of Acetic acid

Concentration of acetic acid (% volume)	Conductivity ( $\mu\text{S}$ )			Mole fraction of acetic acid
	1	2	Average	
0	1385	1377	1381	0
10	1331	1320	1325.5	0.034
20	1280	1295	1287.5	0.073
30	1248	1232	1240	0.119
40	1023	1032	1027.5	0.174
50	761	775	768	0.240
60	479	495	487	0.321
70	255	268	261.5	0.424
80	125	118.5	121.75	0.558
90	22.9	20.5	21.7	0.739
100	0.8	0.8	0.8	1

**Table B.2** The Refractive index of Ethanol

Concentration of ethanol (% volume)	Refractive index				Mole fraction of ethanol
	1	2	3	Average	
0	0	0	0	0	0
10	3	3	3	3	0.033
20	6.4	6.6	6.2	6.4	0.072
30	9.8	9.8	9.8	9.8	0.117
40	12.6	12.1	12.2	12.3	0.171
50	15.1	15.2	15	15.1	0.2362
60	17	17	17	17	0.317
70	18.2	18.2	18.2	18.2	0.419
80	19	19	19	19	0.553
90	21	21.4	21.2	21.2	0.736
100	23	23.2	23.1	23.1	1



**Table B.3** The conductivity of acetic acid and the refractive index of ethanol obtain from the experimental at reflux ratio 0.80.

Time (min)	reboiler		distillate	
	conductivity ( $\mu\text{S}$ )	mole fraction of acetic acid	refractive index	mole fraction of ethanol
0	230.5	0.454	18.4	0.453
1	215	0.469	18.3	0.436
2	198	0.485	18.2	0.419
3	163	0.518	18.0	0.402
4	121	0.559	17.3	0.343
5	107	0.585	16.6	0.300
6	94	0.608	15.0	0.240
7	72	0.648	15.5	0.253
8	66	0.659	12.3	0.171
9	58	0.673	10.4	0.130
10	45	0.697	9.8	0.117
11	31	0.721	9.7	0.116
12	18	0.785	9.5	0.113
13	12	0.86	9.2	0.109

**Table B.4** The conductivity of acetic acid and the refractive index of ethanol obtain from the experimental at reflux ratio 0.825

Time (min)	reboiler		distillate	
	conductivity ( $\mu\text{S}$ )	mole fraction of acetic acid	refractive index	mole fraction of ethanol
0	230	0.454	18.3	0.436
1	226	0.458	18.0	0.402
2	218	0.466	17.8	0.385
3	153	0.528	16.6	0.300
4	174	0.508	16.2	0.283
5	162	0.519	15.4	0.249
6	149	0.532	15.3	0.245
7	83	0.628	12.8	0.183
8	105	0.588	13.2	0.192
9	98	0.601	10.6	0.134
10	72	0.648	10.1	0.123
11	63	0.664	9.8	0.117
12	55	0.679	10.0	0.121
13	38	0.71	8.9	0.105
14	17	0.798	7.3	0.084
15	14	0.835	9.1	0.108
16	12	0.86	7.2	0.083
17	10	0.885	7.1	0.081
18	8	0.91	7.0	0.080

**Table B.5** The conductivity of acetic acid and the refractive index of ethanol obtain from the experimental at reflux ratio 0.85

Time (min)	reboiler		distillate	
	conductivity ( $\mu\text{S}$ )	mole fraction of acetic acid	refractive index	mole fraction of ethanol
0	225	0.459	18.2	0.419
1	207	0.476	18	0.402
2	179	0.503	17.7	0.377
3	148	0.533	17.5	0.360
4	166	0.516	17.0	0.317
5	151	0.53	16.8	0.308
6	143	0.538	15.8	0.266
7	109	0.581	13.8	0.206
8	79	0.635	13.5	0.199
9	81	0.632	12.9	0.185
10	66	0.659	12.2	0.167
11	85	0.624	12.4	0.166
12	47	0.693	11.6	0.156
13	31	0.722	10.9	0.141
14	29	0.726	10.4	0.130
15	16	0.749	9.5	0.113
16	14	0.835	9.3	0.110
17	20	0.76	9.0	0.106
18	17	0.798	8.8	0.104
19	13	0.848	8.8	0.104
20	10	0.885	8.8	0.104

**Table B.6** The conductivity of acetic acid and the refractive index of ethanol obtain from the experimental at reflux ratio 0.875

Time (min)	reboiler		distillate	
	conductivity ( $\mu\text{S}$ )	mole fraction of acetic acid	refractive index	mole fraction of ethanol
0	230.5	0.454	18.5	0.469
1	224	0.46	18.3	0.436
2	217	0.467	18.0	0.402
3	203	0.48	17.7	0.377
4	186	0.496	16.9	0.313
5	151	0.53	16.0	0.274
6	125	0.555	15.8	0.266
7	102	0.594	15.5	0.253
8	104	0.59	15.1	0.236
9	101	0.596	14.2	0.215
10	97	0.603	11.2	0.147
11	96	0.605	12.4	0.166
12	82	0.63	11.6	0.156
13	79	0.635	10.9	0.141
14	74	0.644	9.7	0.116
15	70	0.651	10.4	0.130
16	63	0.664	9.8	0.117

17	55	0.679	9.3	0.110
18	21	0.748	9.2	0.109
19	32	0.72	9.0	0.106
20	16	0.81	8.2	0.095
21	14	0.835	7.3	0.084
22	11	0.873	7.5	0.087
23	9	0.898	7.3	0.084
24	7	0.923	7.3	0.084
25	6	0.935	7.0	0.080

**Table B.7** The conductivity of acetic acid and the refractive index of ethanol obtain from the experimental at reflux ratio 0.90

Time (min)	reboiler		distillate	
	conductivity ( $\mu\text{S}$ )	mole fraction of acetic acid	refractive index	mole fraction of ethanol
0	225	0.459	18.6	0.486
1	219	0.465	18.4	0.453
2	215	0.469	18.1	0.411
3	208	0.475	17.8	0.385
4	196	0.487	17.2	0.334
5	157	0.524	16.8	0.308
6	159	0.522	16.4	0.291
7	142	0.539	15.3	0.245
8	103	0.592	13.7	0.204
9	100	0.597	12.6	0.178
10	124	0.556	13.1	0.190
11	148	0.533	12.7	0.180
12	99	0.599	12.5	0.176
13	137	0.543	10.8	0.139
14	106	0.586	11.6	0.156
15	100	0.597	10.9	0.141
16	92	0.612	10.6	0.134
17	55	0.679	10.4	0.130
18	52	0.684	10.1	0.123
19	66	0.659	9.8	0.117
20	61	0.668	10.0	0.121
21	54	0.681	9.8	0.117
22	35	0.715	9.5	0.113
23	26	0.731	9.7	0.116
24	18	0.785	9.5	0.113
25	16	0.810	8.7	0.102
26	15	0.823	8.5	0.100
27	12	0.839	8.4	0.098
28	8	0.910	8.2	0.096
29	5	0.948	8.5	0.100
30	7	0.923	8.1	0.095
31	5	0.948	7.9	0.092

**Table B.8** The conductivity of acetic acid and the refractive index of ethanol obtain from the experimental at reflux ratio 0.925

Time (min)	reboiler		distillate	
	conductivity ( $\mu\text{S}$ )	mole fraction of acetic acid	refractive index	mole fraction of ethanol
0	224	0.460	18.4	0.453
1	221	0.463	18.3	0.436
2	217	0.467	18.2	0.419
3	199	0.484	17.5	0.360
4	186	0.496	16.6	0.300
5	180	0.502	16.3	0.287
6	175	0.507	15.9	0.270
7	170	0.512	15.2	0.240
8	192	0.491	15.1	0.236
9	161	0.520	14.8	0.229
10	148	0.533	13.7	0.204
11	132	0.548	13.3	0.194
12	161	0.520	12.8	0.183
13	173	0.509	12.5	0.176
14	160	0.521	11.4	0.152
15	165	0.517	11.0	0.143
16	163	0.518	9.2	0.109
17	112	0.576	9.3	0.110
18	145	0.536	10.2	0.126
19	126	0.554	10.4	0.130
20	118	0.565	10.7	0.136
21	109	0.581	10.5	0.132
22	97	0.603	10.2	0.126
23	69	0.653	9.8	0.117
24	58	0.673	9.5	0.113
25	76	0.641	9.2	0.109
26	43	0.691	9.1	0.108
27	61	0.668	9.0	0.106
28	29	0.726	8.0	0.093
29	27	0.729	7.9	0.092
30	20	0.760	7.7	0.089
31	15	0.823	7.6	0.088
32	16	0.810	7.3	0.084
33	19	0.773	9.0	0.106
34	18	0.785	8.5	0.100
35	17	0.798	7.7	0.089
36	16	0.810	7.6	0.088
37	14	0.835	7.7	0.089
38	11	0.873	7.5	0.087
39	10	0.885	7.4	0.085
40	8	0.910	7.3	0.084
41	6	0.935	7.3	0.084

**Table B.9** The conductivity of acetic acid and the refractive index of ethanol obtain from the experimental at reflux ratio 0.95

Time (min)	reboiler		distillate	
	conductivity ( $\mu\text{S}$ )	mole fraction of acetic acid	refractive index	mole fraction of ethanol
0	237	0.447	18.4	0.453
1	235	0.449	18.1	0.411
2	230	0.454	18.0	0.402
3	228	0.456	17.9	0.394
4	224	0.460	17.6	0.368
5	220	0.464	16.8	0.308
6	216	0.468	16.5	0.296
7	202	0.481	15.6	0.257
8	223	0.461	14.3	0.217
9	219	0.465	13.1	0.19
10	198	0.485	12.4	0.166
11	212	0.471	11.6	0.156
12	221	0.463	10.9	0.141
13	220	0.464	11.5	0.154
14	218	0.466	11.4	0.152
15	217	0.467	10.9	0.141
16	215	0.469	10.7	0.136
17	210	0.473	10.8	0.139
18	206	0.477	10.6	0.134
19	204	0.479	11.3	0.149
20	208	0.475	10.8	0.139
21	202	0.481	10.2	0.126
22	200	0.483	10.2	0.126
23	196	0.487	10.0	0.121
24	185	0.497	9.9	0.119
25	173	0.509	9.8	0.117
26	169	0.513	9.5	0.113
27	200	0.483	9.3	0.110
28	181	0.501	8.3	0.097
29	179	0.503	8.2	0.095
30	164	0.517	7.5	0.087
31	162	0.519	7.4	0.085
32	149	0.532	7.3	0.084
33	135	0.545	7.2	0.083
34	127	0.553	7.1	0.081
35	114	0.572	7.6	0.088
36	106	0.586	7.9	0.092
37	93	0.610	8.0	0.093
38	85	0.624	8.9	0.105
39	77	0.639	8.6	0.101
40	72	0.648	7.5	0.087
41	60	0.670	7.4	0.085

**Table B.10** The conductivity of acetic acid and the refractive index of ethanol obtain from the experimental at reflux ratio 0.975

Time (min)	reboiler		distillate	
	conductivity ( $\mu\text{S}$ )	mole fraction of acetic acid	refractive index	mole fraction of ethanol
0	236	0.448	18.2	0.419
5	230	0.454	15.8	0.266
10	228	0.456	14.7	0.227
15	224	0.460	13.2	0.192
20	222	0.462	10.5	0.132
25	219	0.465	10.3	0.128
30	217	0.467	9.6	0.114
35	225	0.459	9.3	0.110
40	215	0.469	9.0	0.106
45	212	0.471	8.8	0.104
50	210	0.473	9.1	0.108
55	207	0.476	8.3	0.097
60	198	0.485	9.2	0.109
65	183	0.499	8.0	0.093
70	156	0.525	7.9	0.092
75	133	0.547	8.5	0.100
80	104	0.590	9.4	0.112
85	99	0.599	8.1	0.095

## VITA

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