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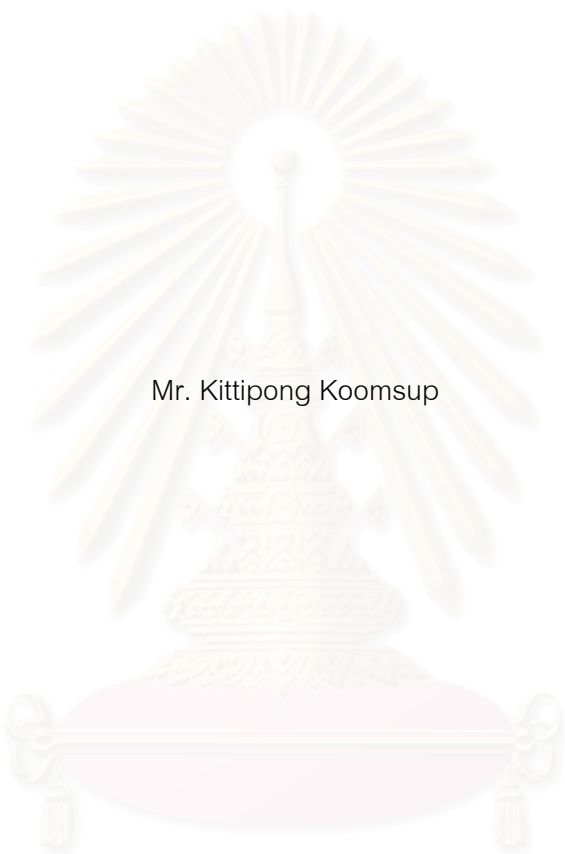
นายกิตติพงศ์ คุ้มทรัพย์

APPLICATION OF REACTIVE DISTILLATION FOR PRODUCTION OF

N-BUTYL ACETATE FROM *N*-BUTANOL AND DILUTE ACETIC ACID

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A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Engineering Program in Chemical Engineering

Department of Chemical Engineering

Faculty of Engineering

Chulalongkorn University

Academic Year 2006

Thesis Title	APPLICATION OF REACTIVE DISTILLATION FOR PRODUCTION OF N-BUTYL ACETATE FROM N-BUTANOL AND DILUTE ACETIC ACID
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งานวิจัยนี้ศึกษาการจำลองการสังเคราะห์นอร์มอลบิวทิวอะซิเททจากนอร์มอลบิวทานอลและกรดอะซิติกเจือจางในหอกลั่นแบบมีปฏิกิริยา ที่ใช้แอมเบอร์ลิส 15 เป็นตัวเร่งปฏิกิริยา โดยใช้ชุดโปรแกรมทางการค้าชื่อแอสเปน พลัส กรดอะซิติกเจือจางที่พิจารณาเป็นผลิตภัณฑ์พลอยได้จากอุตสาหกรรมเคมีบางประเภท วัตถุประสงค์ของงานวิจัยนี้เพื่อสังเคราะห์นอร์มอลบิวทิวอะซิเททที่มีความบริสุทธิ์ไม่ต่ำกว่า 98% โดยโมล โดยรวมระบบหอกลั่นแบบมีปฏิกิริยากับระบบการแยก ได้แก่ ระบบหอกลั่นและระบบเพอร์แวบพอเรชัน งานวิจัยแบ่งออก 2 ส่วน คือ การศึกษาในระดับโรงประลอง และการศึกษาในระดับอุตสาหกรรม ผลการศึกษาในระดับโรงประลองพบว่าระบบหอกลั่นแบบมีปฏิกิริยาที่ติดตั้งอุปกรณ์แยกวัฏภาค (decanter) โดยมีการป้อนกลับวัฏภาคของสารอินทรีย์ทั้งหมดบริเวณชั้นที่ 2 เป็นระบบที่เหมาะสม เมื่อใช้กรดอะซิติกที่มีความเข้มข้นน้อยลงจะทำให้มีความต้องการพลังงานของระบบมากขึ้นสำหรับกรณีระบบหอกลั่นแบบมีปฏิกิริยาหอเดียว ในส่วนของการเพิ่มความเข้มข้นของกรดอะซิติกจาก 35 เป็น 65% โดยน้ำหนัก พบว่าการใช้ระบบเพอร์แวบพอเรชันก่อนป้อนเข้าสู่ระบบหอกลั่นแบบมีปฏิกิริยาต้องการพลังงานทั้งหมดน้อยกว่าระบบการใช้ระบบหอกลั่นร่วมกับระบบหอกลั่นแบบมีปฏิกิริยา และระบบหอกลั่นแบบมีปฏิกิริยาหอเดียว สำหรับการศึกษาในระดับอุตสาหกรรม พบว่าปริมาณการใช้พลังงานให้ผลสอดคล้องกับการศึกษาในระดับโรงประลอง แต่เมื่อพิจารณาค่าใช้จ่ายต่อปีสำหรับกรณีการใช้กรดอะซิติกเจือจาง 35% โดยน้ำหนักเป็นสารตั้งต้น พบว่าการใช้ระบบหอกลั่นแบบมีปฏิกิริยาอย่างเดียวที่มีจำนวนชั้นของปฏิกิริยา 7 ชั้น จำนวนชั้นของสติปปิ้ง 2 ชั้น และไม่มีชั้นของเรคติฟายยิง เสียค่าใช้จ่ายต่อปีน้อยที่สุด รองลงมาคือ การรวมระบบเพอร์แวบพอเรชันกับระบบหอกลั่นแบบมีปฏิกิริยา และการรวมระบบหอกลั่นกับระบบหอกลั่นแบบมีปฏิกิริยา ตามลำดับ

ภาควิชา......วิศวกรรมเคมี......	ลายมือชื่อนิสิต......กิตติพงศ์ คุ้มทรัพย์......	
สาขาวิชา......วิศวกรรมเคมี......	ลายมือชื่ออาจารย์ที่ปรึกษา............	
ปีการศึกษา......2549......	ลายมือชื่ออาจารย์ที่ปรึกษาร่วม......อมรชัย อาภรณ์วิชานพ......	

4870220021 : MAJOR CHEMICAL ENGINEERING

KEYWORDS : n-BUTYL ACETATE/ REACTIVE DISTILLATION/ DILUTE ACETIC ACID/ SIMULATION/ PERVAPORATION/ TOTAL ANNUAL COST

KITTIPONG KOOMSUP : APPLICATION OF REACTIVE DISTILLATION FOR PRODUCTION OF N-BUTYL ACETATE FROM N-BUTANOL AND DILUTE ACETIC ACID. THESIS ADVISOR: ASSOC. PROF. SUTTICHAI ASSABUMRUNGRAT, Ph.D., THESIS COADVISOR: AMORNCHAI ARPORNWICHANOP, D.Eng., 107 pp.

In this research, the simulations of n-butyl acetate synthesis from n-butanol and dilute acetic acid via reactive distillation, in which chemical reactions and separations occur simultaneously, were studied by ASPEN PLUS program. n-Butyl acetate esterification was catalyzed by Amberlyst 15. The objective of this work is to produce n-butyl acetate with a concentration not less than 98 mol%. The studies were divided into 2 main parts of pilot and industrial scales. In the pilot scale study, it was found that the reactive distillation equipped with a decanter with total recycle of the organic phase to the column at stage 2 is a suitable column configuration. For the single reactive distillation column, when the concentration of acetic acid is lowered, higher overall energy of the system is required. Considering the case with a pretreatment of acetic acid from 35 wt% to 65 wt%, the pervaporation-reactive distillation hybrid system requires lower energy than the distillation-reactive distillation hybrid system as well as the case with the single reactive distillation. In the industrial scale study, total energy consumptions of the systems follow similar trend of the pilot scale study. However, when considering the total annual cost for the case with 35 wt% acetic acid feed, it was revealed that the single reactive distillation consisting of 0 rectifying, 7 reaction, and 2 stripping stages offers the lowest total annual cost followed by the pervaporation-reactive distillation hybrid system and the distillation-reactive distillation hybrid system, respectively.

Department ....Chemical Engineering......   Student's signature ...Kittipong Koomsup...

Field of Study ..Chemical Engineering....   Advisor's signature ....

Academic year ....2006..............   Co-advisor's signature Amornchai Arpornwichanop

ACKNOWLEDGEMENTS

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NOMENCLATURE

a_i	activity of species i	[-]
aq	aqueous phase	[-]
A	surface membrane area	[m^2]
D	liquid distillate flowrate	[mol/s]
Di	diffusivity coefficient	[m/s]
DIST	distillation	[-]
E_a	activation energy	[J/mol]
C	coccentration of species i	[wt%]
c_i	concentration of species i	[mol/m^3]
c_{pl}	heat capacity of liquid	[J/mol.K]
F	feed flowrate	[mol/s]
F_i	molar flow rate of species i in the reaction side	[mol/s]
H	enthalpy	[J/s]
H_{vap}	enthalpy of vaporization	[J/s]
HOAc	acetic acid	[-]
J_i	permeate flux of species i	[mol/m^2.s]
k_i	kinetic constant base on mol fraction	[mol/(s mol-H$^+$)]
l	membrane thickness	[m]
L	liquid flowrate to return from stage 1 to stage 2	[mol/s]
M_i	molecular weight of species i	[kg/mol]
MB	membrane	[-]
n-BuAc	n-butyl acetate	[-]
n-BuOH	n-butanol	[-]
N_i	number of stages of reactive distillation or distillation	[mol]
org	organic phase	[-]
P_i	permeability coefficient of species i	[mol/(m^2.s)]
PV	pervaporation	[-]
Q	duty	[W]

Q_i	molar flow rate of species i in the permeate side	[mol/s]
r_i	reaction rate	[mol/(s kg-dry resin)]
RD	reactive distillation	[-]
RF	reflux ratio	[-]
R_g	gas constant (=8.314)	[J/(mol/K)]
S	solubility coefficient	[mol/m^3]
T	operating temperature	[K]
TAC	total annual cost	[\$/year]
W	water	[-]
x_i	liquid mole fraction of component i	[-]
X	conversion of reactant	[%]
Y	yield of product	[%]

Greeks letters

α_i	separation factor of species i	[-]
γ_i	activity coefficients of species i	[-]

Subscripts

0	initial value at $t = 0$
Cond	condenser
F	feed to pervaporation
i	species i
P	permeate side
R	retentate side
Reb	reboiler
Rec	rectifying section
Rxn	reaction section
Strp	stripping section

CHAPTER I

INTRODUCTION

Organic solvents are important chemicals for many industries. Acetate esters have been widely used as solvents for a broad range of resins due to their powerful solvency, high volatility and mild odor. Examples of the commonly used acetate esters are *iso*-amyl acetate, ethoxy ethyl acetate, *n*-butyl acetate, and hexyl acetate. Because *n*-butyl acetate has many potential advantages when compared with other acetate esters, for example, its lower toxicity and lower environmental impact (Steinigeweg, 2002), its demand is increasing progressively.

n-Butyl acetate is produced by esterification, that an organic group replaces hydrogen atom in –OH group of acetic acid through the reaction with *n*-butanol. Up to now, *n*-butyl acetate has been synthesized by this reaction in presence of a strongly acidic catalyst in a liquid phase system. However, since acetic acid is a by-product from many important chemical processes, for example, productions of cellulose acetate, terephthalic acid and glyoxal. Cellulose acetate, commonly used in fiber processing and lacquers and photographic films process, is an ester group of cellulose. It is synthesized by acetylation of cellulose with acetic acid, acetic anhydride and sulfuric acid as reagents. This reaction results in esterification of the accessible hydroxyl groups in the wood cell wall with the formation of a large amount by-product acetic acid containing waste, typically associated with a 35% w/w aqueous solution of acetic acid as a waste stream (Katsuyoshi, 2001). In terephthalic acid production, a by-product containing up to 65% w/w of acetic acid in water is produced (Brunt, 1992). The synthesis of glyoxal from acetaldehyde and nitric acid generates a by-product containing 13-20% w/w of acetic acid.

The conventional separation processes of dilute acetic acid stream are distillation and extraction. However, the distillation requires high energy consumption while liquid-liquid extraction is limited by phase separation and distribution of components involved in the reacting system. Pervaporation is another potential way for separation of liquid mixtures. Its application can be found in dehydration of

organic/water mixtures, removal or recovery of organic compounds from water, and separation of organic mixture. In general, hydrophilic membranes have been used for dehydration of organic solvents. On the other hand, hydrophobic membranes have been used for separation of organics from water.

Another interesting approach for recovering acetic acid from the liquid mixture is to use of dilute acetic acid as a reactant for esterification. It is of growing attention because the by-product is recovered to produce a higher valued ester, which can save raw material cost and environment problem. Because dilute acetic acid is a by-product from many processes in chemical industries, the recovery of dilute acetic acid has been widely investigated. The use of reactive distillation, a multifunction reactor combining chemical reaction and distillation in a single column, is a promising way for utilization of dilute acetic acid for synthesis of high valued chemicals. Dilute acetic acid can be directly used as a reactant in the reactive distillation system. The simultaneous separation of product and chemical reaction inside the column allows the reaction to take place efficiently.

n-Butyl acetate synthesis is an equilibrium limited reaction. The use of reactive distillation is beneficial because there are ranges of operating condition which are suitable for both the reaction and separation. Reactive distillation has demonstrated its potentials for capital productivity improvements, selectivity improvements due to a fast removal of reactants or products from the reaction zone, and reduced energy consumption. It is successfully applied to an exothermic reaction system whose reaction heat can be used for vaporization of liquid. In some applications, the reduction or elimination of solvent used in the process, is realized. Due to the above advantages, reactive distillation has become an attractive unit operation in recent years.

Considering the thermodynamic properties of the reaction system, ternary aceotropic mixture between *n*-butyl acetate, butanol and water is formed as a low-boiling ternary azeotrope at 90 ^{o}C. The ternary azeotrope can be eliminated at temperatures lower than 80 ^{o}C, as well as, if the distillate overhead can be cooled down to sufficiently low temperature, a suitable condition to break azeotropes. In the production of *n*-butyl acetate by esterification via reactive distillation, *n*-butyl acetate

is the highest boiling point product as well as the heaviest key component in the system. *n*-Butyl acetate is withdrawn from the bottom of the column. The overhead distillate consisting of *n*-butanol, water, and *n*-butyl acetate is condensed and cooled to a temperature sufficiently low to allow two phase separation.

In this work, the synthesis of *n*-butyl acetate from dilute acetic acid and *n*-butanol via esterification on Amberlyst 15 catalyst in reactive distillation is investigated by simulation. Because of the presence of high water content in the acetic acid feed, various reactive distillation based systems are considered. A distillation column or a pervaporation unit is included in the process to help remove the water in the system. The commercial Aspen Plus program is employed to simulate the performances of the different systems to find suitable process configuration and operating conditions. In addition, preliminary economic analysis is also carried out to find an optimum system configurations.

CHAPTER II
THEORY

2.1 *n*-Butyl acetate synthesis

n-Butyl acetate is commonly synthesized by the esterification of acetic acid and *n*-butanol as shown in Eq. (2.1). It is a reversible and kinetically controlled reaction which is catalyzed by free protons. Sulfuric acid or sulfonic acid ion-exchange resins are commonly used as catalysts.

$$CH_3COOH \; + \; C_4H_9OH \quad \leftrightarrow \quad CH_3COOC_4H_9 \; + \; H_2O \qquad (2.1)$$
$$\text{(acetic acid)} \quad \text{(\textit{n}-butanol)} \qquad \text{(\textit{n}-butyl acetate)} \quad \text{(water)}$$
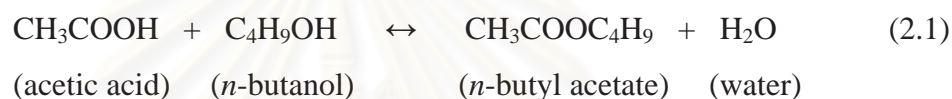
According to thermodynamic properties of the *n*-butyl acetate esterification system, *n*-butyl acetate as the high boiling point product, is obtained as the bottom product in a reactive distillation process. The *n*-butanol-water-*n*-butyl acetate, *n*-butanol-water, and *n*-butyl acetate-water azeotropes have similar boiling points, and therefore, *n*-butanol, *n*-butyl acetate, and water are the main components present in the distillate.

Dilute acetic acid is produced in large quantities in many processes such as manufacture of cellulose esters, terephthalic acid, and dimethyl terephthalate. The recovery of acetic acid from these streams is a problem. Many authors have explored the possibility for esterifying acetic acid from aqueous solution with n-butanol in a reactive distillation column. In this case, one gets an overhead product consisting of a ternary heterogeneous azeotrope of butanol, butyl acetate, and water.

2.2 Reactive distillation

Reactive distillation allows a chemical reaction and multistage distillation to take place simultaneously in a column. The combined unit operation is especially suitable for chemical reactions whose reaction equilibrium limits the conversion in a conventional reactor to a low-to-moderate level. By continuously separating products from reactants while the reaction is carried out, the reaction can proceed to much higher level of conversion. Reactive distillation has been explored as a potentially important process for several reactions. Along with esterification and etherification, other reactions such as acetalization, hydrogenation, alkylation, and hydration have been explored. The objectives of existing and potential applications of reactive distillation are to surpass equilibrium limitation, achieve high selectivity towards a desired product, achieve energy integration and perform difficult separations. Apart from its application as a multifuctional reactor, reactive distillation can be looked upon as an efficient separator for the recovery or purification of chemicals.

2.2.1 Reactive distillation configurations

A conventional configuration for a chemical process usually involves two steps of chemical reaction and subsequent separation. In the chemical reaction step, reactants are brought into contact with solid catalysts at appropriate process conditions in one or more reactors. The stream leaving the reactor section then goes to one or more separation steps where unconverted reactants are separated from the reaction products and the inerts. The unconverted reactants, in some cases, may be recycled to the reaction section. When a substantial amount of inerts are present in the system, at least two separation units for separation of high purity product and for separation of the unconverted reactants from the inerts are required. The separation process by distillation is typically chosen.

A conventional process configuration is shown in Figure 2.1 where a distillation is used for separation. In the case, a reaction product is less volatile than reactants and inert. The flow diagram of the application of reactive distillation to this process is shown in Figure 2.2. The middle section of the column is the reactive section. For a non-azeotropic chemical system, separation of the inerts takes place in

the rectifying section and the purification of the product takes place in the stripping section.
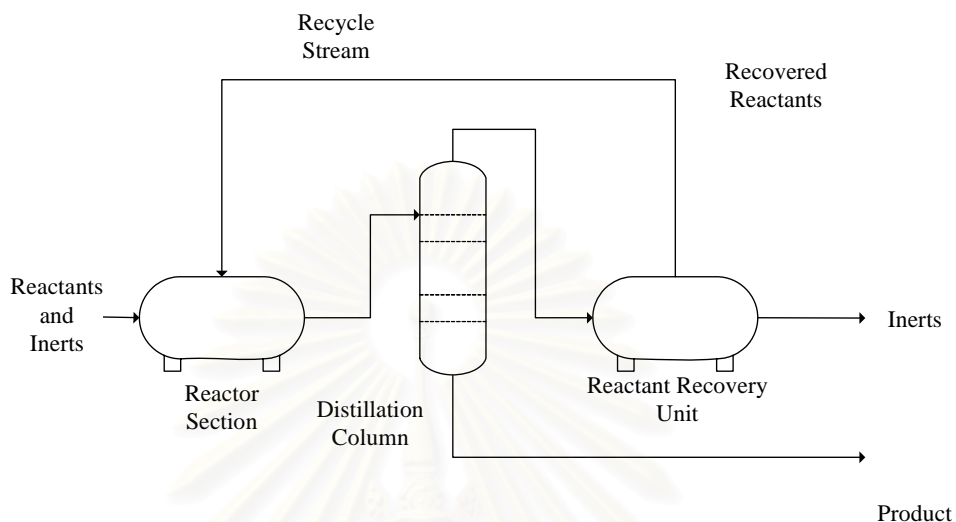
Figure 2.1 Conventional process involving reaction followed by separation.

The reactive distillation column contains both the catalyst contact device and the distillation device. A reaction occurs in the catalyst contact device and then the reacting phase passes to the distillation device for vapor/liquid contact and separation. These two steps occur alternately. By making the steps of infinitely small size, this configuration becomes equivalent to the first one. For both configurations, a rectification section may be located above the reactive distillation section of the column and a stripping section may be located below it, depending upon purity specifications.
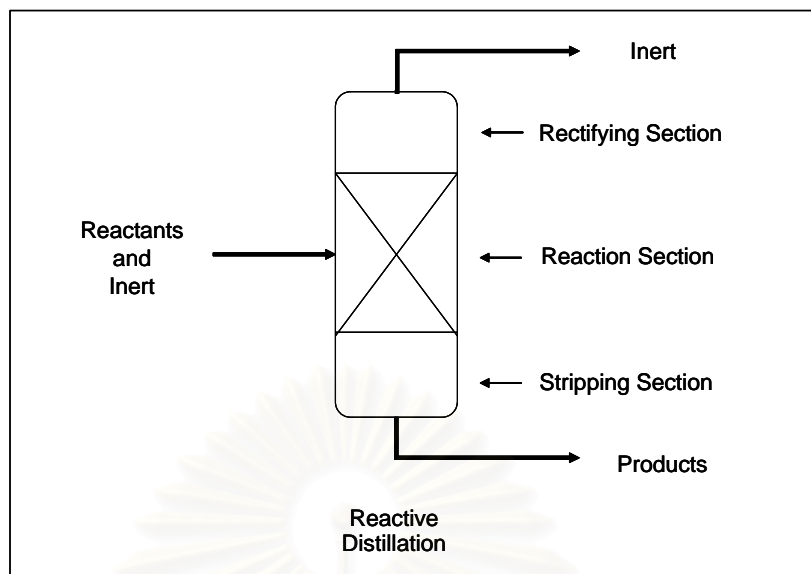
Figure 2.2 Application of reactive distillation for low volatility product process.

2.2.2 Advantages of reactive distillation

Application of reactive distillation to a catalytic chemical reaction using solid catalysts offers many advantages compared to a conventional process as summarized below:

- Two process steps, i.e. separation and reaction, can be carried out in the same device. Such integration leads to lower costs in pumps, piping and instrument.

- The heat released from the reaction can be used for vaporization of liquid, leading to savings of energy costs by the reduction of reboiler duties.

- The maximum temperature in the reaction zone is limited to the boiling point of the reaction mixture, therefore the danger of hot spot formation on the catalyst is reduced significantly. A simple and reliable temperature control can be achieved.

- Product selectivity can be improved due to a fast removal of reactants or products from the reaction zone. By this, the probability of consecutive reactions, which may occur in the sequential operation mode, is lowered.

• If the reaction zone in the reactive distillation column is placed above the feed point, poisoning of the catalyst can be avoided. This leads to longer catalyst lifetime compared to conventional systems.

2.3 Pervaporation process

2.3.1 Definition of pervaporation process

Pervaporation is a membrane separation process for separating liquid mixtures. In the process, a liquid feed mixture is in contact with one side of a selective dense membrane in a membrane module. A gradient in vapor pressure between the feed and the permeate sides of the membrane is a driving force for the permeation. The permeation leaves the membrane as a vapor and is usually condensed and removed from the system as liquid. Heat necessary for evaporation of the permeate stream has to be transported through the membrane, and this transport of energy is coupled to the transport of mass. The evaporation enthalpy is taken from the sensible heat of the liquid feed mixture, leading to a reduction in the liquid mixture temperature. A schematic diagram of the pervaporation process is shown in Figure 2.3.
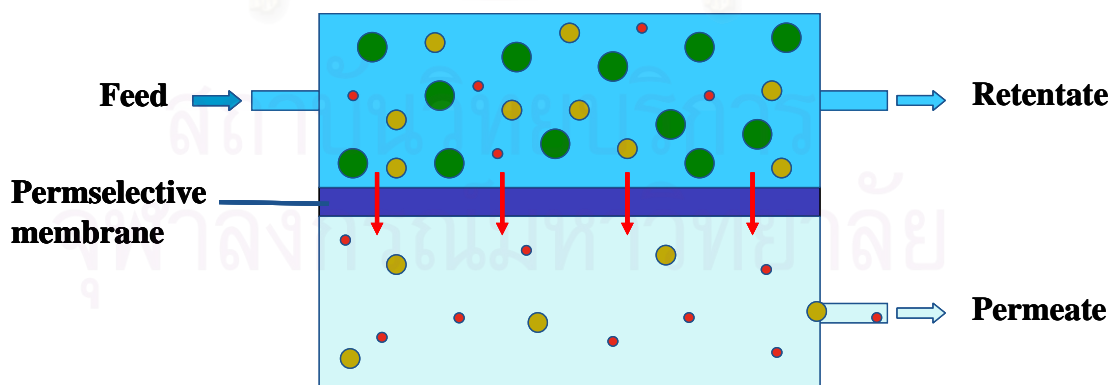
Figure 2.3 Schematic diagram of a pervaporation process.

2.3.2 Definition of membrane

A membrane is a permeable or semi-permeable barrier at the boundary of every cell, often in the form of a thin film deposited on a support. The main function of membrane is to control mass exchanges between two adjacent fluid phases. For this function, the membrane must be able to act as a barrier, which separates different species either by sieving or by controlling their relative rate of transport through itself. Exchange between the two bulk phases across the membrane is caused from the presence of a driving force, which is typically associated with a gradient of pressure, concentration, temperature and electrical potential. Types of membranes used for separation can be classified using different criteria such as by membrane structure (porous and non-porous) and by type of material used to prepare the membrane (organic, polymeric, inorganic, metal, etc.). The ability of a membrane to affect separation of mixtures is determined by two parameters, its permeability, defined as the flux divided by its driving force, and selectivity, defined as the ratio of the individual permeabilities for the two species.

2.3.3 Transport in membrane

Transport of a component through a membrane in the pervaporation process can be described by the solution-diffusion model (Feng *et al*., 1997). The mechanism consists of three consecutive steps (see Figure 2.4) as follows:

1) Sorption of reagent from the liquid feed to the membrane
2) Diffusion of reagent in the membrane and
3) Evaporation or desorption of reagent in vapor phase from the downstream side of the membrane.

In the pervaporation, the components passing through the membrane are sorbed out of a liquid phase but desorbed into a vapor phase.
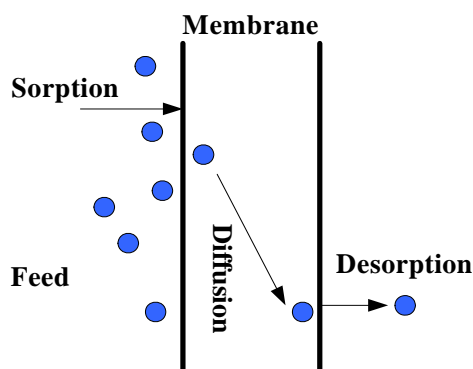
Figure 2.4 Schematic diagram of pervaporation transport by solution-diffusion mechanism.

2.3.4 Applications of membrane pervaporation

The applications of membrane pervaporation process can be defined according to two different membrane classes as follows.

2.3.4.1 Organophilic membrane

Organophilic membranes are mostly applied for removal of volatile organic components (VOC's) from gas stream like waste air or nitrogen. Main applications are treatment of streams originating from evaporation of solvents in coating processes in film and tape production, from purge of products like polymers, from breathing of solvent storage tanks and especially from loading and unloading of gasoline tanks in tank farms.

2.3.4.2 Hydrophilic membrane

The application of hydrophilic membrane pervaporation can be separated in three purposes as:

1. Solvent dehydration: such as the dehydration of alcohols.
2. Removal of water from reaction mixtures.
3. Organic-organic separation.

Pervaporation has been established as a promising membrane technology that is potentially useful in such applications as the dehydration of organic compounds, the removal/recovery of organic compounds from aqueous solutions, and the separation of close-boiling organic mixtures (e.g., structural isomers) and azeotropic mixtures. Polymeric membranes have been traditionally utilized in pervaporation, their respective applications for extraction of water from solutions of ethanol, acetic acid consist of polyamide, poly(acrylic acid), polycarbonate, polysulfonates and poly(vinyl alcohol) etc.

Pervaporation is often applied in combination with another technology as a hybrid process. Of these, pervaporation-distillation and pervaporation-reaction hybrid processes are already finding industrial applications. For pervaporation-membrane-based reactive separations, the membrane either removes the desired product (mostly in biotechnological/wastewater application) or the undesired product (e.g., water for esterification reactions).

2.3.5 Characterization of membranes

2.3.5.1 Permeability and permeation rate

The phase change of the permeating species is one of the most distinguishing features of pervaporation. Based on the solution-diffusion model, the flux equation can be written as (Wijmans and Baker, 1995):

$$J_i = \frac{P_i}{l}(c_{io} - \frac{p_{il}}{H_i}) \qquad (2\text{-}2)$$

where c_{io} is the concentration of components i at the membrane surface and p_{il} is the partial vapor pressure of the permeant at the permeate side and l is the membrane thickness. P_i is the permeability coefficient of the membrane with respect to the driving force expressed in terms of partial vapor pressure and is related to the solubility coefficient (S) and diffusivity coefficient (D).

In the pervaporation process, when the permeate pressure (p_{il}) is kept at low value, the Eq. (2-2) can be expressed as:

$$J_i = \frac{P_i}{l} c_{io} \tag{2-3}$$

and the permeation rate can be expressed as

$$Q_i = P_i A c_i \tag{2-4}$$

where Q_i and c_i are the permeate rate and the concentration of component i, respectively. A is an effective membrane surface area.

The permeability in Eqs. (2-2) to (2-4) are defined as:

$$P_i = D_i S_i \tag{2-5}$$

where D and S are normally dependent on temperature and the temperature dependence can be expressed as Eqs. (2-5) and (2-6), respectively.

$$D_i = D_{i,0} \exp\left(-\frac{E_{a_D}}{R_g T}\right) \tag{2-6}$$

$$S_i = S_{i,0} \exp\left(-\frac{E_{a_S}}{R_g T}\right) \tag{2-7}$$

Thus, the permeability can be written as the following equation.

$$P_i = P_{i,0} \exp\left(-\frac{E_a}{R_g T}\right) \tag{2-8}$$

2.3.5.2 Membrane selectivity

Membrane selectivity of component i is defined as the ratio of the permeability of a desired component to be removed to that of the component i as follow:

$$\alpha_i = \frac{P_d}{P_i} \tag{2-9}$$

where α_i is the separation factor, P_d is the permeability of the desired component to be removed and P_i is the permeability of the component i.

2.4 Aspen Plus program

Aspen Plus program is one of the components in the Aspen Engineering Suite. It is an integrated set of products designed specifically to promote best engineering practices and to optimize and automate the entire innovation and engineering workflow process throughout the plant and across the enterprise. It automatically integrates process models with engineering knowledge databases, investment analyses, production optimization and numerous other business processes. Aspen Plus contains data, properties, unit operation models, built-in defaults, reports and other features. Its capabilities develop for specific industrial applications, such as petroleum simulation.

Aspen Plus is easy to use, powerful, flexible, process engineering tool for the design and steady-state simulation and optimization of process plants. Process simulation with Aspen Plus can predict the behavior of a process using basic engineering relationships such as mass and energy balances, phase and chemical equilibrium, and reaction kinetic. Given reliable thermodynamic data, realistic operating conditions and the rigorous Aspen Plus equipment models, actual plant behavior can be simulated. Aspen Plus can help to design better plants and to increase profitability in existing plants.

2.4.1 Features of Aspen Plus program

Utilize the latest software and engineering technology to maximize engineering productivity through its Microsoft Windows graphical interface and its interactive client-server simulation architecture.

- Contain the engineering power needed to accurately model the wide scope of real-world applications, ranging from petroleum refining to non-ideal chemical systems containing electrolytes and solids.

- Support scalable workflow based upon complexity of the model, from a simple, single user, process unit flowsheet to a large, multi-engineer developed, multi-engineer maintained, plant-wide flowsheet.

- Contain multiple solution techniques, including sequential modular, equation-oriented or a mixture of both, and allow as quick as possible solution times regardless of the application.

2.4.2 Benefits of Aspen Plus program

- Proven track record of providing substantial economic benefits throughout the manufacturing life cycle of a process, from R&D through engineering and into production.

- Allow users to leverage and combine the power of sequential modular and Equation-oriented techniques in a single product, potentially reducing computation times by an order of magnitude while at the same increasing the functionality and suability of the process model.

- Compete effectively in an exacting environment to remain competitive in Process currently industries it is necessary to do more, often with smaller staffs and more complex process.

2.5 Estimating costs

Operating costs are normally simple to estimate. Once we know the flowrate of the raw material streams and the utility flows (fuel, steam, cooling water, power, etc.), we simply multiply the flow by the dollar value of that stream. Care must be taken that the utility values are given on a thermodynamically consistent basis; i.e. fuel and electricity should be more expensive than high pressure steam, which should be more expensive than low pressure steam, etc. After we have determined the stream flows and stream temperature, we can calculate the equipment sizes. Of course, the total processing costs are interested so we must be able to predict the installed equipment costs, rather than the purchased equipment costs.

The total annual cost (TAC) is summation of operating cost and capital cost per year. The total annual cost determined by Douglas (1988) is used to evaluate the appropriateness of a design. The total annual cost is defined as

$$\text{TAC} = \text{operating cost} + \frac{\text{capital cost}}{\text{pay - back period}} \qquad (2\text{-}10)$$

CHAPTER III
LITERATURE REVIEWS

Reactive distillation or catalytic distillation is a process where chemical reaction and distillation are carried out simultaneously in the same vessel. Esterification reactions are important synthesis processes in chemical industry and it is possible that the reactive distillation process will gradually replace the conventional ester production processes. The esterification reaction of acetic acid and alcohol is one of the processes applying reactive distillation technology. *n*-Butyl acetate is one of the most common solvents, used in large quantities in the paint and coating manufacture and other branches of chemical industry. Several researchers have studied the reactive distillation behavior of *n*-butyl acetate esterification.

3.1 Production of *n*-butyl acetate

Leyes and Othmer (1945) and Hatig and Regner (1971) studied the manufacture of butyl acetate by a reactive distillation. However, they could not produce high-purity butyl acetate by using one reactive distillation column, because of lack of sufficient knowledge on the complex phase equilibrium of the system containing water, acetic acid, butanol and butyl acetate.

The traditional acetate production is synthesized by esterification of acetic acid with alcohol in the presence of sulfuric acid or sulfonic acid catalyst as homogeneously catalyzed processes. Esterification of acetic acid with *n*-butanol to produce *n*-butyl acetate is catalyzed by strong acid, sulfuric acid, *p*-toluenesulfonic acid or solid acidic catalysts (Zhicai *et al*., 1998). The production of *n*-butyl acetate has been synthesized by homogeneously catalyzed reaction in different processes (Leyes and Othmer, 1945; Hartig and Regner, 1971), while the heterogeneous catalysis of reaction of *n*-butyl acetate synthesis has been investigated by many authors, indicating that heterogeneously catalyzed reactive distillation offers advantages over the homogeneously catalyzed one.

n-Butyl acetate is commonly synthesized by esterification of acetic acid with *n*-butanol in the presence of strongly acidic catalyst. Therefore, *n*-butyl acetate production by heterogeneously catalyzed reactive distillation is a promising new process which can be conducted either in a batch mode (Venimadhavan *et al*., 1999) or in a continuous mode (Zhicai *et al*., 1998; Hanika *et al*., 1999; Steinigeweg and Gmehling, 2002).

n-Butyl acetate is commonly synthesized by liquid phase reactions of the organic acid with the alcohol, which are catalyzed either homogenously by strong mineral acids, or heterogeneously by acidic ion exchange resins. The conventional process of *n*-butyl acetate from *n*-butanol-acetic acid mixture (49% mol acetic acid) is fed to a pack bed reactor which is packed with strongly acidic ion exchange resin (Hanika *et al*., 1999) before separation of product by distillation.

Blagova *et al*. (2006) investigated side reaction kinetics of the heterogeneously catalyzed esterification of *n*-butanol with acetic acid in an isothermal fixed bed reactor at temperatures between 100 and 120 $^{\circ}$C using three different sulfonation of ion exchange resin catalysts; i.e. Purolite CT 269, Amberlyst 46 and Amberlyst 48. For the fully sulfonated catalysts Purolite CT 269 and Amberlyst 48, side reactions are relatively fast, but almost negligible for the surface-sulfonated catalyst Amberlyst 46. The side reactions occur primarily on the active sites inside the pores of catalysts since the internal diffusion resistance is not so significant for these slow reactions whereas the acetic acid esterification with *n*-butanol takes place mainly on the external surface of catalyst particles since diffusion resistance is significant for this relative fast reaction.

3.2 Application of reactive distillation for *n*-butyl acetate synthesis

Although reactive distillation was proposed in the late 1910s, the first commercial practice started in about 1980s. The integration of reaction and separation process in a single unit improves the conversion of chemical reactants and the selectivity of the desired products, by shifting the chemical equilibrium boundaries, accelerating reactions, reducing by-products, and overcoming azeotropic limitations. The recent utilization of sulfonic acid ion-exchange resin catalysts as well as

heterogeneous catalyst in reactive distillation column, for esterification or etherification, as the replacement for liquid acids (homogeneous catalyst) are gaining importance, less impacts to environment and a dual role of catalyst as well as structure tower packing. Ion-exchange resin catalyst type Amberlyst 15 is successfully applied for *n*-butyl acetate synthesis.

Reactive distillation is an attractive option for the production of many esters and has received much attention in the few last years (Taylor and Krishna, 2000). Hanika *et al*. (1999) experimentally studied butyl acetate synthesis by reactive distillation in a packed column, and computer simulation was also performed to evaluate the experimental data. Steinigeweg and Gmehling (2002) carried out pilot plant experiments using a structured catalytic packing. Both the thermodynamic and the kinetic aspects of the system were investigated. Gangadwala *et al*. (2004) explored various process configurations for the production of butyl acetate in order to eliminate the formation of by-product dibutyl ether, thereby achieving a high purity of the desired product. Liao and Tong (1995) have investigated various aspects of the esterification process for the production of *n*-butyl acetate by catalytic distillation including, for example, catalysts, column packings, esterification kinetics, phase equilibrium of the reaction mixtures, and process development.

Aspen Plus software was used for the simulation of butyl acetate synthesis via reactive distillation. Physicochemical properties such as liquid- and vapor-phase enthalpies as well as phase equilibrium were calculated using the software database. The algorithm of the catalytic distillation process simulation by Aspen Plus and its application has been described in more details. Butyl acetate was synthesized via reactive distillation in both experiment and simulation. The experimental data fitted numerical model very well, so that the equilibrium based model can be used to simulate the process (Hanika, 1999).

Steingeweg and Gmehling (2002) presented the setup of reactive distillation for synthesizing *n*-butyl acetate. The low-boiling reactant is fed above the reactive section of the column. The reactive section consisted of Katapak-S elements filled with Amberlyst 15. For distillate product, the aqueous phase was withdrawn, whereas the organic phase was completely refluxed into the column. It is possible to obtain

high conversions accompanied by high purities of *n*-butyl acetate. In addition, simulations were carried out with the steady state model RADFRAC from the Aspen Plus process simulator. The major design parameters are the column pressure, reboiler duty, feed flow rates, number and location of feed positions, the results indicated that increasing pressure, reboiler duty and number of reactive stage with the increase of conversion. Moreover, for the use of a prereactor is advantageous and the stream leaving the prereactor should be fed into the column directly above the reaction section.

Saha *et al*. (2000) used a 30% acetic acid feed to react with *n*-butanol and *iso*-amyl alcohol for the synthesis of *n*-butyl acetate and *iso*-amyl acetate, respectively in a reactive distillation column with macroporous ion-exchange resin, Indion 130, as a catalyst bed. The effects of variables such as feed flowrate, length of packed section, molar ratio of reactants, location of the feed point and effect of recycle were studied to optimize the reactive distillation column configuration. At higher feed flowrate, the conversion of acetic acid decreased since the residence time of the reactant in the column was lowered. In order to increase the residence time of the reactants in the column, the catalytic section was increased and the length of the non-catalytic rectifying section was also increased. However, no significant change in the conversion of acetic acid was realized with the change in configuration. It was found that with the change in the mode of operation from co-current to counter-current, with 1:2 mole ratio of acetic acid to *n*-butanol, the conversion of acetic acid increased from 32.4 to 52.7%. In a typical configuration, at a 1:2 mole ratio of acetic acid to *n*-butanol, about 58% conversion of acetic acid was achieved.

3.3 Combining reactive distillation with separator for *n*-butyl acetate synthesis

Since the esterification of *n*-butyl acetate generates water as a by-product which can be selectively removed from the system by a separator. The integration of a decanter or pervaporation membrane with a chemical reaction has shown many advantages such as fast separation of the products and high yield for the reaction. In the case of azeotrope reaction mixtures, a simple reactive distillation configuration is not sufficient. Thus decanter or pevaporation membrane is attractive because the decanter is a conventional equipment for separating liquid mixtures of two phases

while the pervaporation does not only depend on the relative volatility of the components but also the qualities of membrane.

Steinigeweg *et al.* (2002) simulated *n*-butyl acetate production by esterification via Aspen Plus simulator. The distillate stream was condensed to two phases and collected in a decanter for removing aqueous phase from the organic phase. Cardona *et al.* (2004) designed a system of reactive distillation for production of *n*-butyl acetate. The part of distillate from the column was refluxed to the column, while another part was fed to the decanter before separating *n*-butyl acetate about 98% purity in the organic phase as the product.

Steinigeweg *et al.* (2004) investigated the hybrid processes by combining a reactive distillation and pervaporation for the production of *n*-butyl acetate by tranesterification of methyl acetate with *n*-butanol. The reaction catalyzed by a strongly acidic Amberlyst 15 ion exchange resin was investigated to find the kinetic parameters for a pseudo homogeneous reaction model. The experimental results were presented in comparison with simulation results.

The concept of using pervaporation to remove by-product species from reaction mixtures was proposed in several pervaporation researches. Among the pervaporation membrane processes, a promising process for separating water/organics or organic/organic mixtures was intensively studied in the past.

For esterification of *n*-butyl acetate, the desired product has the high boiling point, which is the bottom product. The azeotrope of *n*-butanol-water-*n*-butyl acetate, *n*-butanol-water, and *n*-butyl actate-water have similar boiling point. Therefore, *n*-butanol, *n*-butyl acetate and water are main components present in the distillate. The dehydration of water/organic mixtures by pervaporation process with hydrophilic membranes can be used. The removal of water, the product from reaction system would increase the desired product yield.

An alternative approach to reactive distillation for selective removal of certain reaction component is reaction coupled with membrane pervaporation. Pervaporation membrane reactors for esterification reactions have been studied, and the membranes

used are primarily hydrophilic membranes that preferentially permeate water. Especially, poly(vinyl alcohol) based membranes have been used experimentally for removing water from liquid mixture in the synthesis of *n*-butyl acetate from acetic acid and *n*-butanol (Xuehui *et al*., 2001).

Lui *et al*. (2002) studied the modeling of esterification of acetic acid with *n*-butanol in the presence of $Zr(SO_4).4H_2O$ coupled pervaporation. A kinetic model equation was developed for the esterification of acetic acid with *n*-butanol catalyzed by $Zr(SO_4)_2.4H_2O$. Water content in the reactor during the reaction was separated by pervaporation. The separation characteristics of the poly(vinyl alcohol)/ceramic composite membrane were studied by separation of the liquid mixtures quaternary mixtures (water/acetic acid/*n*-butanol/butyl acetate). This research compare between esterification reaction with and without pervaporation in batch reactor. Experiments were conducted to investigate the effects of several operating parameters, such as reaction temperature, initial molar ratio of acetic acid to *n*-butanol, ratio of the membrane area to the reacting mixture volume and catalyst concentration on the pervaporation membrane reactor. The experimental results indicated that the permeation parameter for water is also varied with temperature and it was increased with the increase of temperature. However, concerning the initial molar ratio, water production rate is decreased with the increase of initial molar ratio and, consequently, the rate of water removal was decreased. Water production rate was the same at various ratio of the membrane area to the reacting mixture volume but the rate of water removal was reduced with the decrease of ratio of the membrane area to the reacting mixture volume. Water production rate was increased with the increase of catalyst concentration, resulting in the increase in water permeation flux.

Lui *et al.* (2005) studied the separation of *n*-butyl acetate, *n*-butanol, and acetic acid from dilute aqueous solutions by pervaporation using an organophilic poly(ether block amide) membrane, which is a thermoplastic biphasic elastomer comprising of 80 wt.% poly(tetramethylene oxide) and 20 wt.% nylon 12, its organophilic properties and excellent permselectivity to esters. For binary *n*-butyl acetate-water, *n*-butanol-water and acetic acid-water were tested to determine the membrane permselectivity at various feed concentrations. The membrane preferentially permeates the organic compounds over water. Moreover, pervaporation

of quaternary *n*-butyl acetate-*n*-butanol-acetic acid-water mixture was investigated for the removal of organic compounds from dilute aqueous solutions containing organic compound. After phase separation of permeate stream, the organic phase can be recycled to the reactive distillation column. Nevertheless, this membrane was not very effective for acetic acid removal from water in the separation of quaternary mixtures. The order of the permeation flux in quaternary system was n-butyl acetate > n-butanol > acetic acid > water.

In part of dilute acetic acid pretreatment, to increase the value of dilute acetic acid stream from by-product of several industries, azeotropic distillation is used for separation water at high acetic acid concentrations (Huang, 1988; Ray, 1998). Hung *et al*. (2006) investigated pretreatment dilute acetic acid by distillation column before feed to reactive distillation for esterification of methyl acetate and amyl acetate. Since distillation column use high energy consumption leading to value of total annual cost is high when compared with direct feed of dilute acetic acid to reactive distillation.

Liu *et al*. (2001) investigated the separation characteristics of the crosslinked poly(vinyl alcohol) membranes. The liquid mixtures of both water/acetic acid and water/acetic acid/*n*-butanol/*n*-butyl acetate were considered at a temperature range 60-90 ^{o}C. Isiklan *et al*. (2005) studied the pervaporation of acetic acid/water mixture using poly(vinyl alcohol) (PVA) membranes modified using malic acid (MA). The effects of PVA/MA ratio, membrane thickness, operating temperature, a feed concentration on the permeation rate and separation factor were investigated. As the MA content of the membrane increased, cross-linking density increased. Therefore, separation factors increased with MA content. Increase in feed temperature increased the permeation rate. When the membrane thickness increased, the permeation rate decreased. Optimum PVA/MA ratio was as achieved at a 85/15 (v/v) ratio for 20 wt% acetic acid mixtures at 40 $^{\circ}$C. Mariduraganavar *et al*. (2005) proposed the use of poly(vinyl alcohol) (PVA) and tetraethylorthosilicate (TEOS) hybrid membranes, The performance of these membranes was explained on the basis of a reduction of free-volume and decreased hydrophilic character owing to the formation of covalently bonded crosslinks, for pervaporation separation of water/acetic acid mixtures. The pervaporation performance of these membranes for the separation of water/acetic acid mixtures was investigated in terms of feed concentration and the content of TEOS

used as crosslinking agent. The pervaporation separation index data also supported that membrane with a higher degree of crosslinking density showed an excellent pervaporation performance.

Alghezawi *et al*. (2005) investigated the separation of acetic acid–water mixtures using acrylonitrile grafted poly(vinyl alcohol) (PVA-g-AN) membranes and studied the permeation characteristics of PVA-g-AN membranes as a function of membrane thickness, temperature, feed composition and pressure. The pervaporation separation of acetic acid/water mixtures was performed over a range of 10–90 wt% acetic acid in the feed at temperatures ranging 25–50 ^{o}C. The permeation rate of water increased whereas permeation rate of acetic acid decreased as the water content of the feed increased. Increasing the temperature increased the permeation rate and the downstream pressure increased permeation rate increased whereas separation factor decreased. Li *et al*. (2004) studied pervaporation process of acetic/water with carbon molecular sieve (CMS)-filled polydimethylsiloxane (PDMS) membranes. The effects of feed temperature, feed acetic acid concentration and CMS content on the performance of the membranes were varied. At a CMS content of 20 wt%, both permeation flux and separation factor reached maximum values. As the feed temperature was increased, selectivity decreased and permeate flux increased, because flux of water increased faster than that of acetic acid with temperature. With the increasing in feed concentration, flux and selectivity simultaneously increased.

Moreover, the pervaporation systems of water from water–acetic acid mixtures through prepared poly(vinyl alcohol) membranes by crosslinking with gluteraldehyde (Yeom *et al*., 1996), poly(vinyl alcohol)-g-poly(acrylamide) copolymeric membranes (Aminabhavi *et al*., 2002), and tubular ZSM-5 zeolite membranes (Li *et al*., 2003) were investigated.

CHAPTER IV
SIMULATION

This chapter describes simulation methods for the synthesis of *n*-butyl acetate from *n*-butanol and dilute acetic acid via reactive distillation systems. The simulation studies in this work were divided into two scales of reactive distillation systems, i.e., pilot and industrial scales. Various process configurations and operating variables of the reactive distillation systems were investigated in order to find their effects on reaction performances as well as their energy consumption and economic analysis. The computer simulations were carried out using Aspen Plus program.

4.1 Simulation method

The reactive distillation column was simulated by using Aspen Plus program. The steady state RADFRAC model was used for the *n*-butyl acetate production in the reactive distillation columns. The base case of this work was set at the following condition: no pressure drop in the column (1 atm), pressure of feed stream of 1 atm, temperature of feed stream of 25 $^{\circ}$C, the feed position of acetic acid and *n*-butanol at the first and the fifth stage of reaction, respectively, total condenser and Kettle reboiler. The order of column stages was assigned from the top to the bottom of the column, with stage 1 as the condenser and stage *N* as the reboiler. All simulation results were based on the same product specification that the bottom stream contained *n*-butyl acetate with a concentration not less than 98 mol%.

The reversible esterification of *n*-butanol and acetic acid occurred at the reaction section in the reactive distillation. Kinetic rate constants of both the forward and backward reactions were necessary information for simulations. For Aspen Plus program, the kinetic rate constants based on concentration or mole fraction are required. Since this work used the kinetic rate constants of the reaction on Amberlyst 15 catalyst in activity form from the literature (Steinigeweg and Gmehling, 2002), their kinetic rate constants in activity form were converted to the following rate constants in mole fraction form by following the method described in Appendix B.

$$k_{1x} = \exp\left(11.472 - \frac{6986.3}{T}\right) \tag{4-1}$$

$$k_{-1x} = \exp\left(12.482 - \frac{7937.7}{T}\right) \tag{4-2}$$

Because the acetic acid feed is present in a dilute form, it may be beneficial for the reactive distillation when a pretreatment unit is installed to concentrate the dilute acetic acid. With a lower amount of water in the feed, the reactive distillation should perform even more efficiently. For some cases in this study, a distillation column or a membrane pervaporation unit was installed prior to the reactive distillation to purify the feed.

Concerning the pretreatment unit, RADFRAC was used for distillation simulation while a user-defined Fortran subroutine program of pervaporation was included in the Aspen Plus program for the pervaporation simulation (see Appendix D). Permeability of water and acetic acid are necessary information for the mass transfer across the membrane and in the mass balance equations of the pervaporation model in FORTRAN program. Poly(vinyl alcohol) (PVA) was selected as a membrane for pervaporation unit because of PVA is hydrophilic, allowing water to preferentially permeate through the membrane. The permeability of water and acetic acid were calculated from parameters and equations in the literature (Liu *et al*., 2001) (see Appendix C). Their expressions in the Arrhenius form are shown in Eqs. (4-3) and (4-4), respectively.

$$P_{W} = \exp\left(-0.8961 - \frac{770.02}{T}\right) \tag{4-3}$$

$$P_{HOAc} = \exp\left(-3.7077 - \frac{426.69}{T}\right) \tag{4-4}$$

4.2 Configurations of the reactive distillation systems

4.2.1 Pilot scale

According to the previous work (Steinigeweg and Gmehling, 2002), the reactive distillation in a pilot scale unit for n-butyl acetate esterification from concentrate acetic acid and n-butanol contains totally 28 stages (including condenser and reboiler) which consist of 5 rectifying, 15 reactive and 6 stripping stages. This column configuration was used for preliminary simulation study in order to investigate effects of operating variables on performance of the reactive distillation system. Feed flowrate of pure n-butanol and acetic acid was kept at 35 mol/h for single reactive distillation. The reactive distillation columns with and without a decanter (shown in Fig. 4-1) were considered at different values of reboiler heat duty (Q), reflux ratio (L/D) and position of recycle stream. Then, the suitable reactive distillation system was used to find optimal design variables for the operation of the reactive distillation. The important design variables considered here include the number of rectifying, reaction and stripping stages.

(a)   (b)
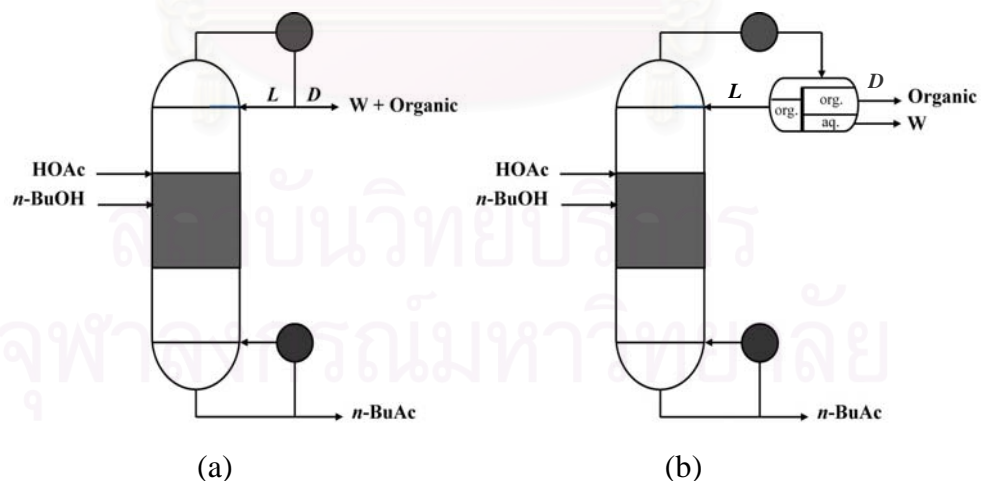
Fig. 4-1 Single reactive distillation system for comparison between (a) only reactive distillation, (b) the reactive distillation equipped with decanter.

The effects of acetic acid concentration (C = 35 and 65 wt%) were studied at different reboiler heat duties for each reactive distillation configuration. Moreover, the systems with the pretreatment unit (distillation column or pervaoration unit as shown in Figs. 4-2 (a), 4-2 (b)) were simulated, using a feed at an acetic acid concentration of 35 wt%. This part was focused on total energy consumption required for each system configuration.
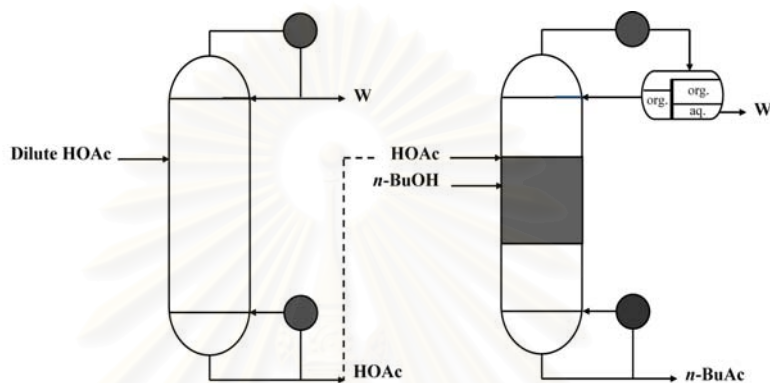
(a) HOAc pretreatment by distillation column followed by reactive distillation.
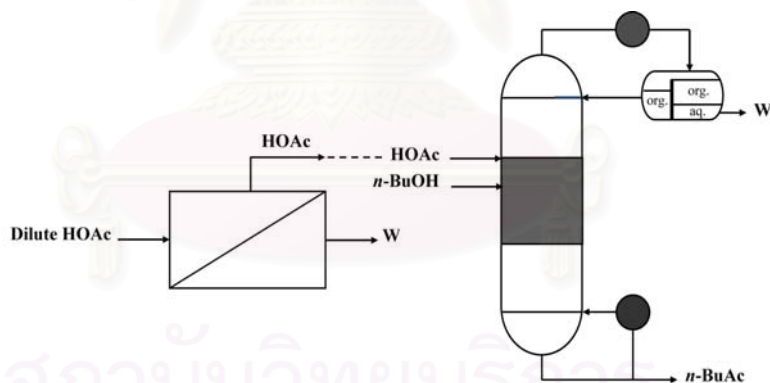
(b) HOAc pretreatment by pervaporation unit followed by reactive distillation

Fig. 4-2 Process of the *n*-butyl acetate production from dilute acetic acid and *n*-butanol.

4.2.2 Industrial scale

The simulations of *n*-butyl acetate in an industrial scale were aimed to determine an optimal configuration of the system by taking into account capital and operating costs. Feed flowrate of the pure *n*-butanol and acetic acid was kept at 50 kmol/h for single reactive distillation. The single-column reactive distillation was investigated to determine effects of design variables such as the number of rectifying, reaction and stripping stages (using the suitable system configuration from the results of the pilot scale study). Acetic acid concentration of 100, 65 and 35 wt% were used to react with *n*-butanol in a single reactive distillation column for design of the column and finding of the minimal cost. A pretreatment unit for the dilute acetic acid feed either by distillation and pervaporation was used for concentrating dilute acetic acid from 35 to 65 wt% before feeding to the reactive distillation. All details of simulations, sizing of equipment and quantity of material in this part were described in Appendix E and total annual cost of the system was calculated from Eq. (2-10).

4.3 Conversion of reactant and yield of product

All system performances were considered in terms of conversion of acetic acid (X_{HOAc}), and yield of *n*-butyl acetate (Y_{BuAc}) defined as follows;

$$X_{AcAc} = \frac{\text{Difference in molar flow rate of inlet and outlet of HOAc} \times 100}{\text{Molar feed flow rate of HOAc}} \quad (4.5)$$

$$Y_{BuAc} = \frac{\text{Molar flow rate of outlet of BuAc} \times 100}{\text{Molar feed flow rate of HOAc}} \quad (4.6)$$

CHAPTER V

RESULTS AND DISCUSSION

5.1 Pilot scale study: energy consumption

5.1.1 The effect of reactive distillation system

In this part, the synthesis of n-butyl acetate from esterification of pure acetic acid (100 wt%) and n-butanol by a reactive distillation is investigated. A single reactive distillation systems with/without a decanter, as shown in Fig. 4-1, is first studied to find whether the decanter should be included in the reactive distillation process. It is noted that the decanter is employed to separate the solution mixture from a column condenser into the aqueous phase and the organic phase. The performance of reactive distillations in terms of the conversion of acetic acid, yield and mole fraction of n-butyl acetate at the bottom is analyzed by varying several operating parameters, i.e., reboiler heat duty, reflux ratio, and the location of reflux stream. It is noted that the reflux ratio is defined as the ratio of molar flow rate of reflux stream (L) and distillate stream (D).

5.1.1.1 Single reactive distillation without decanter

Fig. 5-1 presents the influence of the heat duty on the conversion of acetic acid for different value of the reflux ratio. It can be seen that increasing the reboiler heat duty results in a decrease of the conversion of acetic acid for all value of reflux ratio. As heat duty is increased, more reactants are in the vapor phase and the esterification in the reactive section is decreased. Therefore, less yield and purity of the product, n-butyl acetate, at the bottom are observed as shown in Figs. 5-2 and 5-3. It is noticed that although the conversion of acetic acid is high at any specific value of the reflux ratio and heat duty, the yield of n-butyl acetate at the bottom is very low. This is because some n-butyl acetate product is lost in the distillate stream. This result suggest that the use of a decanter for separating the organic phase which comprises

mostly *n*-butyl acetate from aqueous phase in which water is a major component could be improved the performance of the reactive distillation.
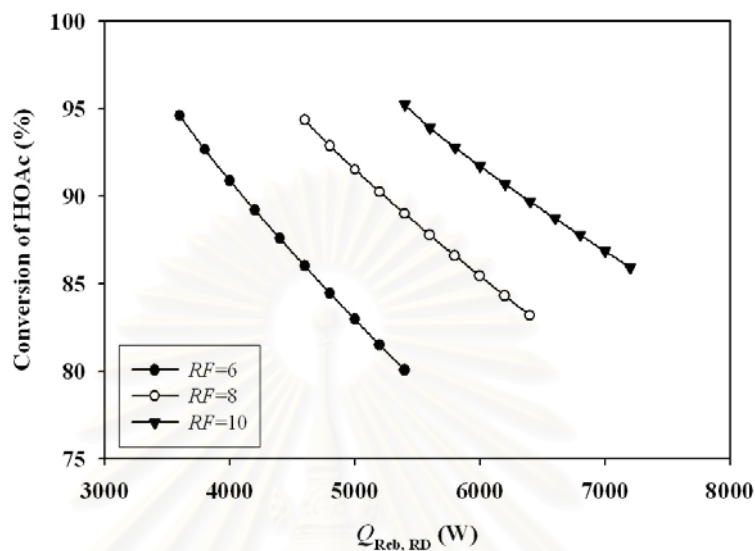
Fig. 5-1 Effect of reboiler heat duty on the conversion of acetic acid at various reflux ratio values (single RD without decanter).
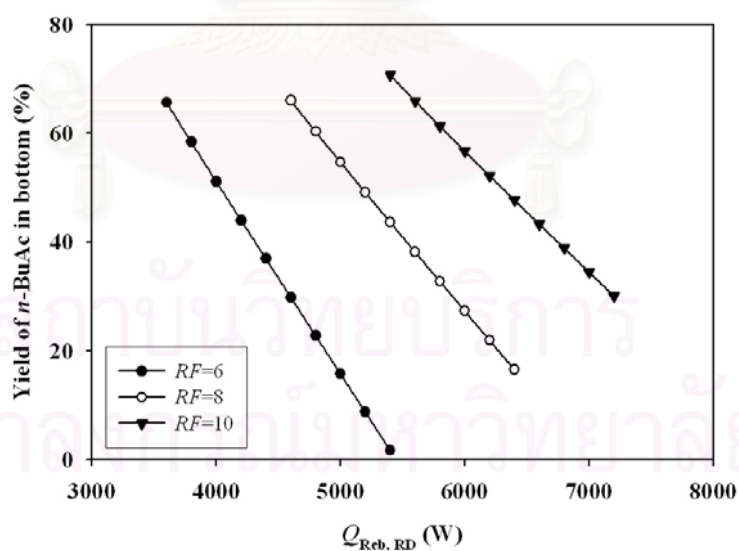
Fig. 5-2 Effect of reboiler heat duty on the yield of *n*-butyl acetate at various reflux ratio values (single RD without decanter).
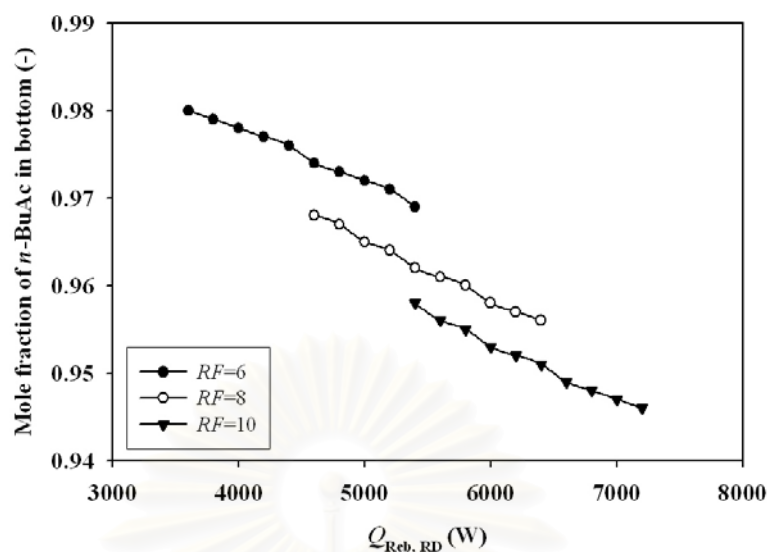
Fig. 5-3 Effect of reboiler heat duty on the mole fraction of *n*-butyl acetate at various reflux ratio values (single RD without decanter).

5.1.1.2 Single reactive distillation with decanter

Since the distillate stream of the reactive distillation consist of organic and aqueous phases, the removal of the aqueous phase consisting mainly of water from the system while recycling only the organic phase in which *n*-butyl acetate, *n*-butanol and acetic acid are main component, to the reactive distillation could enhance the reactive distillation performance. Figs. 5-4 to 5-6 show the effect of the reboiler duty at various reflux ratio values on the conversion of acetic acid, and the yield and mole fraction of *n*-butyl acetate in the bottom, respectively. It can be seen that when the heat duty is less than 1900 W, increasing the heat duty leads to a increase in the conversion of acetic acid, and the yield and mole fraction of *n*-butyl acetate in the bottom. On the other hand, when the heat duty is more than 1900 W, the results show opposite trend; the conversion of acetic acid, and the yield and mole fraction of butyl acetate in the bottom decrease with the reboiler heat duty.

From simulation results, the reactive distillation with decanter consumes less energy, compared to that without decanter since some solution mixture in aqueous phase is separated in the decanter and drawn from the reactive distillation

column as distillate. When comparing the results of the reactive distillation with decanter at various reflux ratio value, it is found that the operation of the reactive distillation with total reflux ratio is the most effective approach for the production of *n*-butyl acetate.
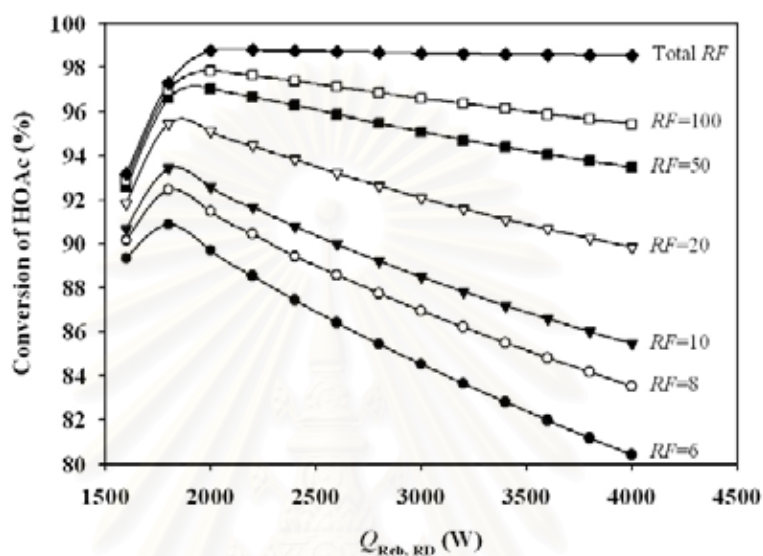
Fig. 5-4 Effect of reboiler heat duty on the conversion of acetic acid at various reflux ratio values (single RD with decanter).
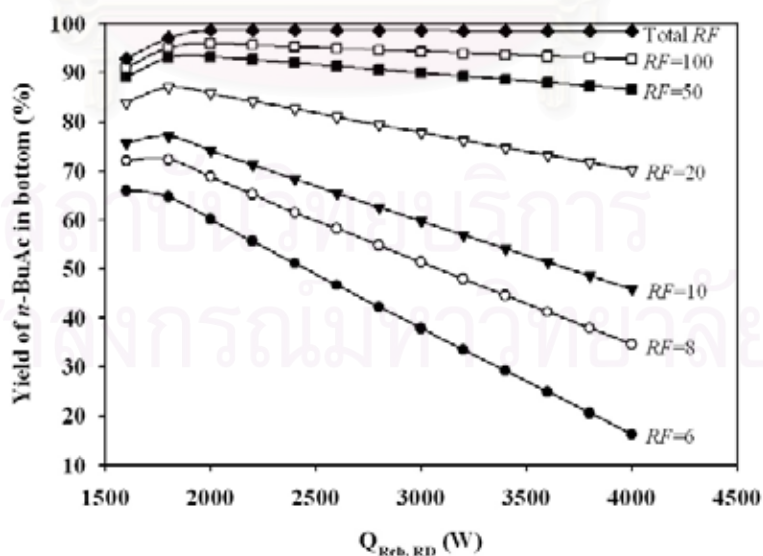
Fig. 5-5 Effect of reboiler heat duty on the yield of *n*-butyl acetate at various reflux ratio values (single RD with decanter).
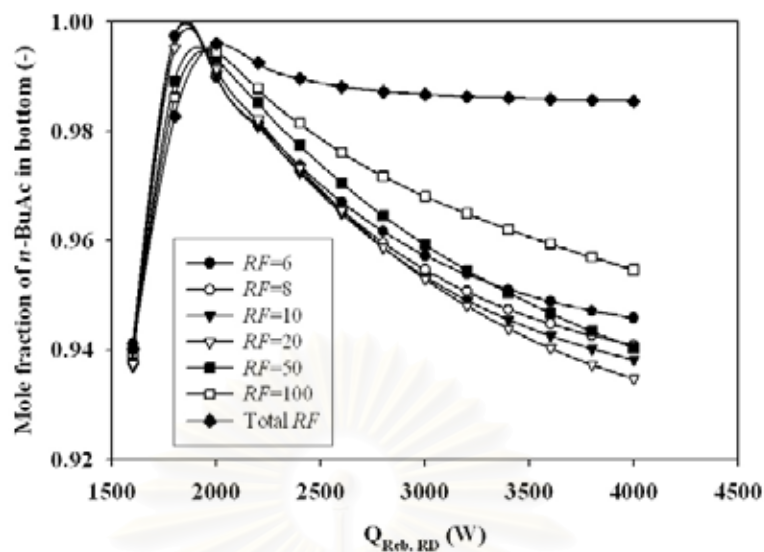
Fig. 5-6 Effect of reboiler heat duty on the mole fraction of *n*-butyl acetate at various reflux ratio values (single RD without decanter).

From previous studies, the production of *n*-butyl acetate in the reactive distillation with decanter which is operated at total reflux ratio is found to be an efficient approach. Next, the effect of the reflux stream location on the performance of reactive distillation is studied. It is assumed that the reflux stream is introduced at the stages 2, 7 and 11. The results in Figs. 5-7 to 5-9 show that the optimal location of reflux stream is at stage 2 because high conversion of acetic acid is expected. With the same heat duty, introducing the reflux stream of organic phase at stages 7 and 11 results in lower conversion.
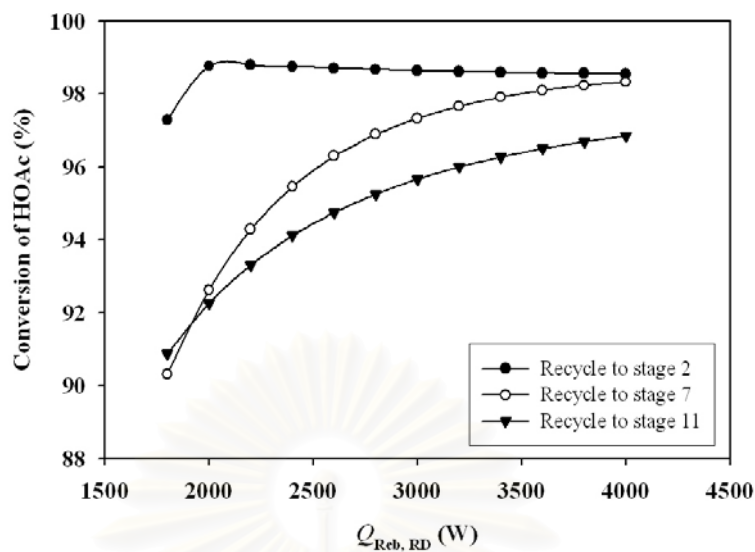
Fig. 5-7 Effect of reboiler heat duty on the conversion of acetic acid at various location of reflux stream (single RD with decanter and total reflux ratio).
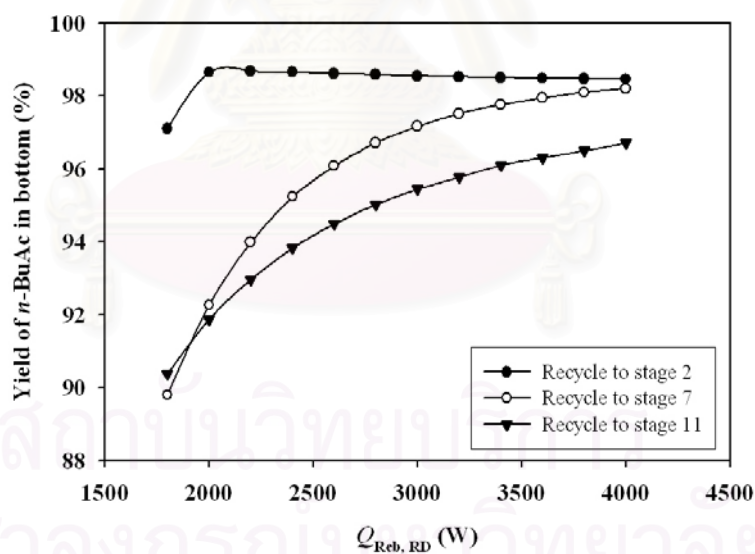
Fig. 5-8 Effect of reboiler heat duty on the yield of *n*-butyl acetate at various location of reflux stream (single RD with decanter and total reflux ratio).
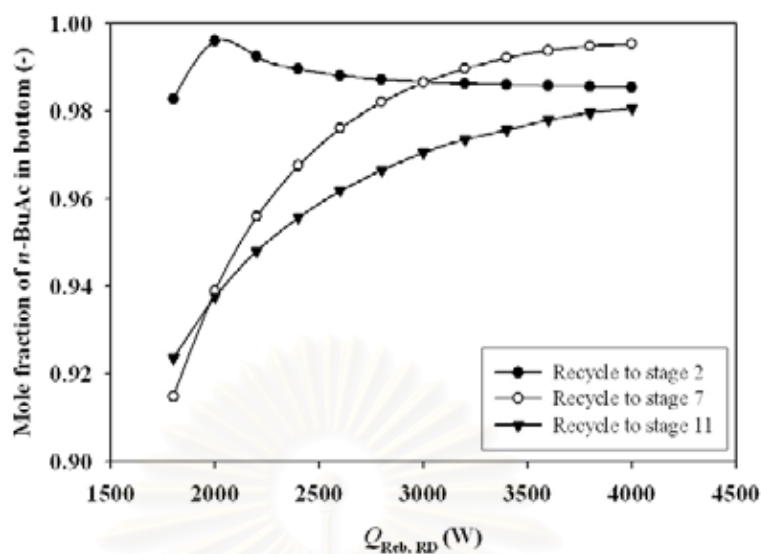
Fig. 5-9 Effect of reboiler heat duty on the mole fraction of *n*-butyl acetate at various location of reflux stream (single RD with decanter and total reflux ratio).

5.1.2 The effect of design variables

A number of stages in rectifying, reaction and stripping section are varied to determine a suitable configuration of the reactive distillation for *n*-butyl acetate production. Esterification of *n*-butyl acetate occurred in reaction zone, while rectifying and stripping supported multi-component distillation. The optimum number of stages should give high conversion of acetic acid and high yield and purity of *n*-butyl acetate.

Firstly, the impact of a number of the stripping stages on the performance of reactive distillation is investigated. With the specified number of the rectifying stages (= 5 stages) as in the standard condition, the number of the stripping stages are varied from 1 to 19 and the results are presented in Fig. 5-10 to 5-12. When the number of stages in the stripping section is increased, more *n*-butanol and acetic acid are separated from the bottom product stream and then returned to the reactive section. This results in an increase in the conversion of acetic acid and the mole fraction of *n*-butyl acetate in the bottom. Fig. 5-10 to 5-12 also show the influence of the number of stages in the reactive section. It can be seen that the performance of the reactive

distillation increased with the increase of the number of reactive stages. This is expected as more reactive stages pronounce the esterification of *n*-butanol and acetic acid. According to the simulation results, the suitable number of stages in the reaction and stripping section is 10 and 7 stages, respectively.
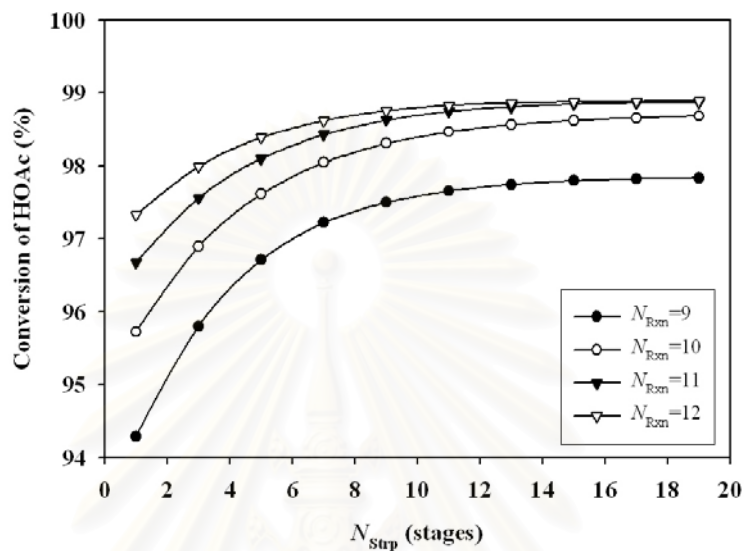
Fig. 5-10 Effect of the number of stripping stages on the conversion of acetic acid for various reaction stages (single RD with decanter and total reflux ratio, rectifying stages = 5).
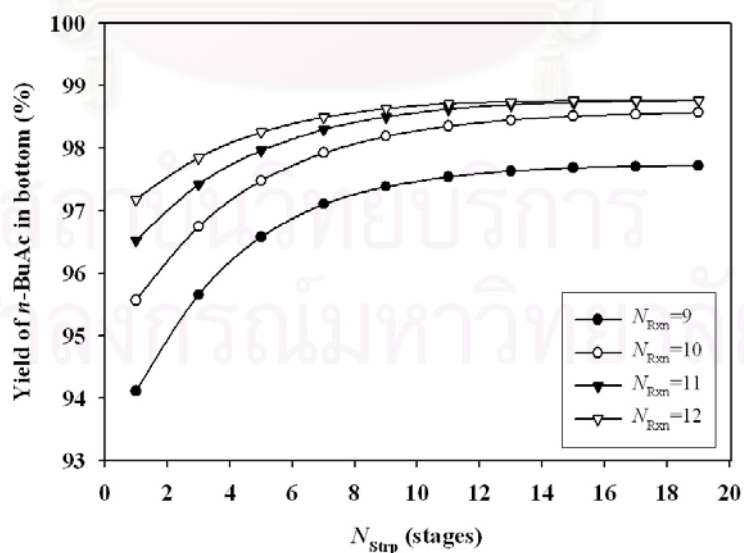
Fig. 5-11 Effect of the number of stripping stages on the yield of *n*-butyl acetate for various reaction stages (single RD with decanter and total reflux ratio, rectifying stages = 5).
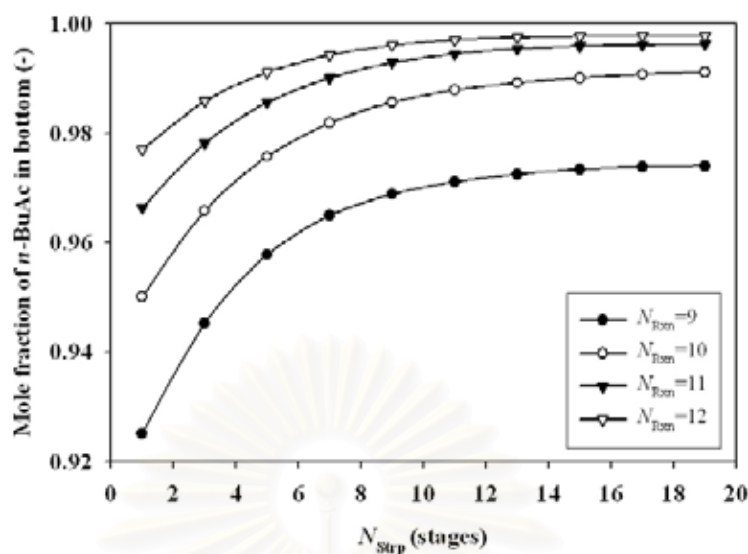
Fig. 5-12 Effect of the number of stripping stages on the mole fraction of *n*-butyl acetate for various reaction stages (single RD with decanter and total reflux ratio, rectifying stages = 5).

Next, the influence of the number of rectifying stages on the performance of reactive distillation is evaluated. It is noted that the number of stripping stages is kept at 7 as a result of the earlier study. According to Fig. 5-13 to 5-15, it is found that the conversion of acetic acid, and the yield and mole fraction of *n*-butyl acetate are increased with the increase of the number of the rectifying stages. Five rectifying stages give a better reactive distillation performance.

From simulation studies, it is found that the optimal configuration for the reactive distillation with a decanter and a total reflux operation policy consists of 5 rectifying, 11 reactive and 7 stripping stages. Figs. 5-16 and 5-17 show the typical composition profile and temperature profile in the reactive distillation with the optimal configuration. It can be seen that the composition of the mixture at the top of the column consists mainly of water, *n*-butyl acetate and *n*-butanol while the bottom products comprise mostly the butyl acetate. It is noted that after the top products are sent to the decanter, they are separated in two phases: organic and aqueous phases. Only the liquid in organic phase is refluxed to the reactive distillation column.
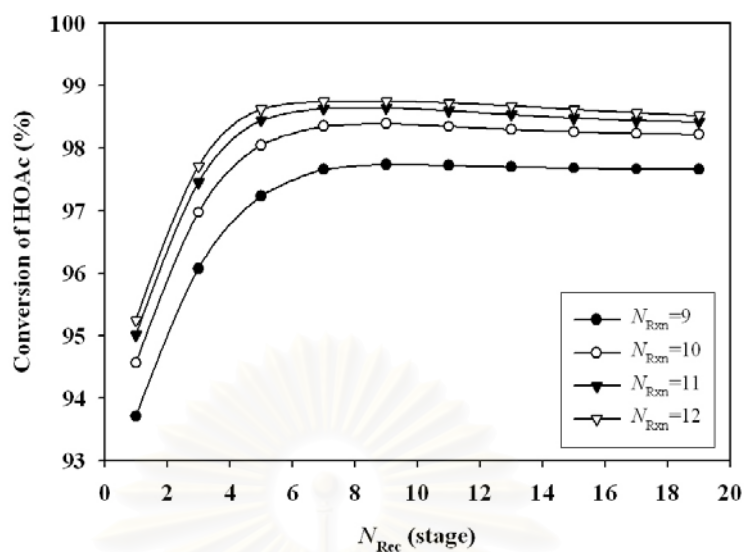
Fig. 5-13 Effect of the number of rectifying stages on the conversion of acetic acid for various reaction stages (single RD with decanter and total reflux ratio, stripping stages = 7).
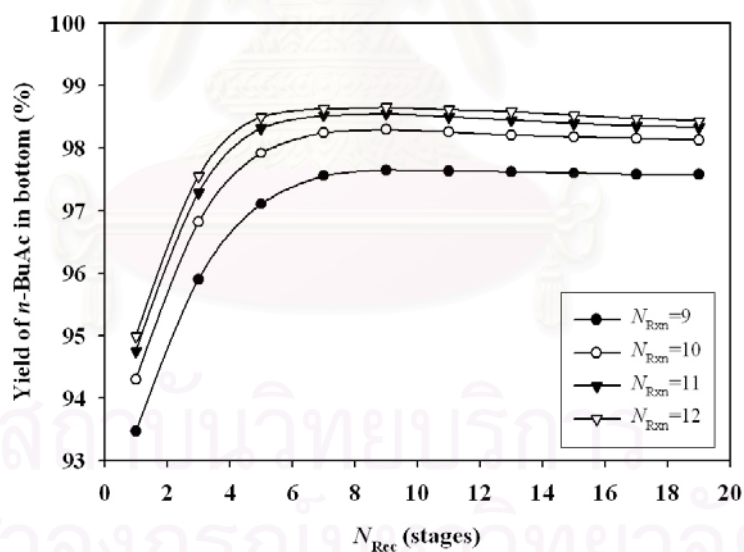
Fig. 5-14 Effect of the number of rectifying stages on the yield of *n*-butyl acetate for various reaction stages (single RD with decanter and total reflux ratio, stripping stages = 7).
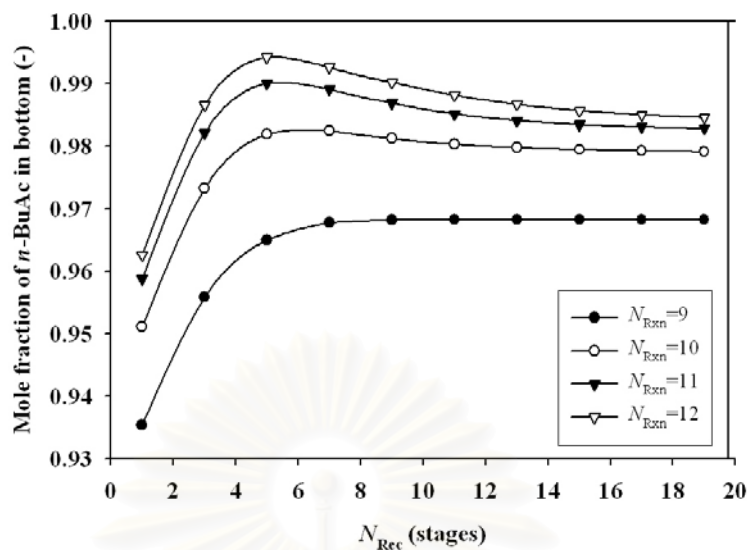
Fig. 5-15 Effect of the number of rectifying stages on the mole fraction of *n*-butyl acetate for various reaction stages (single RD with decanter and total reflux ratio, stripping stages = 7).
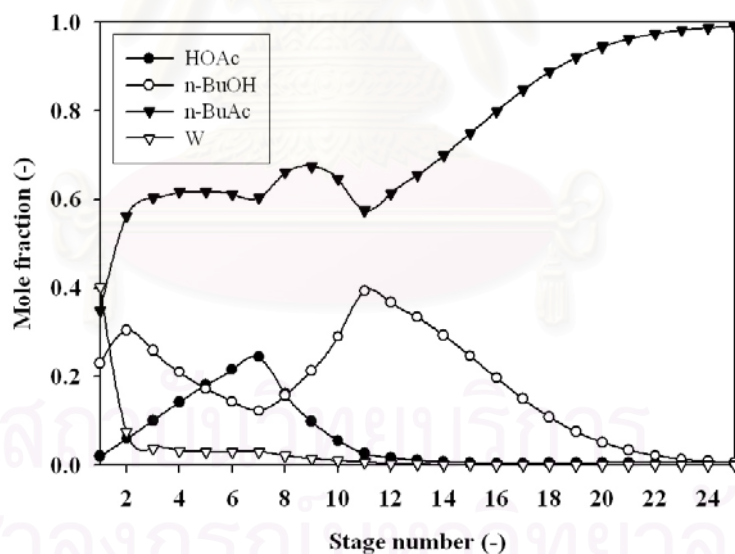
Fig. 5-16 Composition profiles in liquid phase along the reactive distillation column (single RD with decanter and total reflux ratio, reboiler heat duty of 2000 W, rectifying, reaction and stripping stages = 5, 11 and 7, respectively).
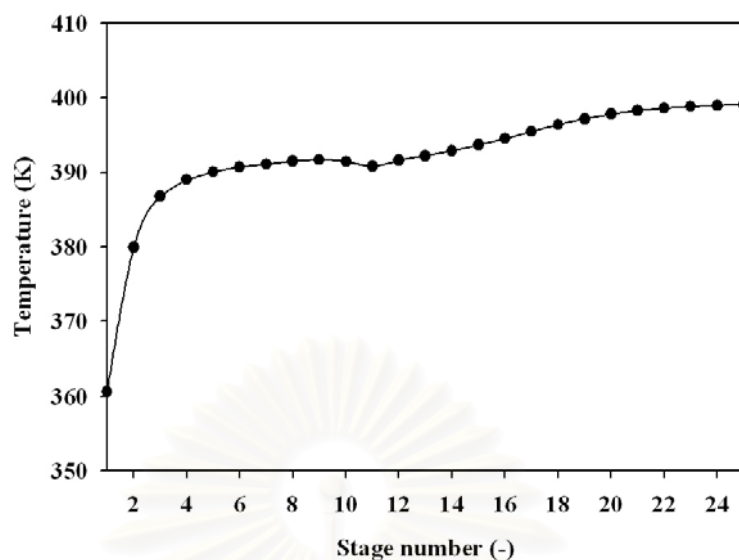
Fig. 5-17 Temperature profile in liquid phase along the reactive distillation column (single RD with decanter and total reflux ratio, reboiler heat duty of 2000 W, rectifying, reaction and stripping stages = 5, 11 and 7, respectively).

5.1.3 The effect of feed acetic acid concentration

In this part, the effect of feed concentration of acetic acid in aqueous solution for *n*-butyl acetate synthesis in the reactive distillation with the optimal configuration as mentioned in Section 5.1.1 and 5.1.3 is investigated. It can be seen from Figs. 5-18 to 5-20 that when the feed acetic acid with low concentration is directly used for esterification in the reactive distillation, more reboiler heat duty is required to obtain the same value of the conversion and yield, compared with using the purity of acetic acid. This can be explained by some of reboiler heat duty required for separating more water from feed stream. Further, it can be observed that by introducing a feed containing 65 wt% of acetic acid and operating at reboiler heat duty of 2000-2200 W, the conversion of acetic acid and the yield and mole fraction of *n*-butyl acetate is similar to those by using the purity of acetic acid. This result shows that the reactive distillation with the optimal configuration designed by the utilization of pure acetic acid can be applied for the production of *n*-butyl acetate from dilute acetic acid of 65 wt%. However, if the feed acetic acid has the concentration less than 65 wt%, it may

require a pretreating unit such as distillations and pervaporations for separating some water from aqueous solution of acetic acid, leading to a higher purity of acetic acid.
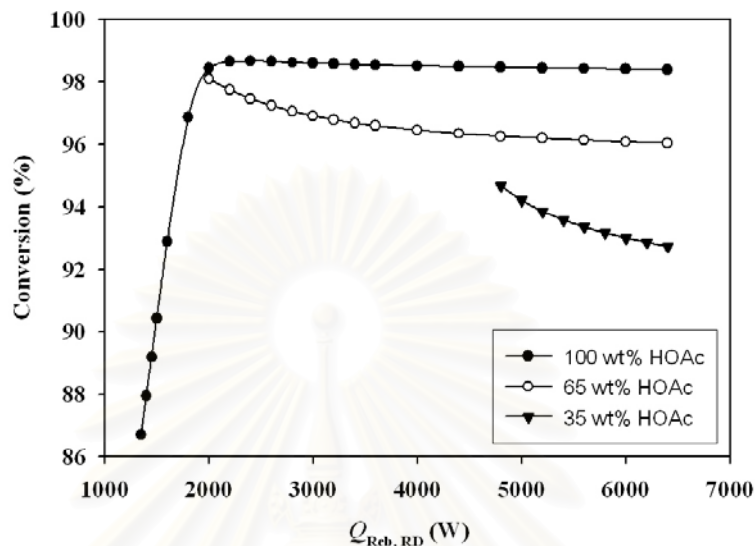
Fig. 5-18 Effect of feed acetic acid concentration on the conversion of acetic acid.
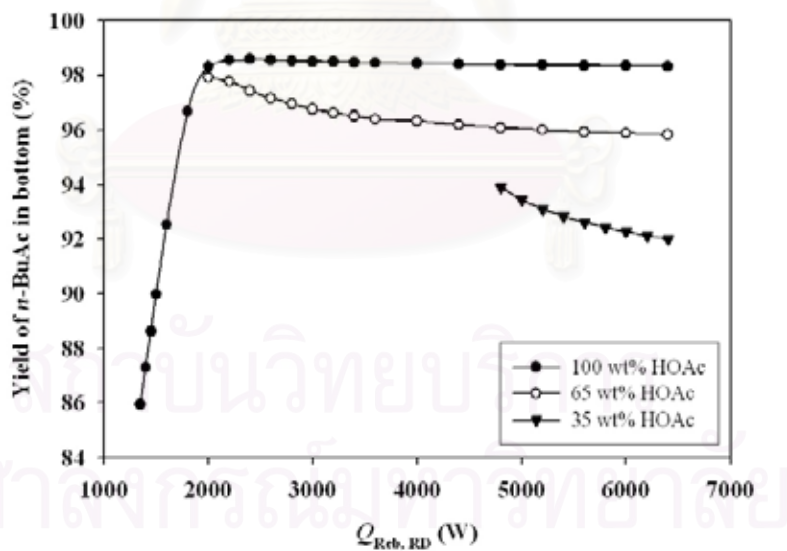
Fig. 5-19 Effect of feed acetic acid concentration on the yield of *n*-butyl acetate.
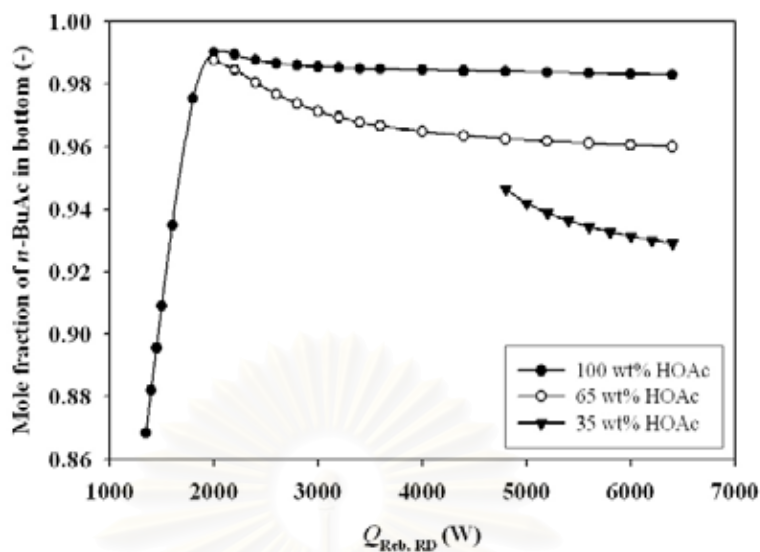
Fig. 5-20 Effect of feed acetic acid concentration on the mole fraction of *n*-butyl acetate.

5.1.4 Model verification

Section 5.1.1-5.1.3 have been investigated about *n*-butyl acetate synthesis in the reactive distillation which was equipped with decanter at the top of the column and recycle all organic phase to stage 2 of the column was the suitable single reactive distillation. In order to kinetic rate constant of *n*-butyl acetate synthesis from *n*-butanol and acetic acid (Steinigeweg and Gmehling, 2002), which was catalyzed by Amberlyst 15 catalyst, was used for simulation in this work. Thus the result from simulation in this research should be compared with the result from experiment of Steinigeweg and Gmehling (2002) to prove that kinetic rate constant can be used for simulation in those systems. Table 5-1 shown that the simulation results in this work were performs similar with experimental data from Steinigeweg and Gmehling (2002).

Table 5-1 Comparision of simulated results and experimental data from Steinigeweg and Gmehling (2002)

Parameters	Steinigeweg and Gmehling (2002) (experiment)	This research (simulation)
Wt% HOAc feed stream	100	100
Feed flowrate (mol/h)		
HOAc	38	35
n-BuOH	36	35
P_1 (mbar)	1,038.45	1,013.25
ΔP (mbar)	20.18	0
N_{Rec}, N_{Rxn}, N_{Strp} (stages)	5, 15, 6	5, 11, 7
Distillate		
$x_{dist, HOAc}$	0.031	0.023
$x_{dist, n\text{-}BuOH}$	0.008	0.010
$x_{dist, n\text{-}BuAc}$	0.003	0.002
$x_{dist, H2O}$	0.958	0.965
Bottom		
$x_{bot, HOAc}$	0.003	0.004
$x_{bot, n\text{-}BuOH}$	0.008	0.016
$x_{bot, n\text{-}BuAc}$	0.969	0.980
$x_{bot, H2O}$	0.020	0.000
Conversion of HOAc (%)	N/A	97.348
Conversion of n-BuOH (%)	98.5	97.344
Bottom flowrate (mol/h)	35.0	34.7
$Q_{reb, RD}$	2,200	1,838

5.1.5 The effect of various system configurations for *n*-butyl acetate production from dilute acetic acid

As mentioned in the previous section, if the dilute acetic acid is employed for the production of *n*-butyl acetate in reactive distillation column, a pretreating unit for increasing the concentration of feed acetic acid is required to improve the reactive distillation performance. In this section, the production of *n*-butyl acetate from dilute acetic acid (35 wt%) by using various system configurations, i.e., a single reactive distillation and a hybrid process consisting of a reactive distillation integrated with a conventional distillation or pervaporation as a pretreating unit is studied.

5.1.5.1 Single Reactive distillation without a pretreating unit

The reactive distillation column is designed for the *n*-butyl acetate synthesis using dilute acetic acid of 35 wt% as reactant. It is found that the suitable column configuration consists of 1 rectifying, 21 reactive and 1 stripping stages for the production of 98 mol% *n*-butyl acetate in bottom product stream. Table 5-1 summarizes the results of applying a single reactive distillation for the production of *n*-butyl acetate from pure acetic acid (100 wt%) and dilute acetic acid (35 and 65 wt%). With the same specification of the purity of *n*-butyl acetate product, the total energy consumption for the operation of the reactive distillation relies mainly on the concentration of acetic acid in feed stream.

5.1.5.2 Reactive distillation with conventional distillation

First, the operating condition of a conventional distillation for removing water from dilute acetic acid of 35 wt% is studied. The aim is to increase the concentration of acetic acid from 35 wt% to 65 wt% that is suitable to be used as a reactant for the reactive distillation. Reboiler heat duty and reflux ratio are varied and the purity and recovery of acetic acid at the bottom stream of the distillation are considered. From Fig. 5-21, it was noticed that to obtain the acetic acid product of 65 wt%, the distillation can be operated at lower reboiler heat duty when the reflux ratio is decreased. In addition, operating at low reboiler duty can take an advantage of obtaining high recovery of acetic acid as can be seen in Fig. 5-22. Table 5-1 show the results when the hybrid distillation-reactive distillation process is applied for the production of *n*-butyl acetate.
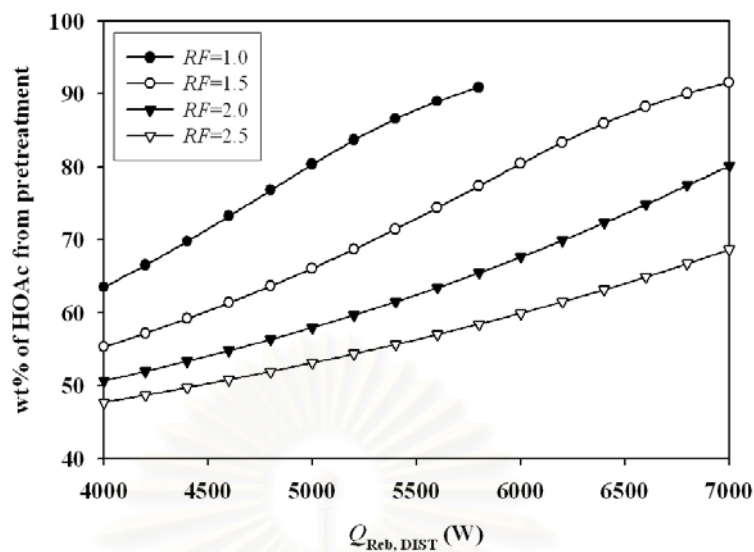
Fig. 5-21 Effects of reboiler heat duty column and reflux ratio of a conventional distillation column on concentration (wt%) of acetic acid product (feed flow rate of acetic acid = 35 mol/hr (35 wt%), feed stage = 4, total stages = 9).
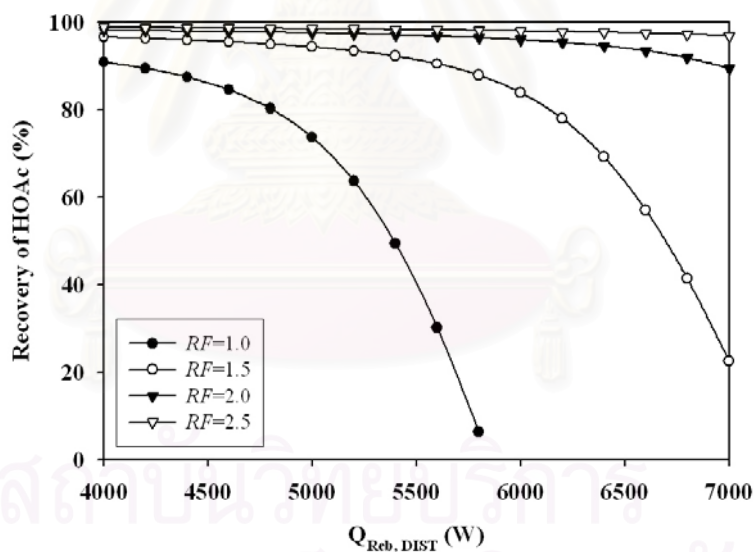
Fig. 5-22 Effects of reboiler heat duty column and reflux ratio of a conventional distillation column on recovery of acetic acid product (feed flow rate of acetic acid = 35 mol/hr (35 wt%), feed stage = 4, total stages = 9).

5.1.5.3 Reactive distillation with pervaporation

The system configuration consisting of a membrane pervaporation as a pretreating unit for dilute acetic acid, followed by a reactive distillation is studied. The isothermal operation of the pervaporation is assumed. The temperature of pervaporation is varied between 30 and 100 ^{o}C so as to investigate its effect on the required membrane area, the recovery of acetic acid, the energy consumption for increasing the concentration of dilute acetic acid from 35 to 65 wt%. The results shows that the required membrane area of pervaporation is decreased with an increase of the operating temperature (Fig. 5-23); increasing the temperature results in the increased permeation, thus reducing the membrane area of pervaporation. It can be observed from Fig. 5-23 that an increase in operating temperature provide more recovery of acetic acid as water can be increasingly separated from aqueous solution of acetic acid. By considering the energy consumption calculated from the energy required for feed stream preheat, pervaporation unit, and power for vacuum pump, the increased operating temperature leads to higher energy consumption as shown in Fig. 5-24. It can also be seen from this figure that the pervaporation unit consumes the highest energy. From the results, the operation of pervaporation at 100 ^{o}C give highest acetic recovery and therefore, this condition is selected for the pervaporation that is used as a pretreating unit of the dilute acetic acid.

Table 5-2 show the results when the hybrid pervaporation-reactive distillation process is applied for the production of *n*-butyl acetate. It is found that when dilute acid acid (35 wt%) is used for the production of *n*-butyl acetate, a hybrid process of pervaporation and reactive distillation seems to require lower total energy consumption than that of distillation and reactive distillation.
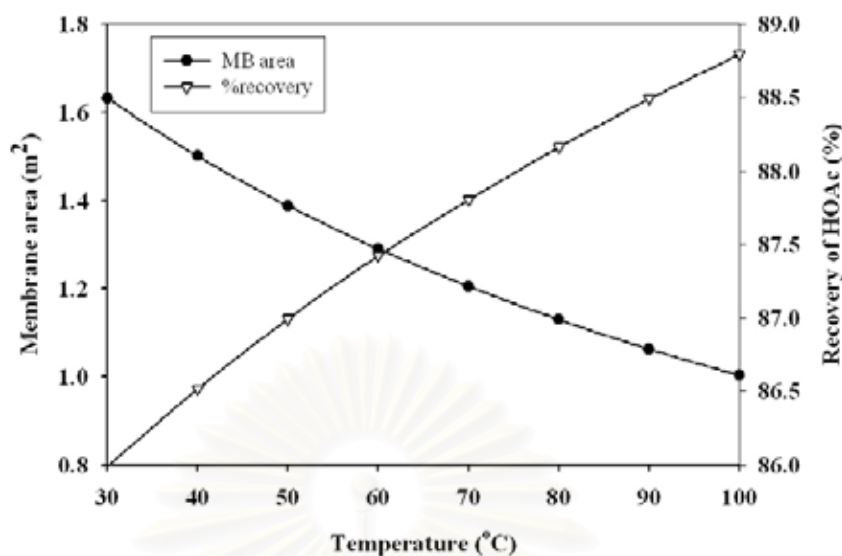
Fig. 5-23 Effects of operating temperature of pervaporation on the required membrane area and the recovery of acetic acid (increasing the dilute acetic acid stream from 35 to 65 wt%, flow rate of feed dilute acetic acid = 35 mol/hr).
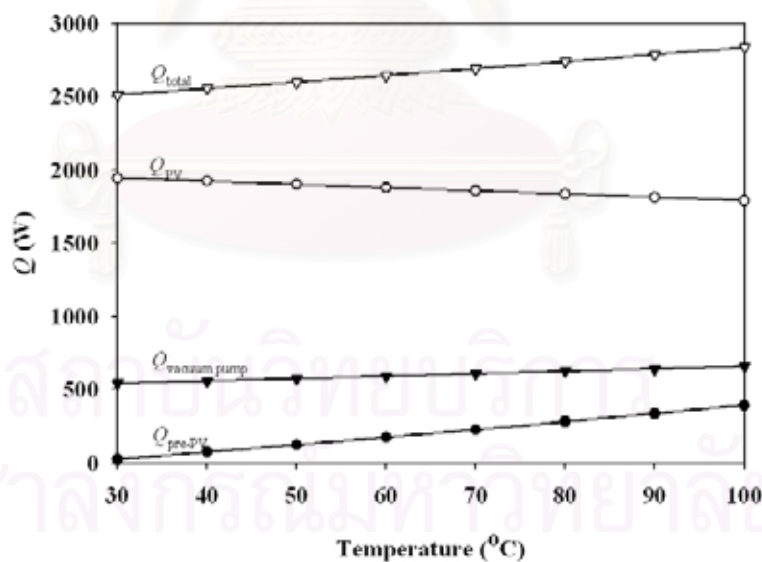
Fig. 5-24 Effects of operating temperature of pervaporation on the energy consumption (increasing the dilute acetic acid stream from 35 to 65 wt%, flow rate of feed dilute acetic acid = 35 mol/hr).

Table 5-2 Summary of the results for *n*-butyl acetate synthesis by difference system configurations.

Parameters	Single column (Only RD)			RD with pretreatment		
				Dist + RD		PV + RD
Wt% HOAc feed stream	100	65	35	35	35	35
Feed flowrate (mol/hr)						
HOAc	35	35	35	35	35	35
n-BuOH	35	35	35	34.109	31.091	31.061
N_{DIST} (stages)	-	-	-	7	7	-
Feed stage of dilute HOAc for DIST	-	-	-	4	4	-
RF_{DIST}	-	-	-	2.5	1	-
Membrane area (m^2)	-	-	-	-	-	1.002
N_{Rec}, N_{Rxn}, N_{Strp} (stages)	5, 11, 7	5, 11, 7	1, 21, 1	5, 11, 7	5, 11, 7	5, 11, 7
Mole fraction in RD						
Distillate						
$x_{dist, HOAc}$	0.023	0.002	0.004	0.003	0.007	0.005
$x_{dist, n\text{-}BuOH}$	0.010	0.009	0.007	0.008	0.003	0.003
$x_{dist, n\text{-}BuAc}$	0.002	0.001	0.001	0.001	0.001	0.001
$x_{dist, H2O}$	0.965	0.988	0.988	0.989	0.989	0.990
Bottom						
$x_{bot, HOAc}$	0.004	0.019	0.020	0.004	0.005	0.005
$x_{bot, n\text{-}BuOH}$	0.016	0.001	0.000	0.016	0.015	0.011
$x_{bot, n\text{-}BuAc}$	0.980	0.980	0.980	0.980	0.980	0.985
$x_{bot, H2O}$	0.000	0.000	0.000	0.000	0.000	0.000
Conversion of HOAc (%)	97.348	97.452	95.106	96.316	87.426	87.095
Yield of *n*-BuAc (%) at bottom	97.194	97.145	94.261	96.10	87.071	87.034
Energy consumption (W)						
$Q_{cond, D}$	-	-	-	6,181.441	3,783.134	-
$Q_{reb, D}$	-	-	-	6,600.000	4,200.000	-
$Q_{pre\text{-}PV}$	-	-	-	-	-	389.302
Q_{PV}	-	-	-	-	-	1,790.600
$Q_{vacuum\ pump}$	-	-	-	-	-	654.457
$Q_{cond, RD}$	1,767.298	2,225.989	4,326.275	1,994.485	1,503.470	1,546.271
$Q_{reb, RD}$	1,838.000	2,400.000	4,760.000	2,000.000	1,495.000	1,550.000
$Q_{Total\ Energy\ Consumption}$	**3,605.298**	**4,625.989**	**9,086.275**	**16,775.926**	**10,981.604**	**5,930.630**
Energy consumption per 35 mol/hr of *n*-BuAc (W)	**3,709.383**	**4,761.942**	**9,639.485**	**17,456.739**	**12,612.241**	**6,814.153**

5.2 Industrial scale study: determination of optimum system

This section is aimed to find an optimum system for the production of n-butyl acetate from n-butanol and dilute acetic acid by using the total annual costs as a criteria. Three reactive distillation systems of a single column reactive distillation, a distillation-reactive distillation hybrid system and a pervaporation-reactive distillation hybrid system were investigated. In all cases, the reactive distillation column equipped with a decanter with total recycle of organic phase to the column at stage 2 was considered as it was demonstrated in the previous section as the most suitable reactive distillation column. The column sizing was carried out by using the tray sizing mode in Aspen Plus program. The distance between trays was kept at 2 ft. For the other equipments, the sizing methods were described in Appendix E. The calculations were based on the following assumptions: 100% tray efficiency, the solid catalyst occupying 50 vol% of the tray holdup and pay-back period of three years for total annual cost calculation. The product specification was set at a purity of 98 mol% of n-butyl acetate at the bottom of the reactive distillation.

5.2.1 Determination of an optimum single column reactive distillation

As an example, an optimum conventional single column reactive distillation fed by n-butanol and pure (100 wt%) acetic acid was determined. The calculations were carried out for columns with different numbers of rectifying (N_{Rec}), reaction (N_{Rxn}) and stripping (N_{Strp}) stages. For each case, the reboiler heat duty was varied until satisfying the bottom product specification of 98 mol% of n-butyl acetate. Figure 5.25 (a) shows the total annual cost (TAC) at different N_{Rec} and N_{Strp} for the case with $N_{Rxn} = 6$. It is obvious that TAC decreases with the increasing number of stripping stage and then slightly increases at higher values. A similar trend is also observed for the effect of number of rectifying stage. From this case the minimum TAC for $N_{Rxn} = 6$ is observed at $N_{Rec} = 7$ and $N_{Strp} = 11$. Figures 5.25 (b), (c) and (d) show the similar results for $N_{Rxn} = 7$, 8 and 9, respectively. The minimum values of TAC and number of rectifying and stripping stages at different number of reaction stage are plotted in Figure 5.26 (a). It is therefore observed that the optimum single column reactive distillation for the case with pure acetic acid feed is at $N_{Rec} = 8$, $N_{Rxn} = 8$, and $N_{Strp} = 9$ with the value of TAC of 686,845 \$/year. Figures 5.26 (b) and (c) provide the results

for the cases with acetic acid concentrations of 65 and 35 wt%. It should be noted that although the acetic acid concentration is lowered, the total extent of acetic acid fed to the column is based on the same amount and, therefore, the comparisons can be made. Details of the optimum reactive distillation columns for three levels of acetic acid concentrations are summarized in Table 5.2.

(a)

(b)
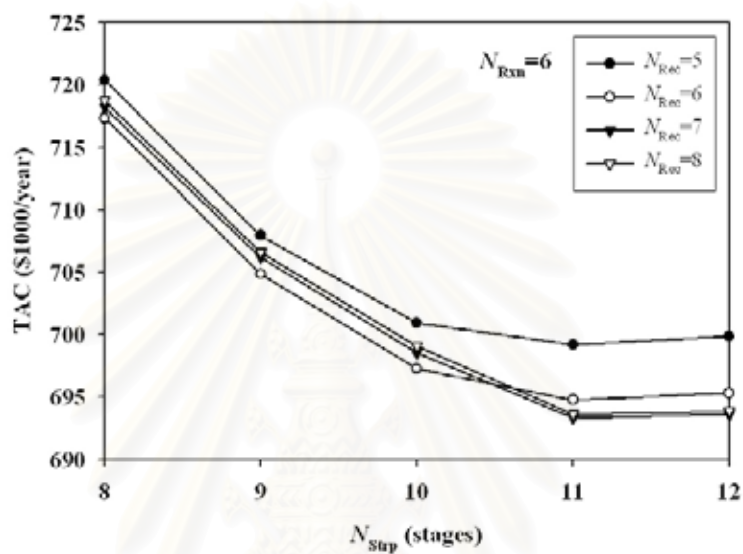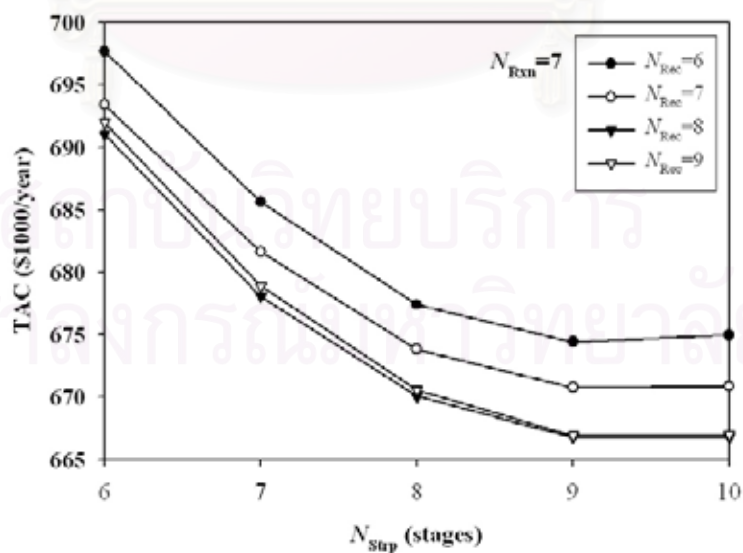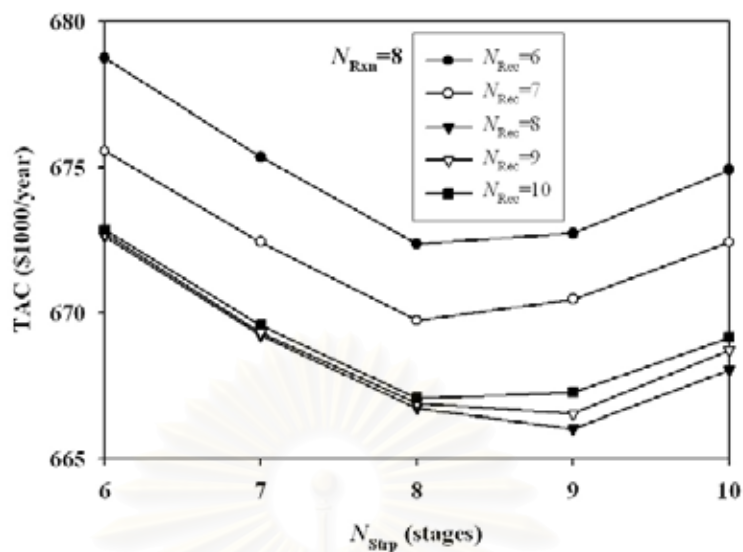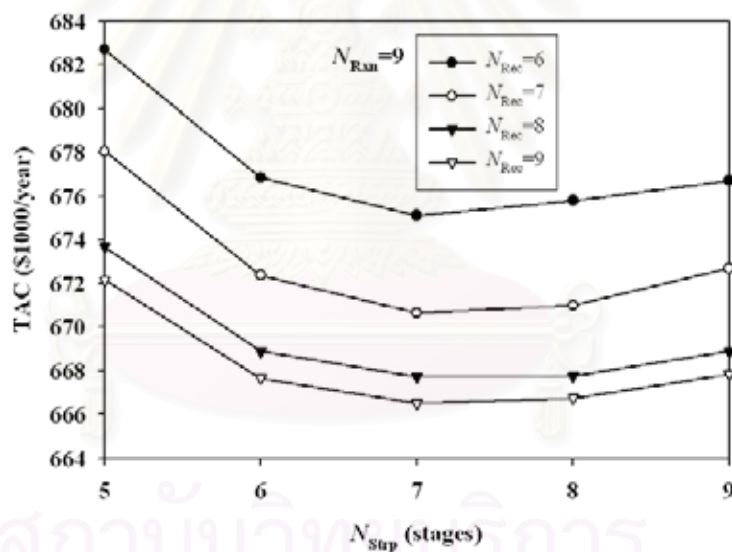
Fig. 5-25 Effect of design stages number of single reactive distillation for *n*-butyl acetate synthesis from concentrate acetic acid and *n*-butanol at various reactive stage number of (a) 6 stages (b) 7 stages (c) 8 stages (d) 9 stages (acetic acid concentration 100 wt%, based on 50 kmol/h HOAc feed).

(a)

(b)

(c)
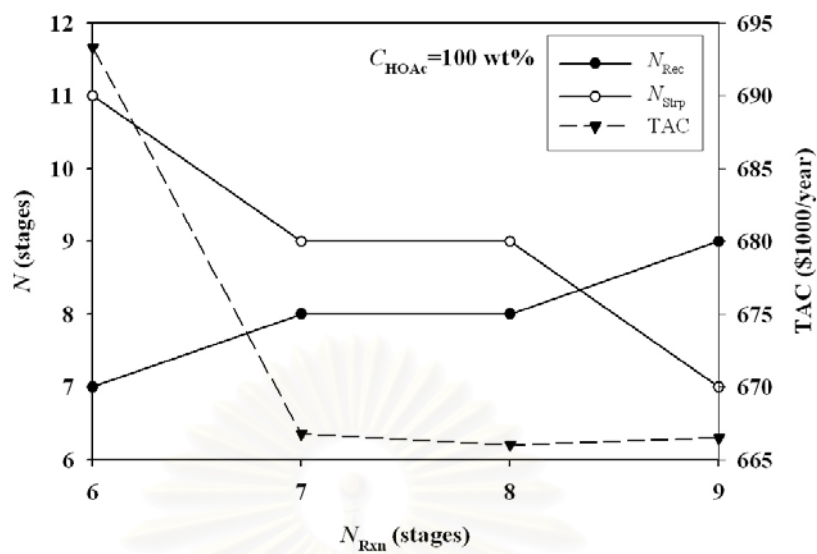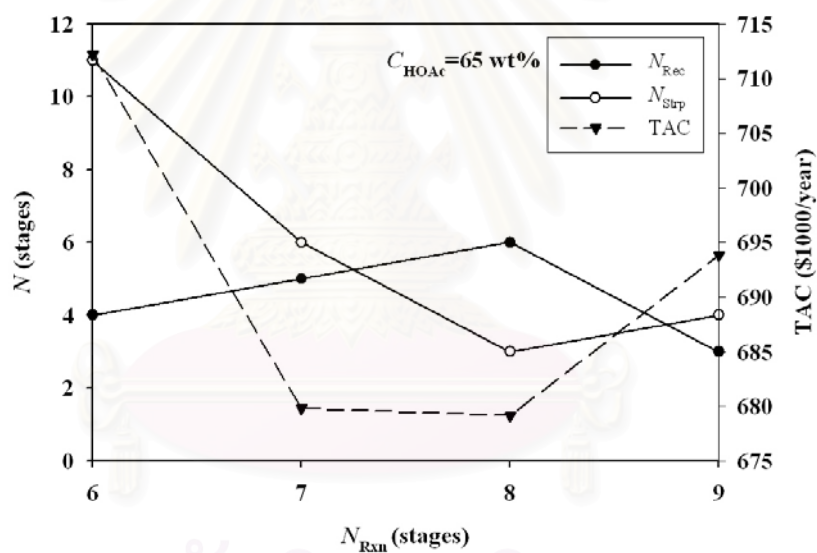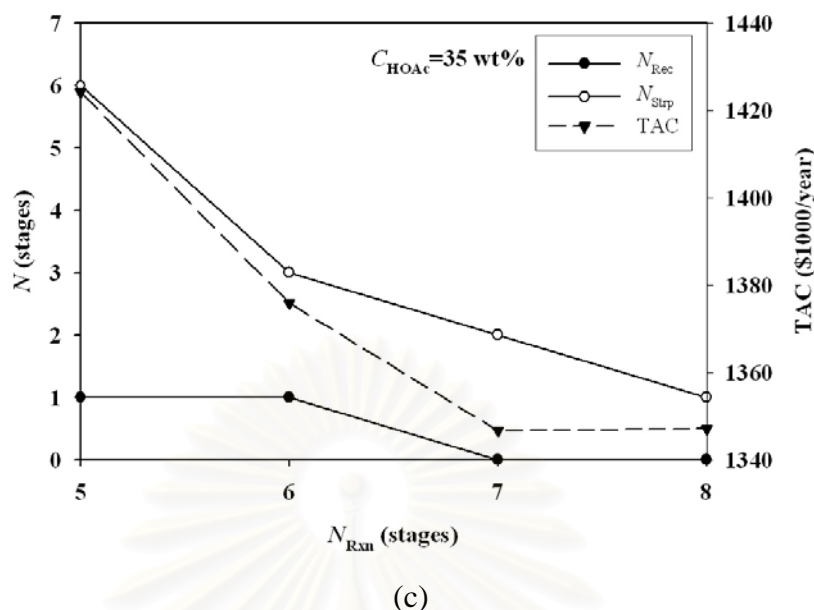
Fig. 5-26 Effect of the number of reactive stages for the design of a single reactive distillation column for *n*-butyl acetate synthesis at acetic acid feed concentration of (a) 100 wt% (b) 65 wt% and (c) 35 wt% (50 kmol/h acetic acid feed).

Due to the presence of more water in the feed at lower acetic acid concentration feed, more energy consumption (condenser and reboiler) and larger column size (column diameter, heat transfer areas and catalyst weight) are required. However, it should be noticed that differences in the energy consumptions, the column diameter and the heat transfer areas required between the cases with pure acetic acid and 65 wt% acetic acid are quite small compared to those of the case with 35 wt% acetic acid. Figure 5.27 indicates that the capital cost, operating cost and TAC follow the order: 35 wt% acetic acid feed > 65 wt% acetic acid feed ≈ 100 wt% acetic acid feed. Similar trend is observed for the equipment and material costs as shown in Figure 5.28. It should be noted that the numbers of rectifying and stripping sections become smaller when the column is fed with acetic acid at lower concentration. This is likely due to the enhancement of phase separation between organic and aqueous phases when more water is present in the system.

Table 5-3 Parameters and results from simulation for *n*-butyl acetate synthesis by difference acetic acid concentration using in single reactive distillation.

Parameters	Single column (Only RD)		
Wt% HOAc feed stream	100	65	35
Feed flowrate (kmol/hr)			
HOAc	50	50	50
n-BuOH	50	50	50
N_{Rec}, N_{Rxn}, N_{Strp} (stages)	8, 8, 9	6, 8, 3	0, 7, 2
Mole fraction in RD			
Distillate			
$x_{dist, HOAc}$	0.028	0.004	0.009
$x_{dist, n\text{-}BuOH}$	0.009	0.003	0.007
$x_{dist, n\text{-}BuAc}$	0.002	0.001	0.001
$x_{dist, H2O}$	0.961	0.992	0.983
Bottom			
$x_{bot, HOAc}$	0.000	0.008	0.002
$x_{bot, n\text{-}BuOH}$	0.020	0.012	0.018
$x_{bot, n\text{-}BuAc}$	0.980	0.980	0.980
$x_{bot, H2O}$	0.000	0.000	0.000
Conversion of HOAc (%)	97.146	96.996	93.228
Yield of *n*-BuAc (%) at bottom	96.968	96.663	92.291
Condenser duty (kW)	2,425.591	2,492.246	5,870.134
Reboiler duty (kW)	2,495.001	2,710.012	6,460.100
Column diameter (m)	1.629	1.695	2.681
Condenser heat-transfer area (m^2)	97.984	121.904	299.461
Reboiler heat-transfer area (m^2)	127.846	137.485	327.732
Catalyst weight (kg)	577.268	625.425	1,368.438
Capital cost ($1000)			
Column	379.961	291.044	284.838
Column trays	33.729	24.405	26.288
Heat exchanger	546.697	596.420	1,057.934
Operating cost ($1000/year)			
Steam	319.986	347.560	828.500
Cooling	8.088	8.310	19.573
Catalyst	17.817	19.304	42.237
TAC ($1000/year) (50 kmol/h of HOAc feed)	666.020	679.130	1,346.663
TAC ($1000/year) (50 kmol/h of *n*-BuAc)	**686.845**	**702.571**	**1,459.157**
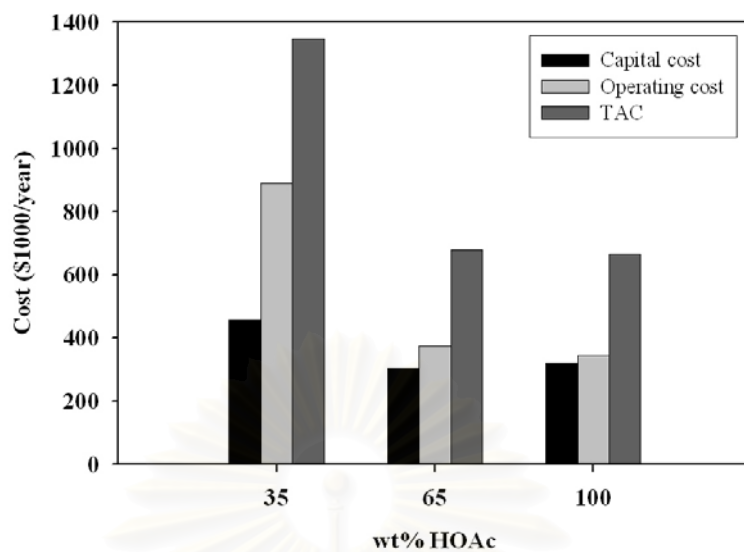
Fig. 5-27 Effect of acetic acid feed concentration on capital and operating cost for single reactive distillation (50 kmol/h acetic acid feed).
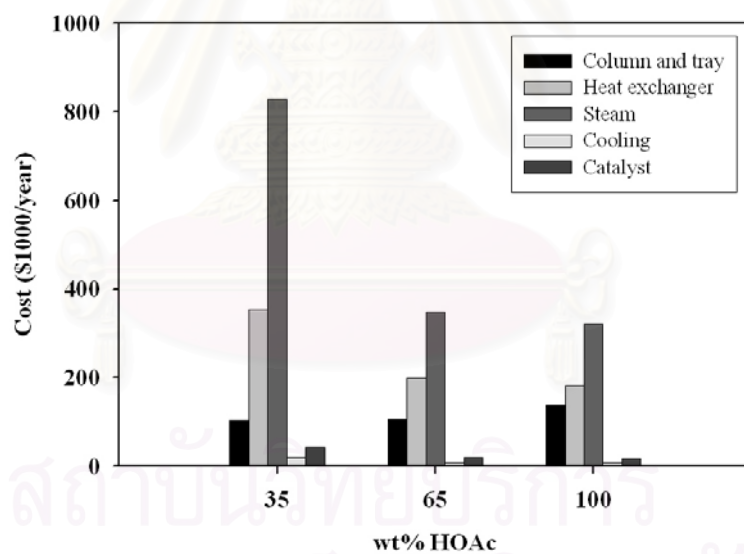
Fig. 5-28 Effect of acetic acid feed concentration on equipments and materials cost for single reactive distillation (50 kmol/h acetic acid feed).

5.2.2 Determination of an optimum reactive distillation system for the *n*-butyl acetate production

It was clearly demonstrated in Section 5.2.1 that the use of a lower acetic acid at 65 wt% does not make a significant difference in term of TAC compared with the case of pure acetic acid feed. Therefore, it is unnecessary to concentrate the dilute acetic acid feed. However, when the acetic acid feed contains a concentration as low as 35 wt%, the TAC increases quite significantly. It is therefore interesting to determine whether the use of hybrid systems by integrating an addition unit to the reactive distillation would be beneficial for the overall system. In this study, two hybrid systems; i.e. distillation-reactive distillation and pervaporation-reactive distillation hybrid systems, are considered. The purpose of using either a distillation or a pervaporation unit is for concentrating the dilute acetic acid feed of 35 wt% to a higher value such as 65 wt% which is considered further in the subsequent studies. It was expected that the use of the hybrid system may help reduce the overall TAC for the production of *n*-butyl acetate.

Considering the distillation-reactive distillation hybrid system, the distillation columns containing different number of distillation stages were simulated to concentrate the dilute acetic acid from 35 wt% to 65 wt% at different values of acid recovery. Figure 5.29 shows that the TAC of the distillation increases with the increase of acetic acid recovery. In addition, by increasing the number of stage, the TAC initially decreases and levels off at higher values. The suitable number of distillation stage is at 12 stages (not including condenser and reboiler). It should be noted that the energy consumptions involved in the distillation are obviously dependent on the level of acid recovery as shown in Figure 5.30 that more energy is required to recover more acetic acid which results in higher TAC. The TAC of the distillation-reactive distillation hybrid system is determined at different value of acid recovery. As shown in Figure 5.31, the TAC of the hybrid system slightly increases as the acid recovery increases.
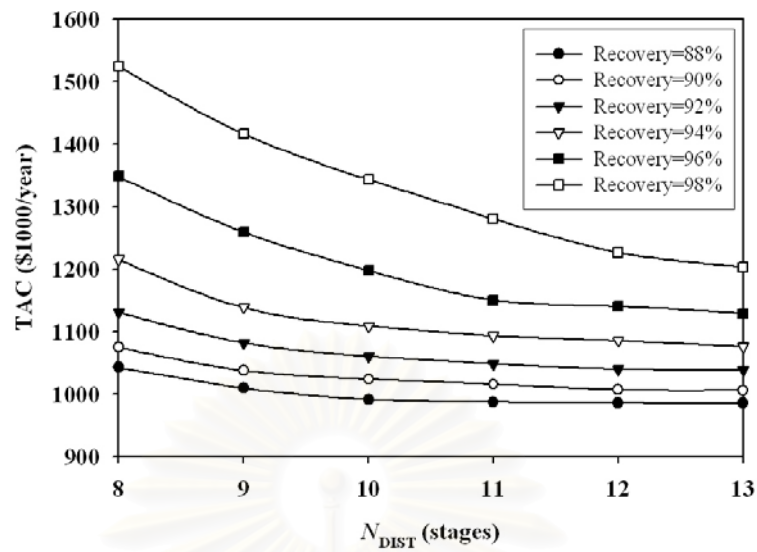
Fig. 5-29 Effect of distillation stage number on total annual cost for pretreatment dilute acetic acid from 35 to 65 wt% (50 kmol/h acetic acid feed).
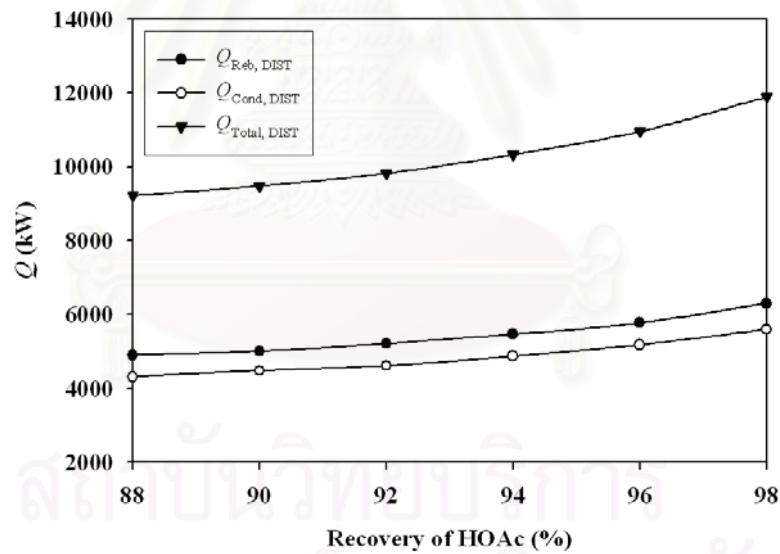
Fig. 5-30 Effect of acetic acid recovery on energy consumption for pretreatment dilute acetic acid from 35 to 65 wt% by distillation column (50 kmol/h acetic acid feed).
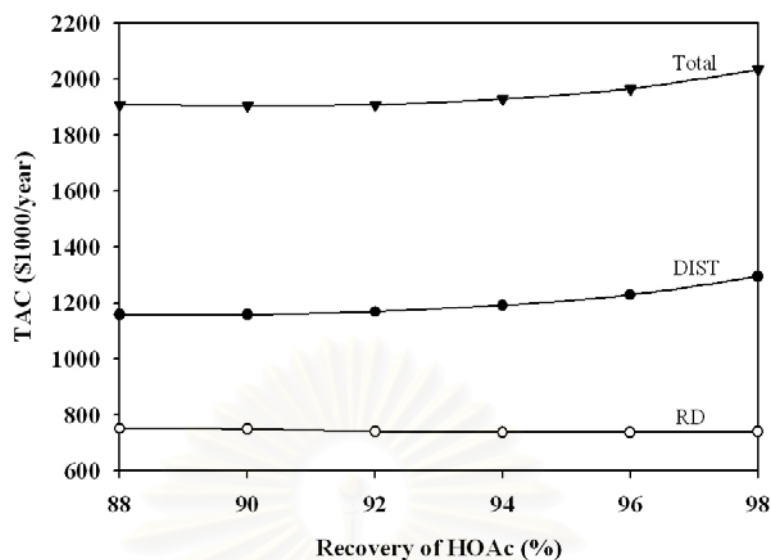
Fig. 5-31 Effect of acetic acid recovery on total annual cost for pretreatment dilute acetic acid from 35 to 65 wt% by distillation column followed by reactive distillation (based on 50 kmol/h *n*-butyl acetate production).

For the pervaporation-reactive distillation hybrid system, the pervaporation unit was used to concentrate the acetic acid from 35 wt% to 65 wt%. The operating temperature was varied between 30 and 100°C. Figure 5.32 shows the required membrane area and the acetic acid recovery at different operating temperature. It is obvious that the requirement of membrane area is smaller when the pervaporation is operated at higher temperature due to the increased permeability at higher temperature. However, the corresponding acetic acid recovery increases due to the more selectivity of the membrane at high temperatures. Therefore, to achieve a high degree of acetic acid recovery, the pervaporation should be operated at a high temperature level unless a better membrane is available; however, the membrane cost would be pronounced. Figure 5.33 provides additional information on the energy consumption for the pervaporation. Comparison with those of the distillation reveals that less energy is required for the pervoparation. Figure 5.34 shows the TAC for the pervaporation-reactive distillation system at different acid recovery. It was found that TAC of the pervaporation is sensitive to the degree of acid recovery unlike the reactive distillation.
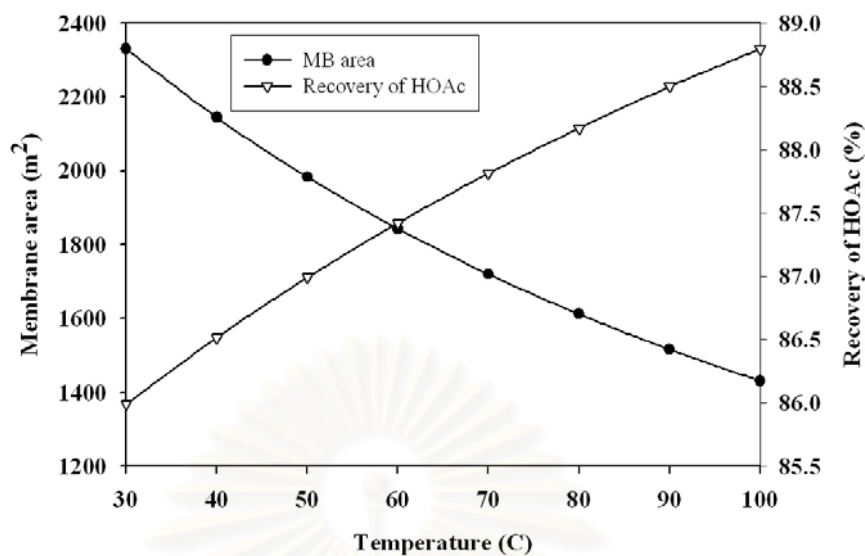
Fig. 5-32 Effects of temperature of pervaporation unit on membrane area and recovery of acetic acid (in retentate stream) for pretreatment of dilute acetic acid from 35 to 65 wt% by pervaporation (50 kmol/h acetic acid feed).
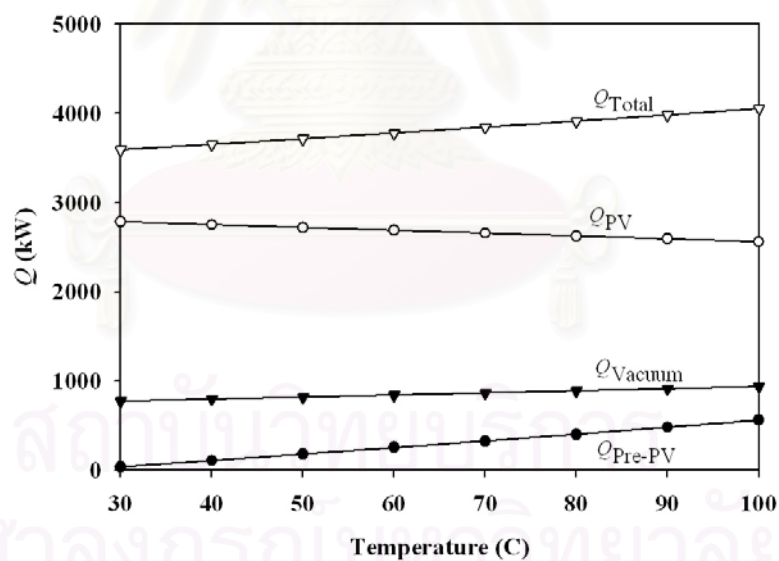
Fig. 5-33 Effects of temperature of pervaporation unit on energy consumption for pretreatment of dilute acetic acid from 35 to 65 wt% by pervaporation (50 kmol/h acetic acid feed).
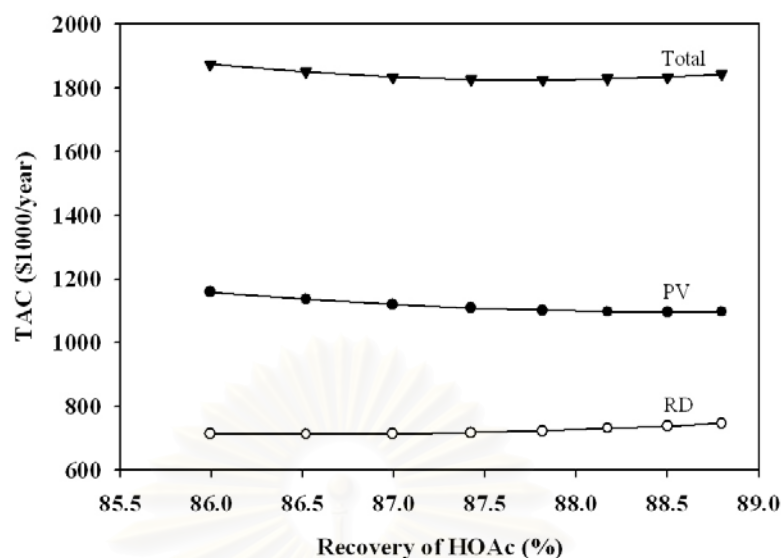
Fig. 5-34 Effects of acetic acid recovery on total annual cost for pretreatment dilute acetic acid from 35 to 65 wt% by pervaporation (based on 50 kmol/h *n*-butyl acetate production).

Table 5.3 summarizes the details of the optimum single column reactive distillation, distillation-reactive distillation hybrid system and pervaporation-reactive distillation hybrid system which show the minimum TACs. It should be noted that the feed flow rate of *n*-butanol for the hybrid systems are smaller than that of the single column reactive distillation because the reactive distillation is operated using the molar feed ratio of acetic acid: *n*-butanol of 1: 1 and not all acetic acid was recovered by either the distillation or pervaporation to the reactive distillation. It is clear that the single column reactive distillation is the most promising system for the production of *n*-butyl acetate from *n*-butanol and dilute acetic acid as it offers the lowest TAC. This would be even more pronounced if the comparisons were based on the same production rate. Considering the energy requirement, the overall reboiler heat duties are 6460, 7567 and 5384 kW for the single column reactive distillation, the distillation-reactive distillation system and the pervaporation-reactive distillation system, respectively, and the condenser heat duties are 5870, 7035 and 2316 kW, respectively. Obviously, in term of energy requirement, the use of the distillation-reactive distillation is not a good choice because it requires even higher energy consumption than the single column reactive distillation. In contrast, the use of

pervaporation is attractive as it consumes less energy; however, it requires additional energy to operate the vacuum pump (864 kW). Figure 5.35 compares the capital cost, operating cost and TAC between different systems. It indicates that the overall capital and operating costs of the hybrid systems are higher than those of the single column reactive distillation. It is therefore not attractive in term of economic analysis to include the additional unit of distillation or pervaporation in this system.
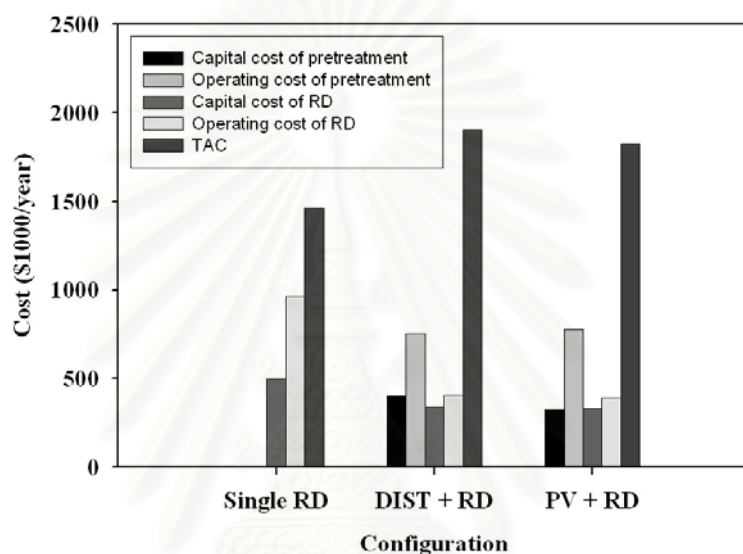
Fig. 5-35 Capital cost, operating cost and total annual cost of difference configurations for using 35 wt% of acetic acid as reactant (based on 50 kmol/h *n*-butyl acetate production).

Table 5-4 Parameters and results from simulation for *n*-butyl acetate synthesis from acetic acid 35 wt% by difference configuration.

Parameter	Single RD	RD with pretreatment	
		Dist + RD	PV + RD
Wt% HOAc feed stream	35	35	35
Feed flowrate (kmol/hr)			
HOAc	50	50	50
n-BuOH	50	44.997	44.907
N_D (stages) (not include Cond and Reb)	-	12	-
RF_D	-	0.70	-
Membrane area (m^2)	-	-	1720
N_{Rec}, N_{Rxn}, N_{Strp} (stages)	0, 7, 2	6, 8, 3	6, 8, 3
Mole fraction in RD			
Distillate			
$x_{dist, HOAc}$	0.009	0.009	0.007
$x_{dist, n\text{-}BuOH}$	0.007	0.004	0.003
$x_{dist, n\text{-}BuAc}$	0.001	0.001	0.001
$x_{dist, H2O}$	0.983	0.986	0.989
Bottom			
$x_{bot, HOAc}$	0.002	0.003	0.004
$x_{bot, n\text{-}BuOH}$	0.018	0.017	0.016
$x_{bot, n\text{-}BuAc}$	0.980	0.980	0.980
$x_{bot, H2O}$	0.000	0.000	0.000
Conversion of HOAc (%)	93.228	87.447	85.674
Yield of *n*-BuAc (%) at bottom	92.291	87.064	85.360
Codenser duty for DIST (kW)	-	4,477.256	-
Reboiler duty for DIST (kW)	-	5,002.085	-
Preheat for PV (kW)	-	-	324.272
Energy for PV (kW)	-	-	2,652.084
Power for vacuum pump (kW)	-	-	864.305
Codenser duty for RD (kW)	5,870.134	2,558.055	2,316.184
Reboiler duty for RD (kW)	6,460.100	2,565.410	2,407.981
Column diameter of DIST (m)	-	1.559	-
Condenser heat-transfer area for DIST (m^2)	-	257.319	-
Reboiler heat-transfer area for DIST (m^2)	-	174.542	-
Heat-transfer area for PV (m^2)	-	-	91.566
Column diameter of RD (m)	2.681	1.643	1.590
Condenser heat-transfer area for RD (m^2)	299.461	119.264	110.590
Reboiler heat-transfer area for RD (m^2)	327.732	130.150	122.163
Catalyst weight (kg)	1,368.438	587.421	550.135

Parameter	Single RD	RD with pretreatment	
		Dist + RD	PV + RD
Capital cost ($1000)			
Column of DIST	-	201.309	-
Column trays of DIST	-	15.130	-
Heat exchanger for DIST	-	834.542	-
Membrane	-	-	737.367
Heat exchanger for PV	-	-	91.566
Column for RD	284.838	281.480	271.811
Column tray for RD	26.288	23.248	22.096
Heat exchanger for RD	1,057.934	580.915	555.438
Operating cost ($1000/year)			
Steam for DIST	-	641.521	-
Cooling for DIST	-	14.929	-
Steam for PV	-	-	381.720
Electricity for PV	-	-	281.764
Steam for RD	828.500	329.016	308.825
Cooling for RD	19.573	8.530	7.723
Catalyst	42.237	18.131	16.980
TAC ($1000/year) (50 kmol/h of HOAc feed)	1,346.663	1,657.667	1,556.663
TAC ($1000/year) (50 kmol of *n*-BuAc)	**1,459.157**	**1,903.968**	**1,823.654**

CHAPTER VI
CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The synthesis of *n*-butyl acetate from *n*-butanol and dilute acetic acid in various reactive distillation systems was simulated by using Aspen Plus program. This research was focused on determining effects of operating variables on performance of reactive distillation and searching for a suitable reactive distillation system by considering total energy consumption and total annual cost of the overall process. Various system configurations were investigated, that includes (i) only reactive distillation without a decanter, (ii) reactive distillation with a decanter, (iii) distillation-reactive distillation hybrid system, and (iv) pervaporation-reactive distillation hybrid system. The installation of either the distillation or pervaporation unit was aimed to concentrate dilute acetic acid from 35 wt% to 65 wt%. The comparisons were based on the same product specification that the bottom product contains *n*-butyle acetate with a concentration not less than 98 mol%. Each configuration was optimized by finding its suitable operating condition. The following conclusions can be drawn from the investigations.

6.1.1 Pilot scale study: energy consumption

Considering the single-column reactive distillations with and without the decanter, the reactive distillation equipped with the decanter at the top of the column for separation of organic and aqueous phases requires lower energy consumption than the one without the decanter for all ranges of the design variables. The refluxed stream of the organic phase is best to be recycled to stage 2 of the column as it gives higher conversion of acetic acid and yield of *n*-butyl acetate at the bottom.

The influences of key design variables on the performance of the reactive distillation were investigated. The results indicate that the optimal design of the column consists of 5 rectifying, 11 reaction, and 7 stripping stages. Under this column

specification, more energy is required when the concentration of acetic acid in the feed becomes lower.

Considering the total energy consumption of n-butyl acetate synthesis from n-butanol and 35 wt% acetic acid in various reactive distillation systems, the process with the pretreatment unit for concentrating dilute acetic acid to 65 wt% by pervaporation requires lowest total energy consumption followed by the single reactive distillation system and the process with the distillation pretreatment unit, respectively.

6.1.2 Industrial scale study: determination of optimum system

An optimum configuration of the reactive distillation system was determined by considering the total annual cost of the system. Preliminary studies were carried out to determine optimum reactive distillation columns, which offer minimum total annual costs, for three cases of different acetic acid feed concentrations (35, 65 and 100 wt%). The total annual cost of the case with 35 wt% of acetic acid is significantly higher than those of the cases with 65 and 100 wt% which show almost in the same value. The suitable system configuration for production of n-butyl acetate by esterification of n-butanol and dilute acetic acid (35 wt%) was investigated by calculating the total annual costs of different reactive distillation systems; i.e. the single-column reactive distillation, distillation-reactive distillation hybrid system and pervaporation-reactive distillation hybrid system. The single-column reactive distillation is the best configuration as it offers the lowest total annual cost. However, the pervaporation-reactive distillation hybrid system becomes the most attractive when considering only the total energy requirement.

6.2 Recommendations

From simulations of *n*-butyl acetate production in this work, it was recommended that some operating parameters such as operating pressure, feed stage location, type of catalyst and kind of membrane should be further taken into account in the studies as these parameters should influence the reactive distillation performance and total annual cost. In addition, because the dilute acetic acid may be present in different concentration ranges other than 35 wt%, more detailed analysis should be carried out. Other system configuration should also be investigated, for example, a reactive distillation with a pervaporation unit for recovering valuable chemicals present in the distillate back to the column.

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APPENDICES

APPENDIX A

UNIFAC METHOD

The basic idea of the UNIFAC (Universal Quasi-Chemical Functional-Group Activity Coefficient) method is that the behavior of a solution is expressible not by the interactions between molecules but by interaction between their functional groups. In other words, the solution is considered to be a mixture of functional group, not of molecules. Nevertheless, it should be understood that all group contribution methods are necessarily approximate because any group within a molecule is not completely independent of the other groups within that molecule. The UNIFAC for estimation of activity coefficient depends on the concept that a liquid mixture may be considered as a solution of the structural units from which the molecules are formed rather than a solution of the molecules themselves. These structural units are called subgroups, and some of them are listed in the second column of Table A.1. A number, designated k, identifies each subgroup. The relative volume R_k and relative surface area Q_k are properties of the subgroups, and values are listed in column 4 and 5 of Table A.1. When it is possible to construct a molecule from more than one set of subgroups, the set containing the least member of different subgroups is the correct set.

The advantages of the UNIFAC method are as follows;
1. Theory is based on UNIQUAC method.
2. Parameters are essentially independent of temperature.
3. Size and binary interaction parameters are available for wide range of types of functional groups.
4. Prediction can be made over a temperature range of 275 to 425 K and for pressure up to a few atmospheres.
5. Extensive comparisons with experimental data are available.

Activity coefficients depend not only on the subgroup properties R_k and Q_k, but also on interactions between subgroups. Here, similar subgroups are assigned to a main group, as shown in the first two columns of Table A.1. The designations of main groups, such as "CH$_2$", "ACH", etc., are descriptive only. All subgroups

belonging to the same main group are considered identical with respect to group interactions. Therefore parameters characterizing group interactions are identified with pairs of main groups. Parameter value a_{mk} for a few such pairs are given in Table A.2.

The UNIFAC method is based on the UNIQUAC equation which treats $g \equiv G^E / RT$ as comprising of two additive parts, a *combinatorial* term g^C to account for molecular size and shape differences, and a *residual* term g^R to account for molecular interactions:

$$g = g^C + g^R \tag{A-1}$$

Function g^C contains pure-species parameters only, whereas function g^R incorporates two binary parameters for each pair of molecules. For a multi-component system,

$$g^C = \sum x_i \ln \frac{\phi_i}{x_i} + 5 \sum q_i x_i \ln \frac{\theta_i}{\phi_i} \tag{A-2}$$

and

$$g^R = -\sum q_i x_i \ln(\sum \theta_j \tau_{ji}) \tag{A-3}$$

where

$$\phi_i = \frac{x_i r_i}{x_j r_{j_i}} \tag{A-4}$$

and

$$\theta_i = \frac{x_i q_i}{x_j q_{j_i}} \tag{A-5}$$

Subscript i identifies species, and j is a dummy index; all summations are over all species. Note that $\tau_{ji} \neq \tau_{i_i}$; however, when $i = j$, then $\tau_{jj} = \tau_{i_i} = 1$. In these equations r_i (a relative molecular volume) and q_i (a relative molecular surface area) are pure-species parameters. The influence of temperature on g enters through the interaction parameters τ_{ji} of Eq. (A-3), which are temperature dependent:

$$\tau_{ji} = \exp \frac{-(u_{ji} - u_{ii})}{RT} \qquad \text{(A-6)}$$

Parameters for the UNIQUAC equation are therefore values of $(u_{ji} - u_{ii})$.

An expression for $\ln \gamma_i$ is applied to the UNIQUAC equation for g [Eqs. (A-1) to (A-3)]. The result is given by the following equations:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \qquad \text{(A-7)}$$

$$\ln \gamma_i^C = 1 - J_i + \ln J_i - 5q_i(1 - \frac{J_i}{L_i} + \ln \frac{J_i}{L_i}) \qquad \text{(A-8)}$$

and

$$\ln \gamma_i^R = q_i(1 - \ln s_i - \sum \theta_j \frac{\tau_{ij}}{s_j}) \qquad \text{(A-9)}$$

where in addition to Eqs. (A-5) and (A-6)

$$J_i = \frac{r_i}{\sum x_j r_j} S \qquad \text{(A-10)}$$

$$L_i = \frac{q_i}{\sum x_j q_j} S \qquad \text{(A-11)}$$

$$s_i = \sum \theta_l \tau_{li} \qquad \text{(A-12)}$$

Again subscript i identifies species, and j and l are dummy indices. All summations are over all species, and $\tau_{ij} = 1$ for $i = j$. Values for the parameters $(u_{ij} - u_{jj})$ are found by regression of binary VLE data.

When applied to a solution of groups, the activity coefficients are calculated by:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \qquad \text{(A-13)}$$

when

$$\ln \gamma_i^C = 1 - J_i + \ln J_i - 5q_i(1 - \frac{J_i}{L_i} + \ln \frac{J_i}{L_i}) \qquad (A-14)$$

and

$$\ln \gamma_i^R = q_i[1 - (\theta_k \frac{\beta_{ik}}{s_k} - e_{ki} \ln \frac{\beta_{ik}}{s_k})] \qquad (A-15)$$

The quantities J_i and L_i are given by:

$$J_i = \frac{r_i}{x_j r_j} \qquad (A-16)$$

$$L_i = \frac{q_i}{x_j q_j} \qquad (A-17)$$

In addition, the following definition of parameters in Eqs. (A-14) and (A-15) apply:

$$r_i = v_k^{(i)} R_k \qquad (A-18)$$

$$q_i = v_k^{(i)} Q_k \qquad (A-19)$$

$$e_{ki} = \frac{v_k^{(i)} Q_k}{q_i} \qquad (A-20)$$

$$\beta_{ik} = e_{mi} \tau_{mk} \qquad (A-21)$$

$$\theta_{ik} = \frac{x_i q_i e_{ki}}{x_j q_j} \qquad (A-22)$$

$$s_k = \theta_m \tau_{mk} \qquad (A-23)$$

$$\tau_{mk} = \exp(\frac{-a_{mk}}{T}) \qquad (A-24)$$

Subscript i identified species, and j is a dummy index running over all species. Subscript k identifies subgroups, and m is a dummy index running over all subgroups. The quantity $v_k^{(i)}$ is the number of subgroups of type k in a molecule of species i. Values of the subgroup parameters R_k and Q_k and of the group interaction parameters, a_{mk} come from tabulation in the literature. Tables A.1 and A.2 show parameter values.

TABLE A.1: UNIFAC-VLE subgroup parameters[†]

Main group	Subgroup	Group name	Rk	Qk
1	1	CH_3	0.9011	0.848
1	2	CH_2	0.6744	0.540
1	3	CH	0.4469	0.228
1	4	C	0.2195	0.000
2	5	$CH_2=CH$	1.3454	1.176
2	6	CH=CH	1.1167	0.867
2	7	$CH_2=C$	1.1173	0.988
2	8	CH=C	0.8886	0.676
2	9	C=C	0.6605	0.485
3	10	ACH	0.5313	0.400
3	11	AC	0.3652	0.120
4	12	$ACCH_3$	1.2663	0.968
4	13	$ACCH_2$	1.0396	0.660
4	14	ACCH	0.8121	0.348
5	15	OH	1.0000	1.200
6	16	CH_3OH	1.4311	1.432
7	17	H2O	0.9200	1.400
8	18	ACOH	0.8952	0.680
9	19	CH_3CO	1.6724	1.488
9	20	CH_2CO	1.4457	1.180
10	21	CHO	0.9980	0.948
11	22	CH_3COO	1.9031	1.728
11	23	CH_2COO	1.6764	1.420
12	24	HCOO	1.2420	1.188
13	25	CH_3O	1.1450	1.088
13	26	CH_2O	0.9183	0.780
13	27	CH-O	0.6908	0.468
13	28	FCH_2O	0.9183	1.100
14	29	CH_3NH_2	1.5959	1.544
14	30	CH_2NH_2	1.3692	1.236
14	31	$CHNH_2$	1.1417	0.924
15	32	CH_3NH	1.4337	1.244
15	33	CH_2NH	1.2070	0.936
15	34	CHNH	0.9795	0.624
16	35	CH_3N	1.1865	0.940
16	36	CH_2N	0.9597	0.632
17	37	$ACNH_2$	1.0600	0.816
18	38	C_5H_5N	2.9993	2.113
18	39	C_5H_4N	2.8332	1.833
18	40	C_5H_3N	2.6670	1.553
19	41	CH_3CN	1.8701	1.724
19	42	CH_2CN	1.6434	1.416
20	43	COOH	1.3013	1.224
20	44	HCOOH	1.5280	1.532
21	45	CH_2Cl	1.4654	1.264
21	46	CHCl	1.2380	0.952
21	47	CCl	1.0060	0.724

TABLE A.2: UNIFAC-VLE Group Interaction Parameters, a_{mk}, in kelvins[†]

a_{mk} / m	k / Name	1 CH₂	2 C=C	3 ACH	4 ACCH₂	5 OH	6 CH₃OH	7 H₂O	8 ACOH	9 CH₂CO	10 CHO	11 CCOO	12 HCOO	13 CH₂O	14 CNH₂	15 CNH₂	16 (C)₃N	17 ACNH₂	18 PYRIDINE	19 CCN	20 COOH
1	CH₂	0	86.02	61.13	76.5	986.5	697.2	1318	1333	476.4	677	232.1	741.4	251.5	391.5	225.7	206.6	920.7	287.7	597	663.5
2	C=C	-35.36	0	38.81	74.15	524.1	787.6	270.6	526.1	182.6	448.8	37.85	449.1	214.5	240.9	163.9	61.11	749.3	0	336.9	318.9
3	ACH	-11.12	3.446	0	167	636.1	637.3	903.8	1329	25.77	347.3	5.994	-92.55	32.14	161.7	122.8	90.49	648.2	-4.449	212.5	537.4
4	ACCH₂	-69.7	-113.6	-146.8	0	803.2	603.2	5695	884.9	-52.1	586.6	5688	115.2	213.1	0	-49.29	23.5	664.2	52.8	6096	603.8
5	OH	156.4	457	89.6	25.82	0	-137.1	353.5	-259.7	84	441.8	101.1	193.1	28.06	83.02	42.7	-323	-52.39	170	6.712	199
6	CH₃OH	16.51	-12.52	-50	-44.5	249.1	0	-181	-101.7	23.39	306.4	-10.72	193.4	-128.6	359.3	266	53.9	489.7	580.5	36.23	-289.5
7	H₂O	300	496.1	362.3	377.6	-229.1	289.6	0	324.5	-195.4	-257.3	72.87	0	540.5	48.89	168	304	-52.29	459	112.6	-14.09
8	ACOH	275.8	217.5	25.34	244.2	-451.6	-265.2	-601.8	0	-356.1	0	-449.4	0	0	0	0	0	119.9	-305.5	0	0
9	CH₂CO	26.76	42.92	140.1	365.8	164.5	108.7	472.5	-133.1	0	-37.36	-213.7	-38.47	-103.6	0	0	-169	6201	165.1	481.7	669.4
10	CHO	505.7	56.3	23.39	106	-404.8	-340.2	232.7	0	128	0	-110.3	11.31	304.1	0	0	0	0	0	0	0
11	CCOO	114.8	132.1	85.84	-170	245.4	249.6	200.8	-36.72	372.2	185.1	0	372.9	-235.7	0	-73.5	0	475.5	0	494.6	660.2
12	HCOO	90.49	-62.55	1967	2347	191.2	155.7	0	0	70.42	35.35	-261.1	0	0	0	0	0	0	0	0	-356.3
13	CH₂O	83.36	26.51	52.13	65.69	237.7	238.4	-314.7	0	191.1	-7.838	461.3	0	0	141.7	0	0	0	0	-18.51	664.6
14	CNH₂	-30.48	1.163	-44.85	0	-164	-481.7	-330.4	0	0	0	0	0	0	63.72	-41.11	-200.7	0	0	0	0
15	CNH₂	65.33	-28.7	-22.31	223	-150	-500.4	-448.2	0	0	0	136	0	-49.3	108.8	0	-189.2	0	0	0	0
16	(C)₃N	-83.98	-25.38	-223.9	109.9	28.6	-406.8	-598.8	0	225.3	0	0	0	0	38.89	865.9	0	0	0	0	0
17	ACNH₂	1139	2000	247.5	762.8	-17.4	-118.1	-367.8	-253.1	-450.3	0	-294.8	0	0	-15.07	0	0	0	0	-281.6	0
18	PYRIDINE	-101.6	0	31.87	49.8	-132.3	-378.2	-332.9	-341.6	-51.54	0	0	0	0	0	0	0	0	0	-169.7	-153.7
19	CCN	24.82	-40.62	-22.97	-138.4	-185.4	157.8	242.8	0	-287.5	0	-266.6	0	38.81	0	0	0	777.4	134.3	0	0
20	COOH	315.3	1264	62.32	268.2	-151	1020	-66.17	0	-297.8	0	-256.3	312.5	-338.5	0	0	0	0	-313.5	0	0

Subgroup classification for *n*-butyl acetate synthesis system

To calculation activity coefficient of each component in *n*-butyl acetate esterification from liquid phase of *n*-butanol and acetic acid as shown in Eq.(2-1), the subgroups of the relevant species are as follows.

Acetic acid (CH_3COOH)	: 1 CH_3, 1 COOH
n-Butanol (C_4H_9OH)	: 1 CH_3, 3 CH_2, 1 OH
n-Butyl acetate ($CH_3COOC_4H_9$)	: 1 CH_3, 3 CH_2, 1 CH_3COO
Water (H_2O)	: 1 H_2O

The parameters used in the UNIFAC calculation for this system are summarized in Table A.3 and Table A.4.

Table A.3 UNIFAC-VLE subgroup parameters (for *n*-butyl acetate esterification system)[†]

Group	Main Group	Subgroup (k)	Rk	Qk
CH_3	1	1	0.9011	0.848
CH_2	1	2	0.6744	0.540
OH	5	15	1.0000	1.200
H_2O	7	17	0.9200	1.400
CH_3COO	11	22	1.9031	1.728
COOH	20	43	1.3013	1.224

Table A.4 UNIFAC-VLE interaction parameters, a_{mk}, in Kelvins (for *n*-butyl acetate esterification system)[†]

Group	Main Group	a_{mk}					
		CH$_3$	CH$_2$	OH	H$_2$O	CH$_3$COO	COOH
		1	1	5	7	11	20
CH$_3$	1	0	0	986.5	1318	232.1	663.5
CH$_2$	1	0	0	986.5	1318	232.1	663.5
OH	5	156.4	156.4	0	353.5	101.1	199
H$_2$O	7	300	300	-229.1	0	72.84	-14.09
CH$_3$COO	11	114.8	114.8	245.4	200.8	0	660.2
COOH	20	3153	3153	-151	-66.17	-2563	0

† Adapted from xLUNIFAC Version 1.0

APPENDIX B

MODIFIED KINETIC PARAMETERS OF
N-BUTYL ACETATE ESTERIFICATION

The reactive distillation unit is simulated via Aspen Plus program in RADFRAC module. The program requires reaction rate constants based on mole fraction or concentration for simulations. The kinetic rate constants of *n*-butyl acetate synthesis from *n*-butanol and acetic acid catalyzed by Amberlyst 15 catalyst is based on activity as given in Table B.1 (Steinigeweg and Gmehling, 2002).

$$\text{HOAc} + n\text{-BuOH} \xleftrightarrow{\text{H}^+} n\text{-BuAc} + \text{H}_2\text{O} \qquad \text{(B-1)}$$

$$r = \frac{1}{m_{cat}}\frac{1}{\nu_i}\frac{dn_i}{dt} = k_1 a_{\text{HOAc}} a_{n\text{-BuOH}} - k_{-1} a_{n\text{-BuAc}} a_{\text{H2O}} \qquad \text{(B-2)}$$

$$k_i = k_i^0 \exp\left(\frac{-E_{\text{A},i}}{RT}\right) \qquad \text{(B-3)}$$

Table B.1 Kinetic parameters for the Pseudohomogeneous kinetic model based on activity (Steinigeweg and Gmehling, 2002).

reaction	i	k^0_i (mol g^{-1} s^{-1})	$E_{\text{A},i}$ (kJ mol^{-1})
esterification	1	6.1084 x 10^4	56.67
hydrolysis	-1	9.8420 x 10^4	67.66

When kinetic parameters are substituted in Eq. (B-3), we can calculate the kinetic rate constant based on activity of esterification and hydrolysis at various temperatures shown in Table B.2.

Table B.2 Kinetic rate constants based on activity at various temperatures.

T (K)	$k_{1,a}$ (mol g^{-1} s^{-1})	$k_{-1,a}$ (mol g^{-1} s^{-1})
333	7.80 x 10^{-5}	2.37 x 10^{-6}
343	1.42 x 10^{-4}	4.83 x 10^{-6}
353	2.49 x 10^{-4}	9.46 x 10^{-6}
363	4.24 x 10^{-4}	1.79 x 10^{-5}

Therefore, the kinetic rate constants based on activity are converted to mole fraction forms by multiplying with average activity coefficients which are estimated from the UNICFAC method (see Appendix A for details).

Then, we calculated average activity coefficients of all components in the system at various temperatures. Table B.3 shows the average activity coefficients that are calculated by using MATLAB.

Table B.3 Activity coefficients calculated by MATLAB.

T (K)	Activity Coefficient (average)			
	HOAc	n-BuOH	n-BuAc	H$_2$O
333	0.8044	1.1830	1.7454	2.8346
343	0.8201	1.1792	1.7300	2.8101
353	0.8342	1.1752	1.7150	2.7873
363	0.8469	1.1711	1.7002	2.7660

Since
$$a_i = \gamma_i x_i \tag{B-4}$$

Substituting the activity of each component (a_i), as shown in Eq. (B-4), in Eq. (B-2) allows the kinetic rate constants based on activity to be converted to the mole fraction forms as given in Eq. (B-5).

$$
\begin{aligned}
r &= k_{1a}\left(\gamma_{\text{HOAc}} x_{\text{HOAc}}\right)\left(\gamma_{n\text{-BuOH}} x_{n\text{-BuOH}}\right) - k_{-1a}\left(\gamma_{n\text{-BuAc}} x_{n\text{-BuAc}}\right)\left(\gamma_{\text{H}_2\text{O}} x_{\text{H}_2\text{O}}\right) \\
&= \left(k_{1a}\gamma_{\text{HOAc}}\gamma_{n\text{-BuOH}}\right)\left(x_{\text{HOAc}} x_{n\text{-BuOH}}\right) - \left(k_{-1a}\gamma_{n\text{-BuAc}}\gamma_{\text{H}_2\text{O}}\right)\left(x_{n\text{-BuAc}} x_{\text{H}_2\text{O}}\right) \\
&= k_{1x} x_{\text{HOAc}} x_{n\text{-BuOH}} - k_{-1a} x_{n\text{-BuAc}} x_{\text{H}_2\text{O}}
\end{aligned} \tag{B-5}
$$

where $k_{1x} = k_{1a}\gamma_{\text{HOAc}}\gamma_{n\text{-BuOH}}$

$k_{-1x} = k_{-1a}\gamma_{n\text{-BuAc}}\gamma_{\text{H}_2\text{O}}$

Then, the new values of the modified kinetic rate constant based on mole fraction are calculated at several temperatures as follows.

At $T = 333$ K,

$$k_{1x} = k_{1a}\gamma_{\text{HOAc}}\gamma_{n\text{-BuOH}}$$
$$= (7.80 \text{ x } 10^{-5})(0.8044)(1.1830)$$
$$= 7.42 \text{ x } 10^{-5}$$

$$k_{-1x} = k_{-1a}\gamma_{n\text{-BuAc}}\gamma_{\text{H}_2\text{O}}$$
$$= (2.37 \text{ x } 10^{-6})(1.7454)(2.8346)$$
$$= 1.17 \text{ x } 10^{-5}$$

In the same way, we calculate the new values of the modified kinetic rate constants at other temperatures:

At $T = 343$ K $k_{1x} = 1.37$ x 10^{-4} $k_{-1x} = 2.35$ x 10^{-5}

At $T = 353$ K $k_{1x} = 2.44$ x 10^{-4} $k_{-1x} = 4.52$ x 10^{-5}

At $T = 363$ K $k_{1x} = 4.20$ x 10^{-4} $k_{-1x} = 8.40$ x 10^{-5}

Next, we use Arrenius plot to find kinetic rate constant expression and activation energy by ln k_1 versus 1/T.
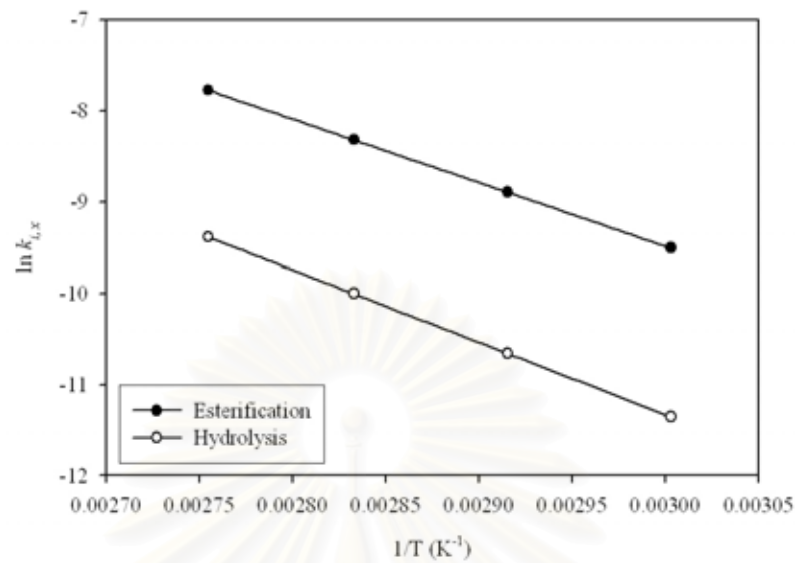
F**igure B.1** Arrenius plot rate constant and activation energy of esterification (k_{1x}) and hydrolysis (k_{-1x}).

From Fig. B.1, we obtain the kinetic rate constant expressions of the forward and the backward reactions as follows:

$$\ln k_{1x} = 11.472 - \frac{6986.3}{T}$$

$$k_{1x} = \exp\left(11.472 - \frac{6986.3}{T}\right)$$

$$\ln k_{-1x} = 12.482 - \frac{7937.7}{T}$$

$$k_{-1x} = \exp\left(12.482 - \frac{7937.7}{T}\right)$$

Table B.4 Kinetic parameters for the kinetic model based on mole fraction.

Reaction	i	k^0_i (mol g^{-1} s^{-1})	$E_{A,i}$ (kJ mol^{-1})
esterification	1	9.5990 x 10^4	58.06
hydrolysis	-1	2.6355 x 10^5	65.96

APPENDIX C

MODELLING OF PERVAPORATION

Fig. C.1 shows a conventional pervaporation unit. A feed liquid mixture contacts one side of a membrane; the permeate is removed as a vapor from the other side. A vacuum pump is used to draw a vacuum on the permeate side of the system. The pervaporation unit can be modeled by performing material and energy balances around the system. Additional data such as heat capacity and heat of vaporization of each component are required for the energy balance caluculations.
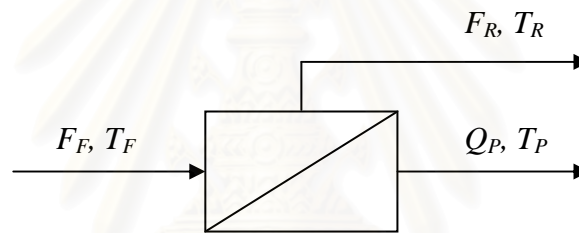
Figure C.1 Schematic diagram of membrane pervaporation.

Assumption system is isothermal ($T_F = T_R = T_P$).

Mass balance

$$\text{Input} \quad = \quad \text{output}$$

$$F_{F,i} \quad = \quad F_{R,i} + Q_{P,i} \tag{C-1}$$

Since

$$Q_{P,i} = AP_i x_i \tag{C-2}$$

So,

$$F_{F,i} = F_{R,i} + AP_i x_i \tag{C-3}$$

where $F_{F,\,i}$ = molar flow rate of species i in the side stream (mol/s)

$F_{R,\,i}$ = molar flow rate of species i in the retentate stream (mol/s)

$Q_{P,i}$ = molar flow rate of species i in the permeate stream (mol/s)

A = membrane area (m^2)

P_i = permeability coefficient of species i (mol/m^2.s)

x_i = mole fraction of species i (-)

Calculation of permeability value

We used data of permeation coefficients of component i through a membrane from the literature (Liu, 2001) for calculation of permeation flux of component i. The data was based on the study of the pervaporation system of water–acetic acid mixtures through the crosslinked polyvinyl alcohol (PVA) membranes. The permeation flux expressions of water and acetic acid are developed as given in Eqs. (C-4) and (C-5).

$$J_{H_2O} = P_{H_2O} C_{H_2O} \qquad \text{(C-4)}$$

$$J_{HOAc} = P_{HOAc} C_{HOAc} + m \qquad \text{(C-5)}$$

where J_i = permeation flux of component i (mol/m^2.h)

P_i = permeability coefficient of species i (l/m^2.h)

C_i = concentration of component I (mol/l)

Table C.1 Parameters for Eqs. (C-4) and (C-5) at different temperatures

T (K)	P_{H2O} (l m^{-2} h^{-1})	P_{HOAc} (l m^{-2} h^{-1})	m
363	4.2	0.054	1.83
353	3.87	0.053	1.70
343	3.52	0.053	1.57
333	3.50	0.052	1.52

From   permeation rate; $$Q_{P,i} = AP_i x_i \qquad\qquad\qquad \text{(C-2)}$$

so,   permeation flux; $$\frac{Q_{P,i}}{A} = P_i x_i \qquad\qquad\qquad \text{(C-6)}$$

permeability; $$P_i = \frac{Q_i}{Ax_i} \qquad\qquad\qquad \text{(C-7)}$$

The compositions of dilute acetic acid of 35 wt% (36.711 mol of water per liter) are corresponding to the mole fractions of acetic acid and water of 0.139 and 0.861, respectively.

Then, the permeability of components i in the system is calculated at various temperatures as following.

At $T = 363$ K,

$$P_i = \frac{Q_i}{Ax_i}$$

$$P_{H_2O} = \frac{154.186 \left(\dfrac{\text{mol}}{\text{m}^2\text{h}}\right)}{0.861}$$

$$= 4.974 \times 10^{-2} \quad \frac{\text{mol}}{\text{m}^2\text{s}}$$

$$P_{HOAc} = \frac{3.812 \left(\dfrac{\text{mol}}{\text{m}^2\text{h}}\right)}{0.139}$$

$$= 7.619 \times 10^{-3} \quad \frac{\text{mol}}{\text{m}^2\text{s}}$$

In the same way, we calculated permeability of water and acetic acid based on polyvinyl alcohol membrane at the other temperatures whose results are summarized in Table C.2.

Table C.2 The permeability of water and acetic acid based on polyvinyl alcohol membrane at various temperature.

T (K)	P_{H2O} (mol/m^2 s)	P_{HOAc} (mol/m^2 s)
363	4.974 x 10^{-2}	7.619 x 10^{-3}
353	4.584 x 10^{-2}	7.286 x 10^{-3}
343	4.169 x 10^{-2}	7.026 x 10^{-4}
333	4.145 x 10^{-2}	6.852 x 10^{-4}

Next, we use Arrhenius plot to find permeability of water and acetic acid based through polyvinyl alcohol membrane by plotting ln Q_i versus 1/T.
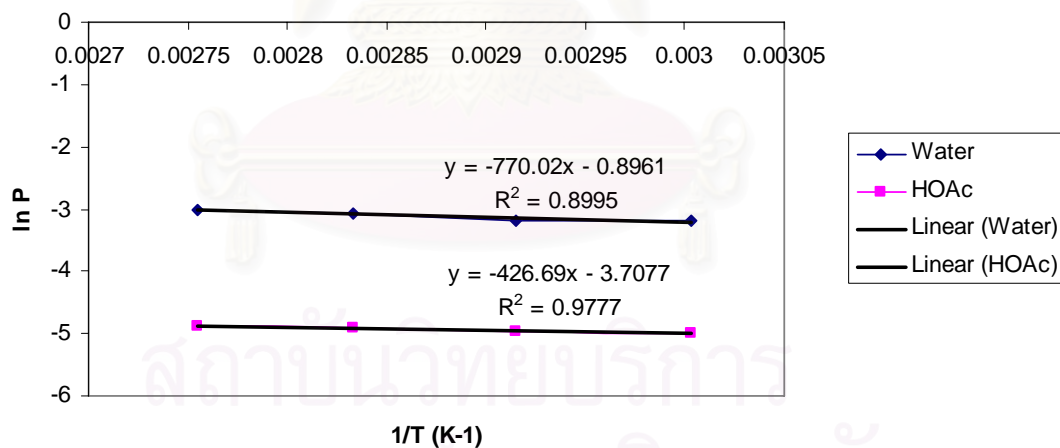
Figure C.2 Arrhenius plot permeability in pervaporation unit based on polyvinyl alcohol membrane.

From Fig. C.1, the permeability of water and acetic acid are rearranged as Arrhenius equation by following;

$$P_{H_2O} = \exp\left(-0.896 - \frac{770.02}{T}\right)$$

$$P_{HOAc} = \exp\left(-3.708 - \frac{426.69}{T}\right)$$

Energy balance

$$\text{Input} = \text{output}$$

$$H_{F,i} + Q = H_{R,i} + H_{P,i} \tag{C-6}$$

$$F_{F,i}\int_{T_F}^{T_F} C_{pl}\,dT + Q = F_{R,i}\int_{T_F}^{T_R} C_{pl}\,dT + Q_{P,i}\left(\int_{T_F}^{T_P} C_{pl}\,dT + H^T_{vzp,i}\right) \tag{C-7}$$

Since $T_F = T_R = T_P$

So

$$Q = Q_{P,i}H^T_{vap,i} \tag{C-8}$$

The enthalpy of vaporization (H^T_{vap}) can calculate from Watson equation shown in Eq. (C-9), which is a function of temperature.

$$H^T_{vap} = A(1 - \frac{T}{T_c})^n \tag{C-9}$$

Table C.2 Parameters for enthalpy of vaporization calculation

Component	A	Tc	n
HOAc	11.575	592.71	-0.65
H$_2$O	52.053	647.13	0.321

Moreover, output stream of the pervaporation system in the permeate side is in vapor phase. If a vacuum pump is equipped at the permeate side, it can help improve the separation due to the increased driving force. We kept the values of the pressure in the suction and the discharge stream at 1 and 0.01 atm, respectively. The energy consumption in the part of vacuum pump is calculated as work form in Eq. (C-10).

$$W = nRT \ln\left(\frac{P_1}{P_2}\right) \qquad \text{(C-10)}$$

APPENDIX D

FORTRAN USER MODEL

Aspen Plus program includes various conventional unit operations which can be combined to any flow scheme. However, pervaporation is not included in the standard version, but Aspen plus allows a user to define a Fortran user-subroutine in the program. Therefore, the implementation of any additional unit operation is possible. This section describes the procedure to write and compile Fortran user model, and to specify the location of the Fortran user models during Aspen Plus runs.

1. Program requirement

There are two essential programs to be installed, as shown below, in computer before writing and compiling the Fortran user models.

- Aspen Plus 10.2 or higher
- Fortran language program (eg., Compaq Visual Fortran 6.6)

An Aspen Plus Fortran user model generally consists of one or more subroutines written to extend the capabilities of Aspen Plus. There are six kinds of Fortran user models for use in Aspen Plus:

- User unit operation models
- User physical property models for the calculation of various major, subordinate and intermediate physical properties
- User models for sizing and costing
- User models for special stream properties
- User stream reports
- User models for performing various types of calculations within Aspen Plus unit operation models

2. Writing Fortran user models

User models written in Fortran should follow these rules:

- **Filename:** Files may be given any name, but should end with a ".f" file extension.

- **Subroutine Names:** The name of all Fortran user model should contain no more than six characters.

- **Double Precision:** All real variables must be declared as double precision (REAL*8).

- **Units:** All variables in the argument list are in SI units, unless the variable description states otherwise.

3. Compiling Fortran user models

All Fortran user models must be compiled before beginning an Aspen Plus run. In order to insure consistent compiler options, use the "aspcomp" command for compiling:

Version	Command[†]
Windows	aspcomp *.f [dbg]

† *dbg is optional. Use it if you plan to debug these routines.*

4. Supplying Fortran user models to Aspen Plus

The simplest method of supplying Fortran user models to Aspen Plus is by putting the user model's object module files (the results of the "aspcomp" command) in the run directory that a project file is saved. By default, whenever Aspen Plus spawns a subprocess to link a run-specific Fortran user model, it includes all object module files from the run directory.

5. User unit operation model

The unit operation models User allow a user to interface his own unit operation model with Aspen Plus by supplying a subroutine and entering its name in the Model or Report field on the User Input Specifications sheet.

Calling Sequence for User

SUBROUTINE subrname† (NSIN, NINFI, SIN1, SIN2, SIN3,
 SIN4, SINFI, NSOUT, NINFO, SOUT1,
 SOUT2, SOUT3, SOUT4, SINFO, NSUBS,
 IDXSUB, ITYPE, NINT, INT, NREAL,
 REAL, IDS, NPO, NBOPST, NIWORK,
 IWORK, NWORK, WORK, NSIZE, SIZE,
 INTSIZ, LD)

Argument List Description for User

Variable	I/O†	Type	Dimension	Description
NSIN	I	INTEGER	-	Number of inlet streams (both material and information)
NINFI	I	INTEGER	-	Number of inlet information streams
SIN1	I/O	REAL*8	(1)	First inlet material stream
SIN2	I/O	REAL*8	(1)	Second inlet material stream
SIN3	I/O	REAL*8	(1)	Third inlet material stream
SIN4	I/O	REAL*8	(1)	Fourth inlet material stream
SINFI	I/O	REAL*8	-	Inlet information stream
NSOUT	I	INTEGER	-	Number of outlet streams (both material and information)
NINFO	I	INTEGER	-	Number of outlet information streams
SOUT1	O	REAL*8	(1)	First outlet material stream
SOUT2	O	REAL*8	(1)	Second outlet material stream
SOUT3	O	REAL*8	(1)	Third outlet material stream
SOUT4	O	REAL*8	(1)	Fourth outlet material stream
SINFO	O	REAL*8	-	Outlet information stream
NSUBS	I	INTEGER	-	Number of substreams in material streams
IDXSUB	I	INTEGER	NSUBS	Location of substreams in stream vector
ITYPE	I	INTEGER	NSUBS	Substream type vector (1-MIXED, 2-CISOLID, 3-NC)

Variable	I/O†	Type	Dimension	Description
NINT	I	INTEGER	-	Number of integer parameters
INT	I/O	INTEGER	NINT	Vector of integer parameters
NREAL	I	INTEGER	-	Number of real parameters
REAL	I/O	REAL*8	NREAL	Vector of real parameters
IDS	I	INTEGER	2, 13	Block IDs: (*,1) - Block ID (*,2) - User model subroutine name (*,3) - User report subroutine name (*,4) to (*,8) - inlet stream IDs (*,9) to (*,13) - outlet stream IDs
NPO	I	INTEGER	-	Number of property option sets (always 2)
NBOPST	I	INTEGER	6, NPO	Property option set array
NIWORK	I	INTEGER	-	Length of integer work vector
IWORK	W	INTEGER	NIWORK	Integer work vector
NWORK	I	INTEGER	-	Length of real work vector
WORK	W	REAL*8	NWORK	Real work vector
NSIZE	I	INTEGER	-	Length of size results vector
SIZE	O	REAL*8	NSIZE	Real sizing results
INTSIZ	O	INTEGER	NSIZE	Integer size parameters
LD	I	INTEGER	-	Plex location of the material stream class descriptor bead

APPENDIX E

SIZING OF EQUIPMENT AND CALCULATION
OF COST

Table E.1 Sizing of equipment and catalyst weight calculation

Parameter	Remarks	Equations
A_{Reb} [m^2]	reboiler heat-transfer area	$A_{\text{Reb}} = \dfrac{Q_{\text{Reb}}}{U_{\text{Reb}} \Delta T_{\text{Reb}}}$
A_{Cond} [m^2]	condenser heat-transfer area	$A_{\text{Cond}} = \dfrac{Q_{\text{Cond}}}{U_{\text{Cond}} \Delta T_{\text{Cond}}}$
H [m]	column hight	$H = (\text{tray spacing})(N_{\text{tray}})$
m_{cat} [kg]	catalyst weight	$m_{\text{cat}} = \dfrac{\pi D_{\text{C}}^{2}}{4}(0.9)(h_{\text{weir}})(0.5)(\rho_{\text{cat}})$

Table E.2 Notation and parameter values for sizing of equipment and cost calculation (hung, 2006).

Parameter	Value	Remarks
C_{MS} [\$]	1,108.1	Marshall and Swift index (as of 2000)
U_{Reb} [W/m^2.K]	788.45	overall heat-transfer coefficient of reboiler
ΔT_{Reb} [K]	25	temperature driving force of reboiler
U_{Cond} [W/m^2.K]	473.07	overall heat-transfer coefficient of condenser
ΔT_{Cond} [K]	calculated	log-mean temperature driving force of condenser (temperature of process stream cooling water inlet and outlet temperature of 32 and 49 $^{\text{o}}$C, respectively)
ρ_{cat} [kg/m^3]	770	catalyst density for Amberlyst 15
h_{weir} [m]	0.1	weir height for tray

Capital and operating costs can be calculated by following the previous work by Douglas (1988), Fahmy (2002) and Hung (2006). Details are as follows:

Capital cost

Column cost

$$\text{Cost}, \$ = \left(\frac{C_{\text{MS}}}{280}\right)101.9D^{1.066}H^{0.802}\left(2.18 + F_m F_p\right); \qquad F_m = 3.67, F_p = 1.00$$

Tray cost

$$\text{Cost}, \$ = \left(\frac{C_{\text{MS}}}{280}\right)4.7D^{1.55}H\left(F_s + F_t + F_m\right); \qquad F_s = 1.00, F_t = 0.00, F_m = 1.70$$

where D = diameter of the column (ft)

H = high of the column (ft)

Heat-exchanger cost

$$\text{Cost}, \$ = \left(\frac{C_{\text{MS}}}{280}\right)101.3A^{0.65}\left(2.29 + \left(F_d + F_p\right)F_m\right); \quad F_d = 1.350 \text{ for reboiler}$$

$F_d = 1.000$ for condenser, $F_p = 0.000$, $F_m = 3.750$

where A = heat transfer area (ft^2)

Membrane material and membrane modules cost

Membrane material; Cost, €$= 80 A_{\text{MB}}$

Membrane modules; Cost, €$= 250 A_{\text{MB}}$

where A_{MB} = membrane area (m^2)

Vacuum pump cost

Cost, $\text{€} = 203V^{0.8}$

where V = volumetric flow rate in suction side (m^3/h)

Operating cost

Steam cost

$$\text{Cost, \$/y} = \left(\frac{\$\,C_s}{1,000\ \text{lb}}\right)\left(\frac{Q_\text{Reb}}{\Delta H_s}\frac{\text{lb}}{\text{h}}\right)\left(8150\frac{\text{hr}}{\text{y}}\right)$$

where C_s = cost of steam (\$/1,000 lb steam)

Cooling cost

$$\text{Cost, \$/y} = \left(\frac{\$\,C_w}{1,000\ \text{gal}}\right)\left(\frac{1}{8.34}\frac{\text{gal}}{\text{lb}}\right)\left(\frac{Q_\text{Cond}}{30}\frac{\text{lb}}{\text{h}}\right)\left(8150\frac{\text{hr}}{\text{y}}\right)$$

where C_w = cost of cooling water (\$/1,000 gal cooling water)

Catalyst cost

$$\text{Cost, \$/y} = \left(m_\text{cat}\ [\text{kg}]\right)\left(7.7162\frac{\$}{\text{kg}}\right)(4)\ \text{for a catalyst life of 3 months}$$

Electricity cost

$$\text{Cost, \$} = \left(\frac{0.04}{\text{kW - h}}\right)$$

<u>**Example of calculations**</u>

1. Reactive distillation equipped with decanter system for using acetic acid 35 wt% (50 kmol/h acetic acid feed)

$$A_{\text{Reb}} = \frac{(6,460,100 \text{ W})}{\left(788.45 \dfrac{\text{W}}{\text{m}^2\text{K}}\right)(25 \text{ K})} = 327.732 \text{ m}^2 = 3,527.670 \text{ ft}^2$$

$$A_{\text{Cond}} = \frac{(5,870,134 \text{ W})}{\left(473.07 \dfrac{\text{W}}{\text{m}^2\text{K}}\right)(44.849 \text{ K})} = 299.849 \text{ m}^2 = 3,223.364 \text{ ft}^2$$

$$H = (\text{tray spacing})(N_{\text{tray}}) = (2 \text{ ft})(9) = 18 \text{ ft}$$

$$m_{\text{cat}} = \frac{\pi(2.681^2 \text{ m}^2)}{4}(0.9)(0.1 \text{ m})(0.5)\left(770 \frac{\text{kg}}{\text{m}^3}\right)$$
$$= 1,368.438 \text{ kg}$$

<u>Capital cost</u>

Column cost;

$$\text{Cost} = \left(\frac{1,108.1}{280}\right)(101.9)(8.796^{1.066})(18^{0.802})(2.18 + 3.67) = \$284,838$$

Tray cost;

$$\text{Cost, \$} = \left(\frac{1,108.1}{280}\right)(4.7)(8.796^{1.55})(18)(1 + 0 + 1.7) = \$26,288$$

Heat-exchanger cost;

$$\text{Cost, \$} = \left(\frac{1,108.1}{280}\right)(101.3)\left(3,527.67^{0.65}\right)\left(2.29 + (1.35 + 0)(3.75)\right) = \$596,119$$

For reboiler

$$\text{Cost, \$} = \left(\frac{1,108.1}{280}\right)(101.3)\left(3,223.364^{0.65}\right)\left(2.29 + (1.000 + 0)(3.75)\right) = \$461,815$$

For condenser

<u>Operating cost</u>

Steam cost;

$$\text{Cost, \$/y} = \left(\frac{\$\,3.72}{1,000\,\text{lb}}\right)\left(\frac{22,042,424\,\dfrac{\text{Btu}}{\text{h}}}{806.617\,\dfrac{\text{Btu}}{\text{lb}}}\right)\left(8150\,\frac{\text{h}}{\text{y}}\right) = \$/y\,828,500$$

Cooling cost;

$$\text{Cost, \$/y} = \left(\frac{\$\,0.03}{1,000\,\text{gal}}\right)\left(\frac{1}{8.34}\,\frac{\text{gal}}{\text{lb}}\right)\left(\frac{20,029,719}{30}\,\frac{\text{lb}}{\text{hr}}\right)\left(8,150\,\frac{\text{hr}}{\text{y}}\right) = \$/y\,19,573$$

Catalyst cost;

$$\text{Cost, \$/y} = (1,368.438\,[\text{kg}])\left(7.7162\,\frac{\$}{\text{kg}}\right)(4) = \$/y\,42,237$$

So

$$\text{TAC} = \text{operating cost} + \frac{\text{capital cost}}{\text{pay - back period}}$$
$$= 890,310 + \frac{1,369,060}{3}$$
$$= \$/y\,1,346,663$$

2. Pretreatment dilute acetic acid 35 to 65 wt% by distillation followed by reactive distillation

Distillation system

$$A_{\text{Reb}} = \frac{Q_{\text{Reb}}}{U_{\text{Reb}} \Delta T_{\text{Reb}}} = \frac{(5{,}002{,}085 \text{ W})}{\left(788.45 \frac{\text{W}}{\text{m}^2\text{K}}\right)(25 \text{ K})} = 257.319 \text{ m}^2 = 2{,}769.759 \text{ ft}^2$$

$$A_{\text{Cond}} = \frac{Q_{\text{Cond}}}{U_{\text{Cond}} \Delta T_{\text{Cond}}} = \frac{(4{,}477{,}256 \text{ W})}{\left(473.07 \frac{\text{W}}{\text{m}^2\text{K}}\right)(54.22 \text{ K})} = 174.542 \text{ m}^2 = 1{,}878.756 \text{ ft}^2$$

$$H = (\text{tray spacing})(N_{\text{tray}}) = (2 \text{ ft})(12) = 24 \text{ ft}$$

Capital cost

Column cost;
$$\text{Cost} = \left(\frac{1{,}108.1}{280}\right)(101.9)(5.115^{1.066})(24^{0.802})(2.18 + 3.67) = \$201{,}309$$

Tray cost;
$$\text{Cost, \$} = \left(\frac{1{,}108.1}{280}\right)(4.7)(5.115^{1.55})(24)(1 + 0 + 1.7) = \$15{,}130$$

Heat-exchanger cost;
$$\text{Cost, \$} = \left(\frac{1{,}108.1}{280}\right)(101.3)(2{,}769.759^{0.65})(2.29 + (1.35 + 0)(3.75)) = \$509{,}393$$

For reboiler

$$\text{Cost, \$} = \left(\frac{1{,}108.1}{280}\right)(101.3)(1{,}878.756^{0.65})(2.29 + (1.000 + 0)(3.75)) = \$32{,}5150$$

For condenser

Operating cost

Steam cost;

$$\text{Cost, \$/y} = \left(\frac{\$\,3.72}{1{,}000\,\text{lb}}\right)\left(\frac{17{,}067{,}814\,\dfrac{\text{Btu}}{\text{h}}}{806.617\,\dfrac{\text{Btu}}{\text{lb}}}\right)\left(8{,}150\,\frac{\text{h}}{\text{y}}\right) = \$/\text{y}\,509{,}393$$

Cooling cost;

$$\text{Cost, \$/y} = \left(\frac{\$\,0.03}{1{,}000\,\text{gal}}\right)\left(\frac{1}{8.34}\,\frac{\text{gal}}{\text{lb}}\right)\left(\frac{15{,}277{,}024}{30}\,\frac{\text{lb}}{\text{hr}}\right)\left(8{,}150\,\frac{\text{hr}}{\text{y}}\right) = \$/\text{y}\,325{,}150$$

Reactive distillation system

$$A_{\text{Reb}} = \frac{(2{,}565{,}410\,\text{W})}{\left(788.45\,\dfrac{\text{W}}{\text{m}^2\text{K}}\right)(25\,\text{K})} = 130.150\,\text{m}^2 = 1{,}400.917\,\text{ft}^2$$

$$A_{\text{Cond}} = \frac{(2{,}558{,}055\,\text{W})}{\left(473.07\,\dfrac{\text{W}}{\text{m}^2\text{K}}\right)(45.339\,\text{K})} = 119.264\,\text{m}^2 = 1283.744\,\text{ft}^2$$

$$H = (\text{tray spacing})(N_{\text{tray}}) = (2\,\text{ft})(17) = 34\,\text{ft}$$

$$\begin{aligned}
m_{\text{cat}} &= \frac{\pi(1.643^2\,\text{m}^2)}{4}(0.9)(0.1\,\text{m})(0.5)\left(770\,\frac{\text{kg}}{\text{m}^3}\right)\\
&= 587.421\,\text{kg}
\end{aligned}$$

Capital cost

Column cost;
$$\text{Cost} = \left(\frac{1{,}108.1}{280}\right)(101.9)\left(5.390^{1.066}\right)\left(34^{0.802}\right)(2.18 + 3.67) = \$281{,}480$$

Tray cost;
$$\text{Cost, \$} = \left(\frac{1{,}108.1}{280}\right)(4.7)\left(5.390^{1.55}\right)(34)(1 + 0 + 1.7) = \$23{,}248$$

Heat-exchanger cost;
$$\text{Cost, \$} = \left(\frac{1{,}108.1}{280}\right)(101.3)\left(1400.917^{0.65}\right)(2.29 + (1.35 + 0)(3.75)) = \$327{,}064$$

For reboiler

$$\text{Cost, \$} = \left(\frac{1{,}108.1}{280}\right)(101.3)\left(1{,}283.774^{0.65}\right)(2.29 + (1.000 + 0)(3.75)) = \$253{,}851$$

For condenser

Operating cost

Steam cost;
$$\text{Cost, \$/y} = \left(\frac{\$\,3.72}{1{,}000\ \text{lb}}\right)\left(\frac{8{,}753{,}538\,\frac{\text{Btu}}{\text{h}}}{806.617\,\frac{\text{Btu}}{\text{lb}}}\right)\left(8150\,\frac{\text{h}}{\text{y}}\right) = \$/\text{y}\,329{,}016$$

Cooling cost;
$$\text{Cost, \$/y} = \left(\frac{\$\,0.03}{1{,}000\ \text{gal}}\right)\left(\frac{1}{8.34}\,\frac{\text{gal}}{\text{lb}}\right)\left(\frac{8{,}728{,}440}{30}\,\frac{\text{lb}}{\text{hr}}\right)\left(8{,}150\,\frac{\text{hr}}{\text{y}}\right) = \$/\text{y}\,8{,}530$$

Catalyst cost;

$$\text{Cost, \$/y} = (587.421\,[\text{kg}])\left(7.7162\,\frac{\$}{\text{kg}}\right)(4) = \$/\text{y}\,18{,}131$$

so

$$\text{TAC} = \text{operating cost} + \frac{\text{capital cost}}{\text{pay - back period}}$$

$$= (656{,}450 + 355{,}676) + \left(\frac{1{,}050{,}980 + 885{,}643}{3}\right)$$

$$= \$/\text{y}\,1{,}657{,}667$$

3. Pretreatment dilute acetic acid 35 to 65 wt% by pervaporation followed by reactive distillation

Pervaporation system

$$A = \frac{Q}{U\Delta T} = \frac{(324{,}272 + 2{,}652{,}084\ \text{W})}{\left(788.45\,\dfrac{\text{W}}{\text{m}^2\text{K}}\right)(131.393\ \text{K})} = 28.875\,\text{m}^2 = 310.808\,\text{ft}^2$$

Capital cost

Heat-exchanger cost;

$$\text{Cost, \$} = \left(\frac{1{,}108.1}{280}\right)(101.3)(310.808^{0.65})(2.29 + (1.35 + 0)(3.75)) = \$91{,}566$$

Membrane material and membrane modules cost;

Membrane material; Cost, €$= 80 A_{\text{MB}} = 80(1720) = $ €137,600 $= \$178{,}756$

Membrane modules; Cost, €$= 250 A_{\text{MB}} = 250(1720) = $ €430,000 $= \$558{,}611$

Vacuum pump cost;

Cost, €= $203V^{0.8} = 203(4.502^{0.8}) = \$879$

<u>Operating cost</u>

Steam cost;

$$\text{Cost, \$/y} = \left(\frac{\$\,3.72}{1{,}000\,\text{lb}}\right)\left(\frac{10{,}155{,}745\,\dfrac{\text{Btu}}{\text{h}}}{806.617\,\dfrac{\text{Btu}}{\text{lb}}}\right)\left(8{,}150\,\frac{\text{h}}{\text{y}}\right) = \$/\text{y}381{,}720$$

Electricity cost;

$$\text{Cost, \$} = \left(\frac{0.04}{\text{kW - h}}\right) = \left(\frac{0.04}{\text{kW - h}}\right)(864.305\,\text{kW})(8150\,\text{h}) = \$281{,}764$$

Reactive distillation system

$$A_{\text{Reb}} = \frac{(2{,}407{,}981\,\text{W})}{\left(788.45\,\dfrac{\text{W}}{\text{m}^2\text{K}}\right)(25\,\text{K})} = 122.163\,\text{m}^2 = 1{,}314.948\,\text{ft}^2$$

$$A_{\text{Cond}} = \frac{(2{,}316{,}184\,\text{W})}{\left(473.07\,\dfrac{\text{W}}{\text{m}^2\text{K}}\right)(44.308\,\text{K})} = 110.500\,\text{m}^2 = 1{,}189.407\,\text{ft}^2$$

$$H = (\text{tray spacing})(N_{\text{tray}}) = (2\,\text{ft})(17) = 34\,\text{ft}$$

$$\begin{aligned}
m_{\text{cat}} &= \frac{\pi(1.590^2\,\text{m}^2)}{4}(0.9)(0.1\,\text{m})(0.5)\left(770\,\frac{\text{kg}}{\text{m}^3}\right) \\
&= 550.135\,\text{kg}
\end{aligned}$$

Capital cost

Column cost;

$$\text{Cost} = \left(\frac{1,108.1}{280}\right)(101.9)\left(5.217^{1.066}\right)\left(34^{0.802}\right)(2.18 + 3.67) = \$27,181$$

Tray cost;

$$\text{Cost, \$} = \left(\frac{1,108.1}{280}\right)(4.7)\left(5.217^{1.55}\right)(34)(1 + 0 + 1.7) = \$22,096$$

Heat-exchanger cost;

$$\text{Cost, \$} = \left(\frac{1,108.1}{280}\right)(101.3)\left(1,314.948^{0.65}\right)(2.29 + (1.35 + 0)(3.75)) = \$313,874$$

For reboiler

$$\text{Cost, \$} = \left(\frac{1,108.1}{280}\right)(101.3)\left(1,189^{0.65}\right)(2.29 + (1.000 + 0)(3.75)) = \$241,564$$

For condenser

Operating cost

Steam cost;

$$\text{Cost, \$/y} = \left(\frac{\$\,3.72}{1,000\,\text{lb}}\right)\left(\frac{8,216,368\,\frac{\text{Btu}}{\text{h}}}{806.617\,\frac{\text{Btu}}{\text{lb}}}\right)\left(8150\,\frac{\text{h}}{\text{y}}\right) = \$/y\,308,825$$

Cooling cost;

$$\text{Cost, \$/y} = \left(\frac{\$\,0.03}{1,000\,\text{gal}}\right)\left(\frac{1}{8.34}\,\frac{\text{gal}}{\text{lb}}\right)\left(\frac{7,903,143}{30}\,\frac{\text{lb}}{\text{hr}}\right)\left(8,150\,\frac{\text{hr}}{\text{y}}\right) = \$/y\,7,723$$

Catalyst cost;

$$\text{Cost, \$/y} = \left(550.135\,[\text{kg}]\right)\left(7.7162\,\frac{\$}{\text{kg}}\right)(4) = \$/\text{y}\,16{,}980$$

so

$$
\begin{aligned}
\text{TAC} &= \text{operating cost} + \frac{\text{capital cost}}{\text{pay - back period}} \\
&= \left(663{,}484 + 333{,}528\right) + \left(\frac{829{,}811 + 849{,}346}{3}\right) \\
&= \$/\text{y}\,1{,}556{,}663
\end{aligned}
$$

VITA

Mr. Kittipong Koomsup was born on January 21, 1983 in Bangkok, Thailand. He finished high school from Samsenwittayalai School. He received Bachelor's Degree of Science in Chemical Technology from the department of Chemical Technology, Faculty of Science, Chulalongkorn University, Bangkok, Thailand in 2005 and Master's degree of Engineering in Chemical Engineering from the department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, Thailand in 2007.