รายงานวิจัยฉบับสมบูรณ์

โครงการการนำกรดอะซิติกเจือจางกลับมาใช้ประโยชน์ในการผลิตสารบิวทิลอะซิเตตโดยใช้หอกลั่นแบบมีปฏิกิริยา

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มิถุนายน 2551

สัญญาเลขที่ MRG4980069

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สนับสนุนโดยสำนักงานคณะกรรมการการอุดมศึกษา และสำนักงานกองทุนสนับสนุนการวิจัย

Abstract

Project Code : MRG4980069

Project Title : Recovery of Dilute Acetic Acid for Butyl Acetate Production by a Reactive Distillation Column

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The objective of this research is to apply a reactive distillation to recover dilute acetic acid. The direct use of dilute acetic acid as a reactant for esterification with butanol to produce butyl acetate in the reactive distillation is investigated via simulation studies. The performance of a single reactive distillation and that integrated with a distillation column or a pervaporation as a pretreatment unit is evaluated with the aim to determine the effect of design variables on the performance of a reactive distillation and to search for a suitable reactive distillation system by considering total energy consumption. Considering the operation of a reactive distillation, two alternative control strategies, i.e., the indirect and direct control of product composition, are studied for the closed-loop control of the reactive distillation. Further, the application of the reactive distillation for other reaction systems, i.e., the etherification reaction of ethanol and tertiary-amyl alcohol is also studied in this work.

Keywords : Dilute Acetic Acid; Reactive Distillation; Butyl Acetate; Simulation; Control

บทคัดย่อ

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งานวิจัยนี้มีวัตถุประสงค์เพื่อประยุกต์ใช้หอกลั่นแบบมีปฏิกิริยาสำหรับนำกรดอะซิติกเจือจากกลับมาใช้ประโยชน์ โดยทำการศึกษาการใช้กรดอะซิติกเจือจางเป็นสารตั้งต้นโดยตรงสำหรับปฏิกิริยาเอสเทอริฟิเคชันร่วมกับบิวทานอลเพื่อผลิตสารบิวทิลอะซิเตตโดยใช้หอกลั่นแบบมีปฏิกิริยา สมรรถนะการดำเนินงานของระบบที่มีเพียงหอกลั่นแบบมีปฏิกิริยาจะถูกนำมาเปรียบเทียบกับระบบที่ใช้หอกลั่นแบบมีปฏิกิริยาร่วมกับหอกลั่นธรรมดาหรือเพอร์แวบพอเรชัน ทั้งนี้เพื่อศึกษาผลของตัวแปรออกแบบที่มีต่อสมรรถนะของหอกลั่นแบบมีปฏิกิริยา รวมทั้งหาระบบหอกลั่นแบบมีปฏิกิริยาที่เหมาะสมโดยคำนึงถึงการใช้พลังงานรวมของระบบ เมื่อพิจารณาการดำเนินงานของหอกลั่นแบบมีปฏิกิริยา งานวิจัยนี้ได้ศึกษาแผนการควบคุม 2 รูปแบบ ได้แก่ การควบคุมองค์ประกอบผลิตภัณฑ์ทางตรงและทางอ้อม สำหรับควบคุมหอกลั่นแบบมีปฏิกิริยา นอกจากนี้ ในงานวิจัยนี้ยังได้ศึกษาเพิ่มเติมเกี่ยวกับการประยุกต์ใช้หอกลั่นแบบมีปฏิกิริยาสำหรับระบบปฏิกิริยาอีเทอร์ริฟิเคชันระหว่างเอทานอลกับเทอร์เชียร์รี เอมิล อัลกอฮอล์

คำหลัก : กรดอะซิติกเจือจาง หอกลั่นแบบมีปฏิกิริยา บิวทิลอะซิเตต การจำลอง การควบคุม

Executive Summary

สารละลายกรดอะซิติกเจือจางในน้ำเป็นผลิตภัณฑ์พลอยได้ (by-product) ที่สำคัญอย่างหนึ่งจากกระบวนการในอุตสาหกรรมปิโตรเคมีและอุตสาหกรรมเคมี โดยเฉพาะอย่างยิ่งในกระบวนการผลิตที่มีการใช้กรดอะซิติกเป็นสารตั้งต้น (reactant) ยกตัวอย่างเช่น การผลิตสารเซลลูโลสอะซิเตตซึ่งเป็นสารเคมีที่ใช้ในอุตสาหกรรมการผลิตเลกเกอร์ สิ่งทอ และฟิล์มถ่ายรูป พบว่าในกระบวนการผลิตสารเซลลูโลสอะซิเตตจากปฏิกิริยาอะซิติเลชั่นระหว่างเซลลูโลสและกรดอะซิติก มีการใช้กรดอะซิติกในกระบวนการผลิตประมาณ 65% โดยน้ำหนัก ส่วนที่เหลืออีประมาณ 35% โดยน้ำหนักจะ พบในน้ำที่ออกจากกระบวนการผลิต หรือกระบวนการผลิตกรดเทเลฟทาเลตซึ่งใช้เป็นสารเคลือบผิวในการเตรียมเรซินและในอุตสาหกรรมพอลิเมอร์ พบว่ามีปริมาณกรดอะซิติกที่เหลือในน้ำสูงถึง 65% โดยน้ำหนัก นอกจากนี้ยังพบว่าในกระบวนการผลิสารเคมีบางชนิดนั้นจะได้กรดอะซิติกเป็น ผลิตภัณฑ์พลอยได้ เช่น กระบวนการสังเคราะห์ glyoxal จากอะซิทาลดีไฮด์และกรดไนตริก พบว่าจะได้กรดอะซิติกเจือจางที่มีความเข้มข้นประมาณ 13-20% โดยน้ำหนักเป็นผลิตภัณฑ์พลอยได้ จากข้อมูลที่กล่าวมาแสดงให้เห็นว่าหากสามารถนำสารละลายกรดอะซิติกเจือจางในน้ำที่ได้จาก กระบวนการผลิตเหล่านี้กลับมาใช้ประโยชน์อีกครั้งนอกจากจะเป็นการช่วยลดภาระในขั้นตอนการบำบัดกรดอะซิติกเจือจางในสารละลายก่อนที่จะปล่อยสู่สิ่งแวดล้อมแล้ว ยังสามารถนำกรดอะซิติกที่ได้ไปใช้ในการผลิตผลิตภัณฑ์ที่มีค่าอื่นๆ

การนำกรดอะซิติกเจือจางที่ได้กลับมาใช้ประโยชน์โดยทั่วไปประกอบด้วย 2 ขั้นตอน ขั้นตอนแรกคือการแยกกรดอะซิติกออกจากสารละลายในน้ำเพื่อเพิ่มความเข้มข้น ทั้งนี้สามารถทำได้ด้วยการใช้การกลั่นแบบสกัดแยก (extractive distillation) ซึ่งเหมาะกับสารละลายกรดอะซิติกเจือจางที่มีความเข้มข้น 50-70% โดยน้ำหนัก หรือใช้การสกัดแยกโดยใช้ของเหลว (liquid-liquid extraction) ซึ่งวิธีนี้เหมาะกับสารละลายกรดอะซิติกที่มีความเข้มข้นน้อยกว่า 50% โดยน้ำหนัก ขั้นตอนที่สองได้แก่การนำกรดอะซิติกที่ได้จากการแยกซึ่งมีความเข้มข้นประมาณ 95-100% โดยน้ำหนัก ไปผ่านกระบวนการเพื่อผลิตเป็นผลิตภัณฑ์ที่ต้องการ ปัจจุบันนิยมนำกรดอะซิติกไปใช้ในการผลิตสารจำพวกเอสเทอร์ซึ่งเป็นผลิตภัณฑ์ที่ได้จากปฏิกิริยาเอสเทอริฟิเคชันระหว่างกรดอะซิติกและแอลกอฮอล์ชนิดต่างๆ ตัวอย่างผลิตภัณฑ์ที่ได้จากกรดอะซิติก ได้แก่ บิวทิลอะซิเตตซึ่งเป็นสารเคมีที่ใช้ในการเคลือบผิววัสดุและใช้เป็นตัวทำละลายได้จากปฏิกิริยาระหว่างกรดอะซิติกกับบิวทานอล สารไอโซ-เอมิล อะซิเตตซึ่งเกิดจากปฏิกิริยาระหว่างกรดอะซิติกและไอโซ-เอมิล แอลกอฮอล์ สารเคมีดังกล่าวสามารถนำไปใช้ในการทำสารเคลือบผิว นอกจากนี้ยังสามารถนำกรดอะซิติกไปใช้ในการผลิตสาร 2-เอทิล-1-เฮกซิล อะซิเตตซึ่งเป็นส่วนผสมที่ใช้เป็นสารกันแดดในการผลิตเครื่องสำอาง เป็นต้น

อย่างไรก็ตามในปัจจุบันแนวทางใหม่ที่ได้รับความสนใจในการนำกรดอะซิติกเจือจางกลับมาใช้ ได้แก่การนำสารละลายกรดอะซิติกเจือจางไปผ่านกระบวนการผลิตโดยตรงภายในหอกลั่นแบบมีปฏิกิริยา (reactive distillation column) ข้อดีของวิธีการดังกล่าวคือสามารถนำกรดอะ

ซิติกที่มีความเข้มข้นต่ำไปใช้เป็นสารตั้งต้นในกระบวนการผลิตได้โดยตรง โดยไม่จำเป็นต้องเพิ่มความเข้มข้นของกรดด้วยการแยกก่อนนำกลับไปใช้ใหม่ นอกจากนี้การที่เกิดการแยกสารและปฏิกิริยาเคมีพร้อมกันภายในหอกลั่นนั้น ทำให้ปฏิกิริยาเคมีที่ถูกจำกัดด้วยเงื่อนไขสมดุลเคมี เช่น ปฏิกิริยาเอสเทอริฟิเคชันของกรดอะซิติก เกิดปฏิกิริยาได้สมบูรณ์มากขึ้นเนื่องจากผลิตภัณฑ์ที่ได้ถูกแยกออกโดยการกลั่นแยก ทำให้การเกิดปฏิกิริยาเคมีของสารตั้งต้นเพิ่มมากขึ้นตามหลักสมดุลเคมีส่งผลทำให้ได้ผลิตภัณฑ์มากขึ้น

งานวิจัยที่เกี่ยวข้องกับการใช้หอกลั่นแบบเกิดปฏิกิริยาเอสเทอริฟิเคชันของกรดอะซิติกนั้น ในระยะเริ่มแรกนิยมใช้ตัวเร่งปฏิกิริยาแบบเอกพันธ์ (homogeneous catalyst) เช่น กรดซัลฟูริก ต่อมาเริ่มมีความสนใจในการนำตัวเร่งปฏิกิริยาแบบวิวิธพันธ์ (heterogeneous catalyst) เช่น ตัวเร่งปฏิกิริยาเรซินแบบมีการแลกเปลี่ยนไอออน (ion exhange resins) มาใช้เนื่องจากช่วยลดปัญหาการกัดกร่อนและการแยกตัวเร่งปฏิกิริยาออกจากผลิตภัณฑ์ อย่างไรก็ตามเป็นที่น่าสังเกตว่างานวิจัยที่ผ่านมาทั้งในส่วนที่เกี่ยวข้องกับการศึกษาปฏิกิริยาเอสเทอริฟิเคชันของกรดอะซิติก การดำเนินการทดลองและการจำลองกระบวนการของหอกลั่นแบบมีปฏิกิริยาเอสเทอริฟิเคชันของกรดอะซิติกนั้นมุ่งศึกษาเฉพาะกรณีที่ใช้กรดอะซิติกเข้มข้น (ความเข้มข้น 98-100% โดยน้ำหนัก) งานวิจัยที่ทำการศึกษาในแง่การนำกลับมาใช้ประโยชน์ของสารละลายกรดอะซิติกเจือจางในน้ำซึ่งเป็นผลพลอยได้จากกระบวนการผลิตสารเคมีต่างๆ ดังที่ได้กล่าวไว้ในตอนต้นมีน้อยมาก การศึกษาในประเด็นนี้จึงเป็นเรื่องที่น่าสนใจ ทั้งนี้การนำกรดอะซิติกเจือจางซึ่งมีน้ำเป็นองค์ประกอบในปริมาณมากมาใช้เป็นสารตั้งต้นในการทำปฏิกิริยาจะมีผลต่อสมดุลเคมีซึ่งจะส่งผลกระทบต่อสมรรถนะการดำเนินงานของหอกลั่นแบบมีปฏิกิริยา

ดังนั้นวัตถุประสงค์ของงานวิจัยนี้จึงมุ่งเน้นที่จะศึกษาการประยุกต์ใช้หอกลั่นแบบมีปฏิกิริยาในการนำกรดอะซิติกเจือจางกลับมาใช้ประโยชน์ โดยเลือกศึกษาการผลิตสารบิวทิลอะซิเตตจากปฏิกิริยาเอสเทอริฟิเคชันเนื่องจากสารเคมีชนิดนี้เป็นที่ต้องการในปัจจุบัน โดยใช้เป็นสารเคลือบผิวและตัวทำละลายในแลคเกอร์ซึ่งมีการใช้งานอย่างแพร่หลายในอุตสาหกรรมภายในประเทศ โดยเฉพาะอุตสาหกรรมการผลิตเฟอร์นิเจอร์ งานวิจัยนี้ได้ศึกษาถึงปัจจัยต่างๆ ได้แก่ ความเข้มข้นของสารละลายกรดอะซิติก องค์ประกอบของสายป้อน อัตราการไหลของสายป้อน สัดส่วนการป้อนกลับ (reflux ratio) เป็นต้น ที่มีผลต่อสมรรถนะการดำเนินการของหอกลั่นแบบมีปฏิกิริยาซึ่งเป็นกระบวนการที่ซับซ้อนเนื่องจากเกิดการแยกสารและปฏิกิริยาเคมีพร้อมกันในหน่วยปฏิบัติการเดียว งานวิจัยนี้ยังได้ศึกษาการเลือกรูปแบบวิธีการดำเนินงานและสภาวะการดำเนินงานที่เหมาะสม รวมทั้งการออกแบบระบบการควบคุมหอกลั่นแบบมีปฏิกิริยาสำหรับการผลิตบิวทิลอะซิเตตจากกรดอะซิติกเจือจาง นอกจากนี้แล้ว งานวิจัยนี้ได้ทำศึกษาเพิ่มเติมเกี่ยวกับการประยุกต์ใช้กระบวนการร่วมระหว่างหอกลั่นแบบมีปฏิกิริยากับกระบวนการเพอร์แวบพอเรชัน (pervaporation) สำหรับการผลิตสารออกซิจิเนต ได้แก่ สารเทอร์เชียรีเอมิลเอทิลอีเทอร์ จากเอทานอลและเทอร์เชียรีเอมิลแอลกอฮอล์ โดยใช้ปฏิกิริยาอีเทอร์ริฟิเคชัน

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CHAPTER I

Hybrid Reactive Distillation Systems for *n*-Butyl Acetate Production from Dilute Acetic Acid

1. Introduction

Dilute acetic acid is considered as a by-product from many chemical and petrochemical processes such as productions of terephthalic acid, dimethyl terephthalate, glyoxal and cellulose acetate. It is found that the concentration of dilute acetic acid in aqueous solution is varied between 35 and 65 wt.% [1,2]. As a consequence, the recovery of dilute acetic acid becomes an important issue due to economic and environmental awareness. In practice, the conventional separation processes of a dilute acetic acid stream are distillation and extraction. High purity acetic acid obtained is then utilized for the synthesis of various chemicals. However, the distillation may require high energy consumption while the liquid-liquid extraction is limited by phase separation. Pervaporation is another potential method for a separation of liquid mixtures. Its application can be found in the dehydration of organic/water mixtures, the removal and recovery of organic compounds from water, and the separation of organic mixture. In general, hydrophilic membranes have been used for dehydration of organic solvents whereas hydrophobic membranes have been used for separation of organics from water [3-6].

Another interesting approach for recovering acetic acid from its dilute aqueous solution is to directly use it as a reactant for esterification. This approach has received much attention as the dilute acetic acid can be recovered to produce a higher valued ester, which can save raw material cost and environment problem. The use of a reactive distillation, a multifunctional reactor combining chemical reaction and distillation in a single column, is a promising way for the utilization of the dilute acetic acid to synthesize high valued chemicals. The simultaneous separation of products and chemical reactions inside the column allows the reaction to take place efficiently, especially in esterification processes in which a maximum conversion is limited by reaction equilibrium [7].

n-Butyl acetate is one of the most important esters used in coating and painting industries because it is a low toxic and environment-friendly solvent compared with other esters such as ethoxy ethyl acetate [8]. It is commonly synthesized via the esterification of acetic acid with butanol in the liquid phase system in the presence of a strongly acid catalyze, e.g., sulfuric acid, acidic ion exchange resins and zeolites. Although the synthesis of n-butyl acetate has been widely studied [9-11], a few research works concern on the direct utilization of dilute acetic acid as the reactant to produce butyl acetate via the esterification process. For examples, Saha et al. [1] reported experimental results on the recovery of dilute acetic acid (30 wt.%) through esterification process with higher alcohols such as *n*-butanol and iso-amy alcohol, in a reactive distillation column. Xu et al. [12] studied the separation of dilute acetic acid from water using a catalytic distillation where dilute acetic acid is reacted with methanol via esterification catalyzed by Amberlyst-15 to produce methyl acetate. Singh et al. [13] examined the recovery of acetic acid solution in range of 5-30 wt.% by using reactive distillation in which esterification is occured.

In this study, the synthesis of *n*-butyl acetate from the esterification of dilute acetic acid and *n*-butanol in a reactive distillation is investigated via simulation studies using Aspen Plus program. Due to the presence of high water content in acetic acid feed, hybrid reactive distillation-based systems are considered. The performance of a single reactive distillation and that integrated with a distillation column or a pervaporation as a pretreatment unit is evaluated. This study focuses on determining the effect of design variables on the performance of a reactive distillation and searching for a suitable reactive distillation system by considering total energy consumption.

2. Simulations of Hybrid Reactive Distillation Systems

2.1 Reactive distillation

A reactive distillation column is simulated by using Aspen Plus program. The RADFRAC model, a rigorous equilibrium-stage model for describing a multistage vapor-liquid separation in distillation columns, is used in this study for the *n*-butyl acetate production. The inside-out method is employed to solve the reactive distillation model. In the reactive distillation, it consists of rectifying, reaction, and stripping zones. The reversible esterification of *n*-butanol and acetic acid as shown in Eq. (1) occurs at the reaction section of the reactive distillation. The rate expression and kinetic constants of this reaction catalyzed by Amberlyst 15 are given in Eqs. (2)-(4) [14].

$$\underset{\text{(acetic acid)}}{\mathrm{CH_3COOH}} + \underset{(n\text{-butanol})}{\mathrm{C_4H_9OH}} \xleftrightarrow{\mathrm{H^+}} \underset{(n\text{-butyl acetate})}{\mathrm{CH_3COOC_4H_9}} + \underset{\text{(water)}}{\mathrm{H_2O}} \tag{1}$$

$$r = k_1 C_{\mathrm{HOAc}} C_{n\text{-BuOH}} - k_{-1} C_{n\text{-BuAc}} C_{\mathrm{H2O}} \tag{2}$$

$$k_1 = \exp\left(11.472\text{-}\frac{6986.3}{T}\right) \tag{3}$$

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

According to the previous work by Steinigeweg and Gmehling [14], a pilot-scale reactive distillation for the synthesis of *n*-butyl acetate from esterification of concentrate acetic acid with *n*-butanol contains totally 28 stages (including condenser and reboiler) that consist of 5 rectifying, 15 reaction and 6 stripping stages. This column specification is used for preliminary study in order to analysis the effect of design parameters, i.e., the number of reactifying, reaction and stripping stages, on the performance of the reactive distillation column. Feed flow rate of pure *n*-butanol and acetic acid was kept at 35 mol/h for the case of a single reactive distillation. In the standard case, the following conditions are assumed; the column pressure is 1 atm, the temperature and pressure of feed stream are 25 ^{o}C and 1 atm, respectively, acetic acid and *n*-butanol are introduced to the column at the 6th and 10th stage, respectively. It is noted that since the distillate product which is mainly comprised *n*-butanol and water with less *n*-butyl acetate is separated into aqueous and organic phases [8,10,15], the reactive distillation column with a decanter as shown in Fig. 1 is considered.

It is noted that prior to applying the RADFRAC model of a reactive distillation for simulation studies, the model is validated by comparing the calculated results with data reported by Wang et al. [16]. Under the same column configuration and operating conditions reported in their work, it can be seen from Table 1 that the simulation results of the RADFRAC model are in good agreement with the published data.

2.2 Pretreatment Unit

Since dilute acetic acid is directly used as reactant for the *n*-butyl acetate production process, 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 column feed, the reactive distillation should perform even more efficiently. In this study, a conventional distillation column or a membrane pervaporation unit is chosen to be installed prior to the reactive distillation to purify the feed.

Concerning the pretreatment unit, the RADFRAC model in Aspen Plus is also employed to represent a conventional distillation column. However, since a steady state model of a pervaporation is not provided in Aspen Plus simulator, a user-defined Fortran subrountine ('usrpv') is developed in this study, allowing the simulation of the pervaporation in Aspen Plus. Fig. 2 shows the schematic diagram of a pervaporation membrane process. In *usrpv*, the calculations are performed by solving mass and energy balances as given in Eqs. (5) and (6). The permeability of water and acetic acid are necessary information for determining mass transfer across the membrane. In this study, polyvinyl alcohol (PVA) is selected as a hydrophilic membrane in the pervaporation unit, allowing water to preferentially permeate through the membrane. The permeability of water and acetic acid were calculated from the parameters and equations reported in literature [3] and can be expressed in the Arrhenius form as shown in Eqs. (7) and (8), respectively.

$$F_{f,i} = F_{R,i} + AP_i x_i \tag{5}$$

$$H_{f,i} = H_{R,i} + H_{P,i} \tag{6}$$

$$P_{\mathrm{W}} = \exp\left(-0.8961 - \frac{770.02}{T} \right) \tag{7}$$

$$P_{\mathrm{HOAc}} = \exp\left(-3.7077 - \frac{426.69}{T} \right) \tag{8}$$

where x_i is the mole fraction of species i in the liquid mixture, H_i is the enthalpy of component i in each stream that can be calculated from the heat capacity (C_p) of each component.

Fig. 3 shows the schematic diagram of the hybrid process of a reactive distillation with a pretreatment unit.

3. Results and Discussion

3.1 Effect of design variables

To find optimal design variables for the operation of the reactive distillation, simulations are carried out to study the effects of these variables on the reactive distillation performance. The important design variables considered here include the number of rectifying, reaction and stripping stages. Since esterification of *n*-butyl acetate occurs in the reaction zone whereas the rectifying and stripping zones perform multi-component separation, the optimum number of stages in each section should give both high conversion of acetic acid and high yield and purity of *n*-butyl acetate.

Firstly, the impact of the number of stripping stages on the performance of reactive distillation is investigated. With the specified number of the rectifying stages (= 5 stages) as in the standard case study, the number of the stripping stages is varied from 1 to 19 and the results are presented in Figs. 4(a)-(c). 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 reaction section. This results in an increase in the conversion of acetic acid and the mole fraction of *n*-butyl acetate in the bottom. Fig. 4 also shows the influence of the number of stages in the reactive section. It can be seen that the performance of the reactive distillation is improved when increasing of the number of reaction stages. This is expected as an increase in reaction stages promotes the esterification of *n*-butanol and acetic acid. Considering the conversion of acetic acid, and the yield and the purity of n-butyl acetate in the bottom product stream, the suitable number of stages in the reaction and stripping sections is 11 and 7 stages, respectively.

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 stage is kept at 7 as a result of the earlier study. According to the results shown in Figs. 5(a)-(c), 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. The results indicate that 5 rectifying stages give a better reactive distillation performance.

From the above simulation results, it can be concluded that the optimal configuration for the reactive distillation with a decanter and a total reflux operation policy consists of 5 rectifying, 11 reaction and 7 stripping stages. Fig. 6 shows the typical composition and temperature profiles 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 *n*-butyl acetate. Note that after the top products are sent to the decanter, they are separated in two phases: organic and aqueous phases. Only the liquid in the organic phase is refluxed to the reactive distillation column.

3.2 Effect of feed acetic acid concentration

In this part, the effect of acetic acid feed concentration in aqueous solution for *n*-butyl acetate synthesis in the reactive distillation is investigated. It can be seen from Figs. 7(a)-(c) 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. This is because higher reboiler heat duty is required for separating higher amount of water in the feed stream. Further, it can be observed that by introducing the feed containing 65 wt.% 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 are similar to those with the use of 100 wt.% acetic acid. This result suggests 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 acetic acid feed has the concentration less than 65 wt.%, it would require a pretreatment unit such as distillation and pervaporation for separating some water from aqueous solution of acetic acid, leading to a higher purity of acetic acid and a reduced energy requirement in the reactive distillation.

3.3 Effect of various system configurations for n-butyl acetate production from dilute acetic acid

As mentioned in the previous section, if dilute acetic acid is employed for the production of *n*-butyl acetate in the reactive distillation column, a pretreatment unit for increasing the concentration of feed acetic acid may be required for improving 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 a pervaporation as a pretreatment unit is studied.

3.3.1 Single reactive distillation without a pretreatment unit

The reactive distillation column is designed for the synthesis of *n*-butyl acetate using the dilute acetic acid of 35 wt.% as reactant. With the similar design procedure as explained in previous section, it is found that the suitable column configuration contains 1 rectifying, 21 reaction and 1 stripping stages for the production of 98 mol% *n*-butyl acetate in the bottom product stream. Table 2 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.

3.3.2 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. 8(a), it is noticed that to obtain the acetic acid product of 65 wt.%, the distillation can be operated at a lower reboiler heat duty when the reflux ratio is decreased. In addition, operating at a low reboiler duty can take an advantage of obtaining high recovery of acetic acid as can be seen in Fig. 8(b). Table 2 shows the results when the hybrid distillation-reactive distillation process (with reflux ratio of the conventional distillation = 1 and 2.5) is applied for the production of *n*-butyl acetate. Comparing with the single reactive distillation system, the hybrid reactive distillation-distillation process requires higher total energy consumption; even though, the energy consumption of the reactive distillation in the hybrid reactive distillation-distillation process is less than that of the single reactive distillation system.

3.3.3 Reactive distillation with pervaporation

In this section, the system consisting of a membrane pervaporation as a pretreatment unit for dilute acetic acid and a reactive distillation is studied. The isothermal operation of the pervaporation is assumed. The operating 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 wt.% to 65 wt.%. The results show that the required membrane area of pervaporation is decreased with an increase in operating temperatures (Fig. 9(a)); increasing the temperature results in the increased permeation, thus reducing the membrane area of pervaporation. It can also be observed that an increase in operating temperature provides higher 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 preheating and pervaporation unit, and power for vacuum pump, the increased operating temperature leads to higher energy consumption as shown in Fig. 9(b). The figure also shows that the pervaporation unit consumes the highest energy. From the results, the operation of pervaporation at 100 ^{o}C gives higher acetic recovery and therefore, this condition is selected for the operation of the pervaporation unit. Table 2 shows the results when the hybrid pervaporation-reactive distillation process is applied. It is found that when dilute acetic acid (35 wt.%) is used for the production of *n*-butyl acetate, the hybrid process of the pervaporation-reactive distillation needs lower total energy consumption than the hybrid distillation-reactive distillation system. This is due to less energy consumption of the pervaporation unit compared to that of the conventional distillation.

4. Conclusions

The synthesis of *n*-butyl acetate from *n*-butanol and dilute acetic acid in various reactive distillation systems, i.e., (i) a single reactive distillation, (ii) a hybrid distillation-reactive distillation system, and (iii) a hybrid pervaporation-reactive distillation system, was investigated by using Aspen Plus program. The installation of either the distillation or pervaporation unit was aimed to concentrate the dilute acetic acid from 35 wt.% to 65 wt.%. Considering the single-column reactive distillations, it was found that more energy is required when the concentration of acetic acid in the feed becomes lower. Considering the total energy consumption for *n*-butyl acetate synthesis (98 mol%) from *n*-butanol and 35 wt.% acetic acid in various reactive distillation systems, the hybrid pervaporation-reactive distillation system requires the lowest total energy consumption.

Nomenclature

A	surface membrane area	[m^2]
D	liquid distillate flow rate	[mol/s]
C	concentration of species i	[mol/m^3]
F_i	molar flow rate of species i	[mol/s]
H	enthalpy	[J/s]
HOAc	acetic acid	
k_i	kinetic constant	[mol/(s mol-H$^+$)]
L	reflux flow rate	[mol/s]
n-BuAc	*n*-butyl acetate	
N	number of stages in a reactive distillation or a distillation	
P_i	permeability of species i	[mol/(m^2.s)]
Q	heat duty	[W]
r_i	reaction rate	[mol/(s kg-cat)]
T	operating temperature	[K]
x_i	liquid mole fraction of component i	[-]

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Table 1. Comparison of simulation results and data from Wang et al. [16]

	Wang et al. [16]	Simulation
Number of rectifying stages	11	
Number of reaction stages	13	
Number of stripping stages	15	
Overhead Pressure (atm)	1	
Column Pressure Drop (atm)	0.134	
Reboiler duty (Mkcal/h)	1.98	
Organic reflux rate (kmol/h)	100.76	98.25
Aqueous Distillate rate (kmol/h)	100.75	100.80
Bottom rate (kmol/h)	99.20	99.24
Acetic acid conversion (%)	99.30	99.28
Bottom n-butyl acetate purity (mol %)	99.9	99.9

Table 2. Summary of the results for *n*-butyl acetate synthesis by different configurations of a reactive distillation (RD) system

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	34.11	31.09	31.06
N_{DIST} (stages)	-	-	-	7	7	-
Feed stage of dilute HOAc for DIST	-	-	-	5	5	-
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						
$x_{\mathrm{dist,\ HOAc}}$	0.023	0.002	0.004	0.003	0.007	0.005
$x_{\mathrm{dist,}\ n\mathrm{-BuOH}}$	0.010	0.009	0.007	0.008	0.003	0.003
$x_{\mathrm{dist,}\ n\mathrm{-BuAc}}$	0.002	0.001	0.001	0.001	0.001	0.001
$x_{\mathrm{dist,\ H2O}}$	0.965	0.988	0.988	0.989	0.989	0.990
Bottom						
$x_{\mathrm{bot,\ HOAc}}$	0.004	0.019	0.020	0.004	0.005	0.005
$x_{\mathrm{bot,}\ n\mathrm{-BuOH}}$	0.016	0.001	0.000	0.016	0.015	0.011
$x_{\mathrm{bot,}\ n\mathrm{-BuAc}}$	0.980	0.980	0.980	0.980	0.980	0.985
$x_{\mathrm{bot,\ H2O}}$	0.000	0.000	0.000	0.000	0.000	0.000
Conversion of HOAc (%)	97.35	97.45	95.11	96.32	87.43	87.10
Yield of *n*-BuAc (%) at bottom	97.19	97.15	94.26	96.10	87.07	87.03
Energy consumption (W)						
$Q_{\mathrm{cond,\ D}}$	-	-	-	6,181.44	3783.13	-
$Q_{\mathrm{reb,\ D}}$	-	-	-	6,600.00	4200.00	-
$Q_{\mathrm{pre\text{-}PV}}$	-	-	-	-	-	389.30
Q_{PV}	-	-	-	-	-	1790.60
$Q_{\mathrm{vacuum\ pump}}$	-	-	-	-	-	654.46
$Q_{\mathrm{cond,\ RD}}$	1,767.30	2,225.99	4,326.26	1,994.49	1503.47	1546.27
$Q_{\mathrm{reb,\ RD}}$	1,838.00	2,400.00	4,760.00	2,000.00	1495.00	1550.00
$\boldsymbol{Q}_{\mathbf{Total\ Energy\ Consumption}}$	**3,605.30**	**4,625.99**	**9,086.26**	**16,775.93**	**10981.60**	**5930.63**
Energy consumption per 35 mol/hr of *n*-BuAc (W)	**3709.38**	**4761.94**	**9639.49**	**17456.74**	**12612.24**	**6814.15**

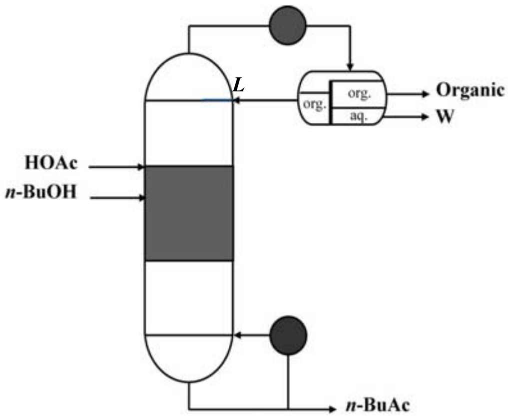


Fig. 1 A Single reactive distillation column with decanter.

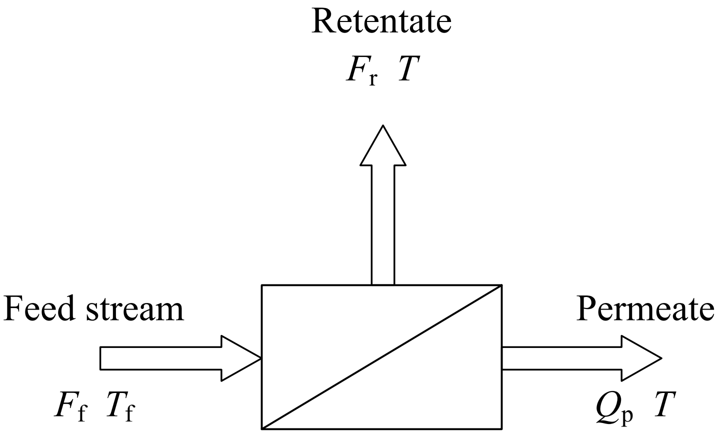


Fig. 2 The schematic diagram of pervaporation membrane.

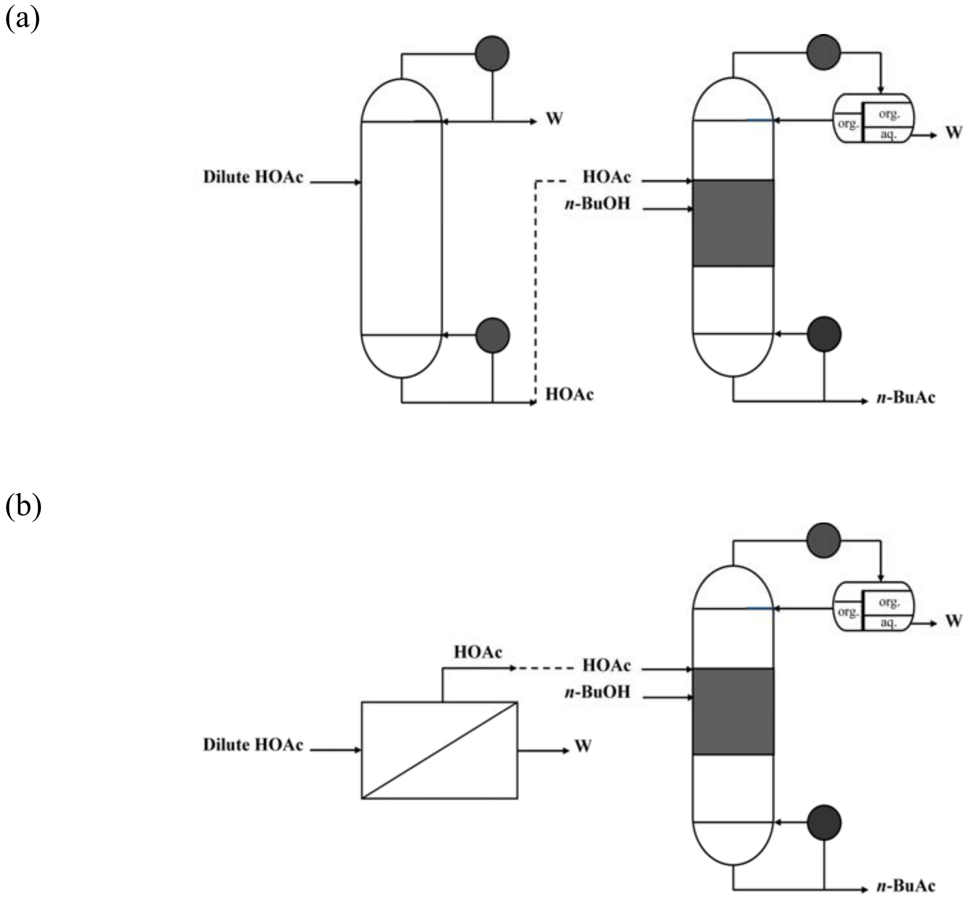
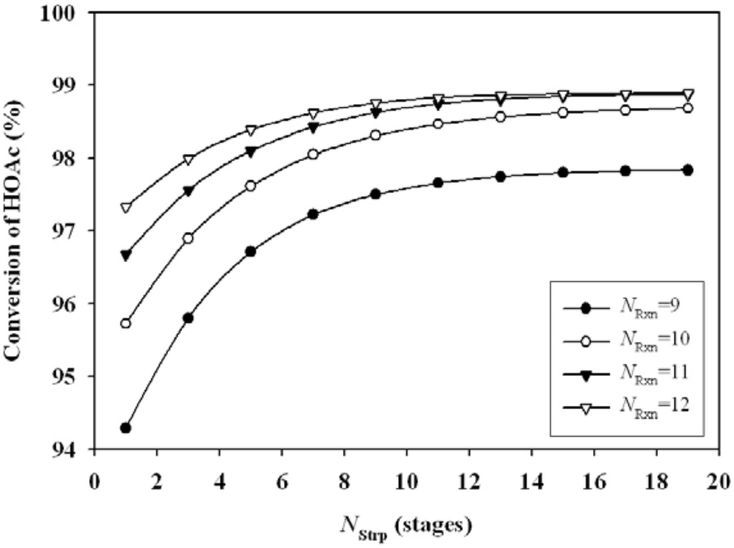
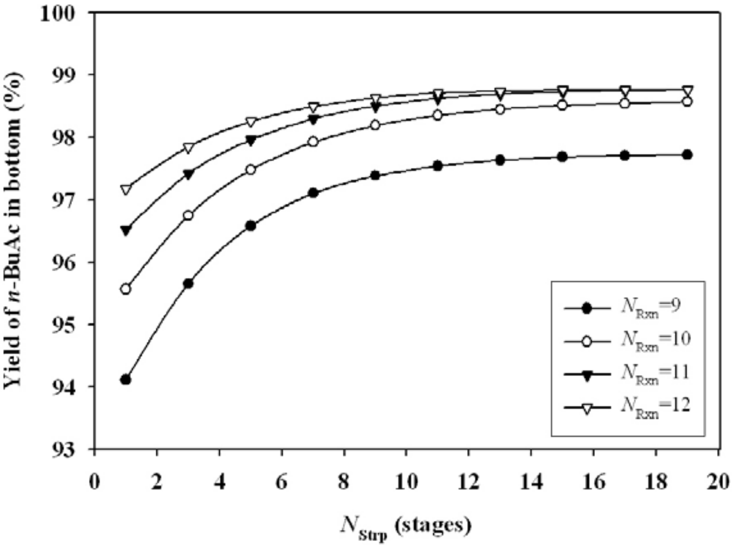


Fig. 3 Hybrid process of a reactive distillation with: (a) a distillation, and (b) a pervaporation.

(a)


Conversion of HOAc (%)
100
99
98
97
96
95
94
0
2
4
6
8
10
12
14
16
18
20
N_{Strp} (stages)
N_{Rxn}=9
N_{Rxn}=10
N_{Rxn}=11
N_{Rxn}=12

(b)


Yield of n-BuAc in bottom (%)
100
99
98
97
96
95
94
93
0
2
4
6
8
10
12
14
16
18
20
N_{Strp} (stages)
N_{Rxn}=9
N_{Rxn}=10
N_{Rxn}=11
N_{Rxn}=12

(c)

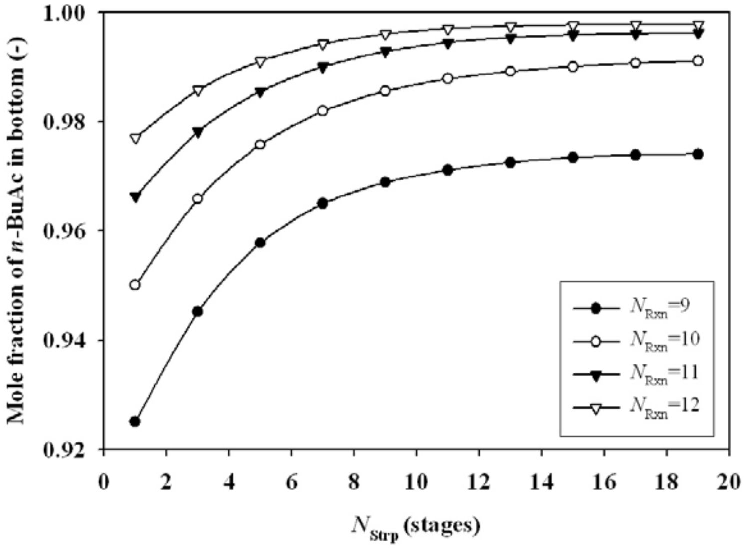
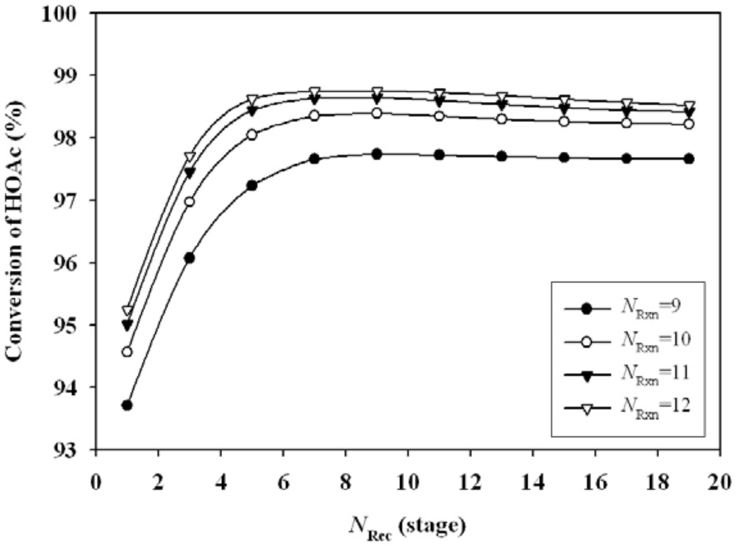


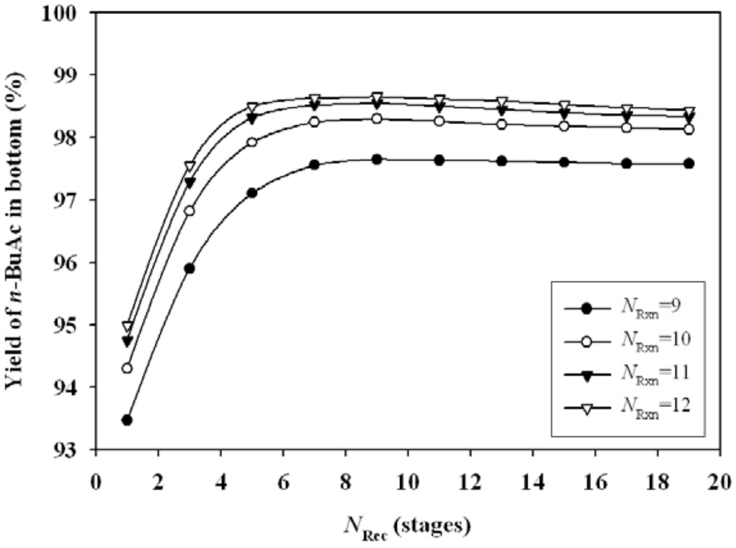
Fig. 4 Effect of the number of stripping stages on (a) the conversion of acetic acid, (b) the yield of *n*-butyl acetate, and (c) the mole fraction of *n*-butyl acetate, at various reaction stages.

(a)



Conversion of HOAc (%)
100
99
98
97
96
95
94
93
0
2
4
6
8
10
12
14
16
18
20
N_{Rec} (stage)
N_{Rxn}=9
N_{Rxn}=10
N_{Rxn}=11
N_{Rxn}=12

(b)



Yield of *n*-BuAc in bottom (%)
100
99
98
97
96
95
94
93
0
2
4
6
8
10
12
14
16
18
20
N_{Rec} (stages)
N_{Rxn}=9
N_{Rxn}=10
N_{Rxn}=11
N_{Rxn}=12

(c)

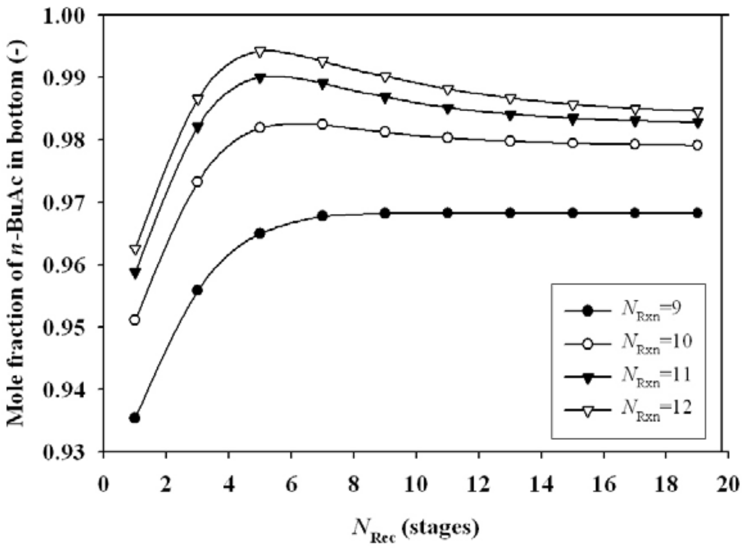
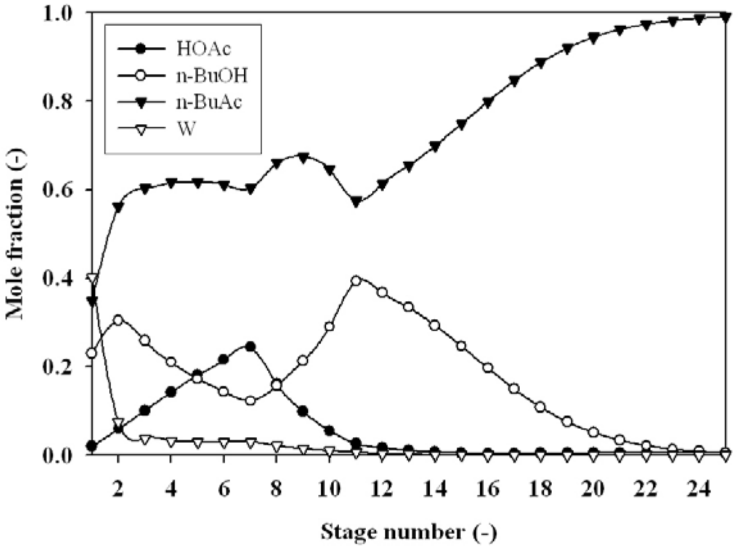


Fig. 5 Effect of the number of rectifying stages on (a) the conversion of acetic acid, (b) the yield of *n*-butyl acetate, and (c) the mole fraction of *n*-butyl acetate, at various reaction stages

(a)



(b)

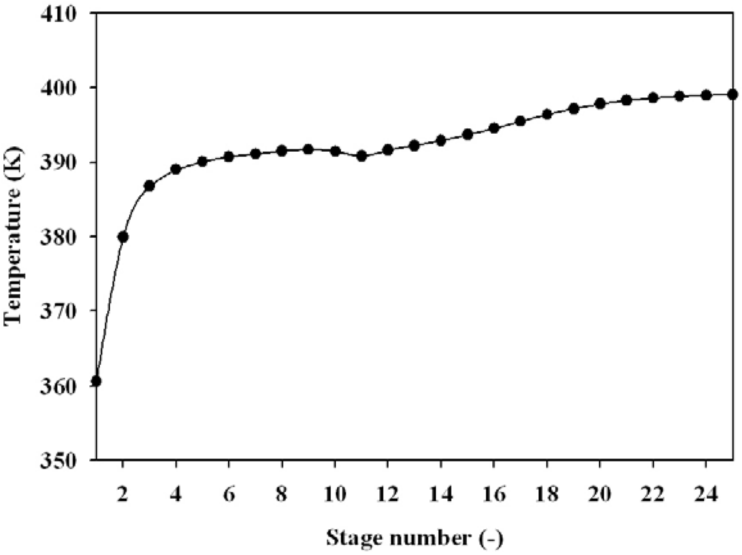
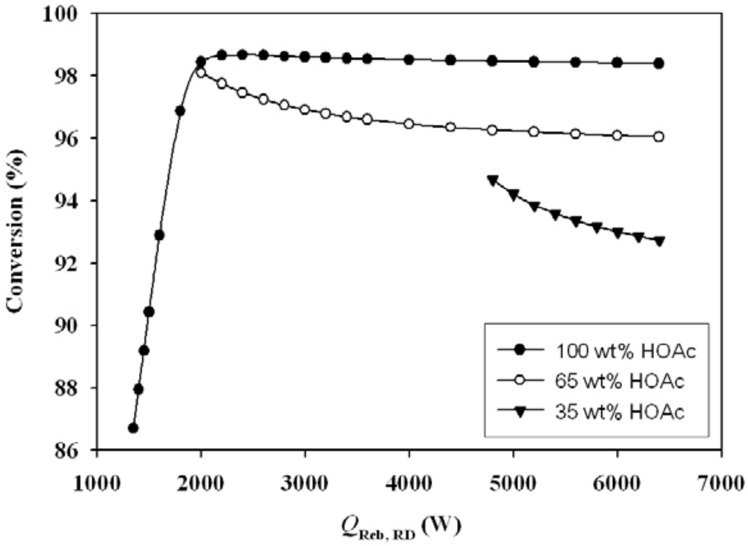
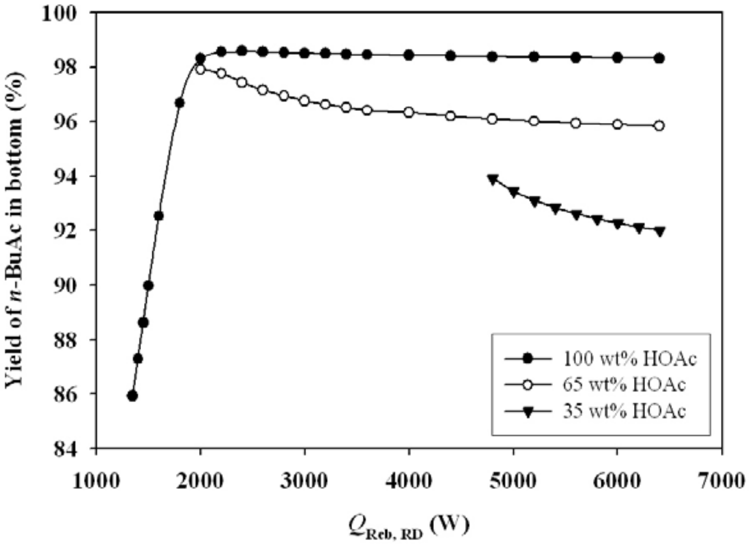


Fig. 6 (a) Composition profiles and (b) Temperature profile in liquid phase along the reactive distillation column (a single RD with decanter and total reflux ratio, reboiler heat duty of 2000 W, rectifying, reaction and stripping stages = 5, 11 and 7, respectively).

(a)


Conversion (%)
100
98
96
94
92
90
88
86
1000
2000
3000
4000
5000
6000
7000
$Q_{\text{Reb, RD}}$ (W)
100 wt% HOAc
65 wt% HOAc
35 wt% HOAc

(b)


Yield of *n*-BuAc in bottom (%)
100
98
96
94
92
90
88
86
84
1000
2000
3000
4000
5000
6000
7000
$Q_{\text{Reb, RD}}$ (W)
100 wt% HOAc
65 wt% HOAc
35 wt% HOAc

(c)

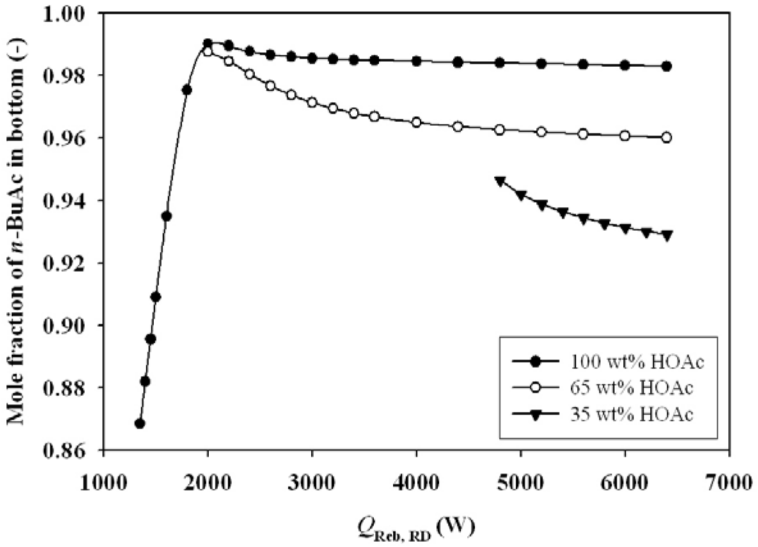
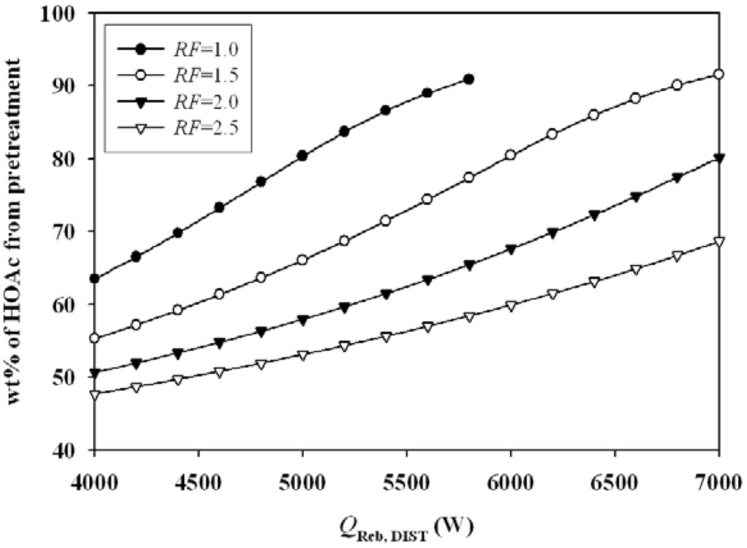


Fig. 7 Effect of feed acetic acid concentration on (a) the conversion of acetic acid, (b) the yield of *n*-butyl acetate, and (c) the mole fraction of *n*-butyl acetate.

(a)



(b)

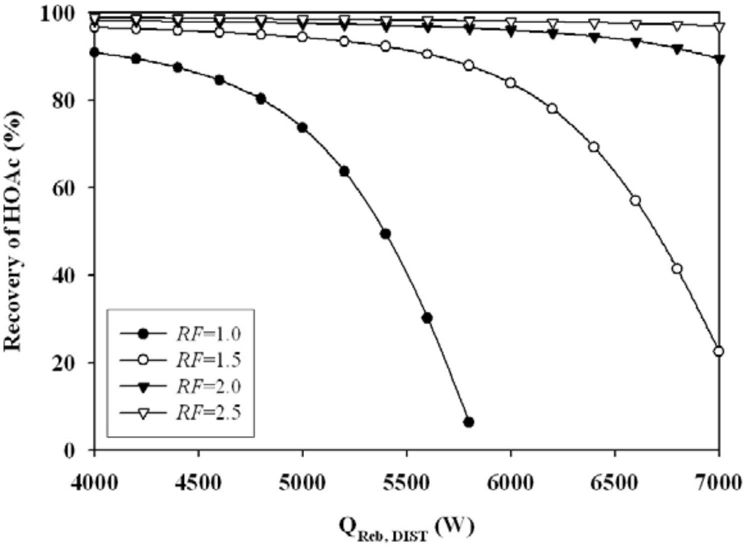


Fig. 8 Effects of reboiler heat duty column and reflux ratio of a conventional distillation column on (a) concentration (wt.%) of acetic acid product, and (b) recovery of acetic acid product (feed flow rate of acetic acid = 35 mol/hr (35 wt.%), feed stage = 4, total stages = 9).

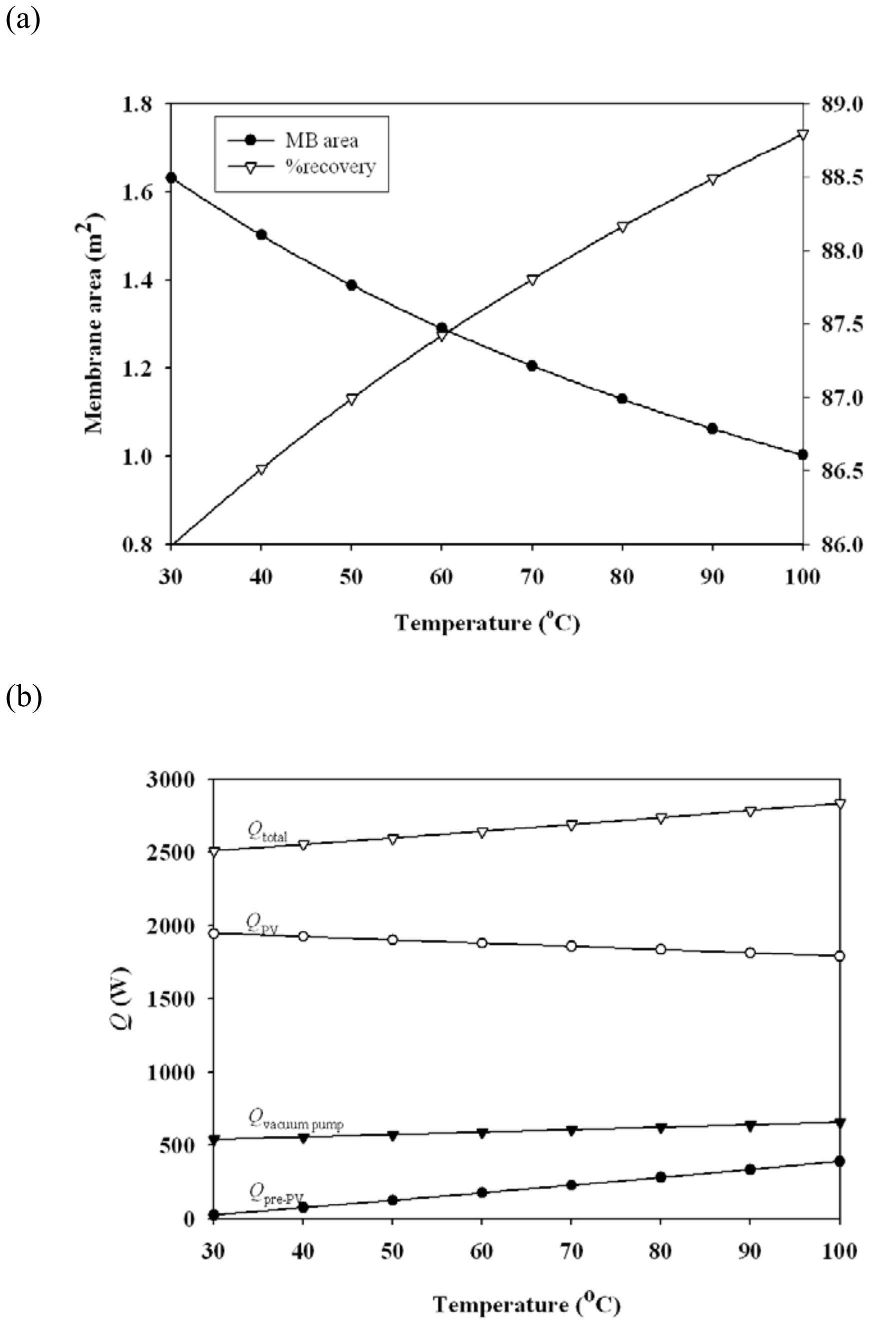


Fig. 9 Effects of operating temperature of pervaporation on (a) the required membrane area and the recovery of acetic acid, and (b) the energy consumption (increasing the dilute acetic acid stream from 35 to 65 wt.%, flow rate of feed dilute acetic acid = 35 mol/hr).

CHAPTER II

The Use of Dilute Acetic Acid for Butyl Acetate Production in a Reactive Distillation: Simulation and Control Studies

1. Introduction

The aqueous solution of acetic acid is normally founded as a by-product from many chemical and petrochemical processes. Examples of such relevant processes include the production of cellulose acetate, an ester group of cellulose used in lacquers and photographic film process, which is typically associated with a 35 wt.% aqueous solution of acetic acid as a waste stream. Other important processes involve the synthesis of terephthalic acid and glyoxal, which have by-products of dilute acetic acid streams of typically 70 wt.% and 13-20 wt.%, respectively (Saha et al., 2000; Xu et al., 1999).

Recovery of dilute acetic acid, therefore, becomes important issues due to economic and environmental awareness. A conventional process applied to separate acetic acid from its aqueous solution involves a dehydration process by using a distillation column and then, high-purity acetic acid obtained is used as a raw material in the synthesis of many valuable chemical compounds. Due to the special properties of acetic acid, the separation with distillation is a difficult and expensive task, requiring the column with many stages and high energy consumption. An alternative process for acetic acid recovery is an extraction by using a suitable solvent; however, it is limited by phase separation (Ragaini et al., 2006; Saha et al., 2000). Furthermore, additional steps to recover and recycle the solvent are necessary.

Recently, a number of researches has been focused on the implementation of a reactive distillation as a promising alternative to recover dilute acetic acid. In comparison with the traditional approach of separation followed by reaction processes, performing the chemical reaction and separation in a single reactive distillation column offers advantages not only to separate acetic acid from its aqueous solution but also to produce a valuable product at the same time, thereby reducing capital and energy costs. Following this approach, the direct utilization of dilute acetic acid as a reactant for the production of a high-valued ester, a common solvent used in chemical industries, has received much attention (Xu et al., 1999; Hung et al., 2006). In general, the esterification of acetic acid and different alcohols is represented by the following reaction:

$$\text{Acetic Acid} + \text{Alcohol} \Leftrightarrow \text{Acetate} + \text{Water} \qquad (1)$$

Since the esterification reaction is equilibrium limited, the use of the reactive distillation is an attractive method by removing products from the reaction mixture that leads to an increase in a reactant conversion. In addition, it was reported that ternary azeotropic mixture of acetate, alcohol and water is found (Cardona et al., 2004; Hanika et al., 1999), thus resulting in difficulties in downstream separation if a traditional production process is utilized. However, the reactive distillation may be effective in order to deal with these difficulties.

Generally, the design and operation of reactive distillation systems are considerably more complex than those of conventional reactors or distillations. Nonlinear phenomena, which are caused by interactions of reaction kinetics, phase equilibrium and mass transfer, and strong influences of various operating parameters, leads to the complicated behavior of the systems (Arpornwichanop et al., 2007). Although a large number of research efforts has been carried out to investigate and design reactive distillations with various systems (Sneesby et al., 1997; Subawalla and Fair, 1999; Luyben, 2000; Assabumrungrat et al., 2004), detailed design of reactive distillation for mixtures exhibiting phase-split behavior in a decanter is less obvious. Another important issue to be considered for the successful application of reactive distillation columns to recover dilute acetic acid is the design of control systems to maintain the columns at a desired condition. However, there are limited researches concerning on the closed-loop control of reactive distillations (Han and Clough, 2006). For examples, Al-Arfaj and Luyben (2000) evaluated six alternative control structures for an ideal two-product reactive distillation column. In all the schemes, a composition analyzer was used in the reactive zone to maintain stoichiometric balance. Wang et al. (2003) studied a reactive distillation column for butyl acetate production from a pure acetic acid under steady-state condition and designed the control strategy of the column. Product quality is maintained by controlling the temperature of the stage inside the column.

In this work, the implementation of a reactive distillation to recover dilute acetic acid via esterification with butanol for the production of butyl acetate, a relatively important solvent, is investigated. Simulation studies of the effect of dilute acetic acid concentration on the reactive distillation performance in terms of acetic acid conversion and butyl acetate production are carried out using HYSYS commercial software. The influences of key design and operating variables on the performance of the reactive distillation are also evaluated in order to determine an optimal configuration of the reactive distillation column. Finally, the closed-loop control of the reactive distillation column based on the obtained suitable column configuration and specifications are considered.

2. Simulation of Reactive Distillation

A steady-state simulation of a reactive distillation for the production of butyl acetate from esterificaiton of dilute acetic acid and butanol is performed using HYSYS commercial software. A rigorous equilibrium stage model and NRTL model for describing thermodynamic properties and phase equilibriums are used (Singh et al., 2006; Sahapatsombud et al., 2005). The configuration of a reactive distillation column under the study is shown in Fig. 1. There are three zones in the column. The rectifying and stripping zones operates exactly as a nonreactive distillation column in order to purify top and bottom products, respectively. Butyl acetate (BuOAc) and water (H_2O) are formed in the reactive zone where the esterification of acetic acid (HOAc) and butanol (BuOH) as in Eq. (2) is carried out. The kinetic expressions of this reaction in the presence of Amberlyst 15 as catalyst reported by Steinigeweg and Gmehling (2002) are used in this study (Eqs. (3)-(5)).

$$\mathrm{HOAc} + \mathrm{BuOH} \xleftrightarrow{\mathrm{H}^+} \mathrm{BuOAc} + \mathrm{H_2O} \tag{2}$$

$$r = k_f \left(a_{HOAc} a_{BuOH} - \frac{a_{BuOAc} a_{H_2O}}{K_{eq}} \right) \tag{3}$$

$$k_f = 6.1084 \times 10^4 \exp\left(-\frac{56.67 \text{ kJ/mol}}{RT}\right) \tag{4}$$

$$K_{eq} = 0.6206 \exp\left(-\frac{10.99 \text{ kJ/mol}}{RT}\right) \tag{5}$$

The molar feed ratio of HOAc to BuOH is kept constant at 1:1 following the stoichiometric ratio of the reaction. BuOH and HOAc feeds are mixed in a single stream and then introduced to the column at the same stage. The overhead vapor having the composition close to a ternary azeotropic mixture of H_2O, BuOH, and BuOAc is condensed in a condenser and then separated into two phases in a decanter (Hanika et al., 1999; Cardona et al., 2004). The aqueous phase is completely withdrawn from the decanter whereas the organic phase is totally recycled back to the column. BuOAc product is removed from the bottom of the column as it is the highest boiling point component in the system. The specifications of the reactive distillation column at standard condition are given in Table 1 (Wang et al., 2003).

Note that in order to use the reactive distillation model from HYSYS for simulating a reactive distillation with confidence, the reliability of the model is verified by comparing the simulation results with the experimental data from Steinigeweg and Gmehling (2002). With the same standard experimental conditions reported in their paper, results of the simulation run in comparison to the experimental data are shown in Table 2, indicating that the simulation results are in good agreement with the experimental data.

3. Steady State Analysis

Reactive distillation column behaves substantially differently from conventional distillation columns due to the interactions between chemical reaction and vapor-liquid equilibrium. In this section, the effects of the concentration of feed acetic acid and key design and operating variables are discussed. It is noted that the specifications of the reactive distillation column as shown in Table 1 for the synthesis of BuOAc is a preliminary configuration. The major design parameters include feed location and a number of reactive and nonreactive stages. After investigating the influence of these parameters, a suitable configuration of the reactive distillation column will be determined and used for a control study.

3.1 Effect of Feed Location

The feed location of HOAc and BuOH is a very important parameter in the operation of the reactive distillation column. For the system to be operated optimally, provision should be made for maximum contact area between the reactants so that the column is more used as a reactor and not as a distillation unit only. Fig. 2 shows the effect of the feed location on the HOAc conversion and mass fraction of BuOAc in the bottom stream at different concentration of feed acetic acid. In all simulations, the reboiler duty is fixed at 1300, 2200, 4700 and 9300 kW for the 100 wt.%, 80 wt.%, 50 wt.% and 30 wt.% of HOAc concentration in the feed stream, respectively. It is noted that at the specified heat duty, the product butyl acetate of 90 wt.% at the bottom stream is obtained and used as a basis for comparing the effect of the feed location. The results show that when the feed location is shifted down from the top stage of the reactive section, the conversion of reactants decreases, leading to a decrease in the BuOAc concentration in the bottom product streams. This result is more evident if acetic acid with lower concentration is applied. From Fig. 2, the feed location at stage 12 provides the highest conversion of

HOAc and bottom product purity. It can be concluded that the most effective approach is to feed both the reactants into the column on the top of the reactive section. Therefore, all the rest simulations are carried out by determining the feed location at this stage.

3.2 Effect of Reactive Stages

In order to increase the conversion of HOAc, the optimum number of stages in the reactive section should be carefully provided. In all simulations presented here, the product purity of BuOAc at the bottom is at 99.5 wt.%. The number of reactive stages is varied from 6 to 14 stages. Fig. 3 shows the influence of the number of reactive stages on the conversion of HOAc and the required reboiler heat duty at different HOAc feed concentrations. For all cases under the conditions studied, it can be seen that increasing the number of reactive stages slightly increases the conversion of HOAc as more reactive stages pronounce the esterification of *n*-butanol and acetic acid. In addition, it was found an increase in reactive stage is less sensitive to the reboiler heat duty.

3.3 Effect of Non-Reactive Stages

Fig. 4 shows the influence of the number of rectification stages on conversion, reboiler duty and product stream at different concentration of HOAc in feed stream. In this study, a number of stages in the reactive section are fixed at 13 and the product specification is also set to 99.5 wt.% of BuOAc. For 100 wt.%, 80 wt.% and 50 wt.% of HOAc, increasing the number of rectifying stages slightly increases both the conversion of HOAc and the reboiler duty. Since more *n*-butanol and acetic acid from the decanter are returned to the column and to the reactive section, higher conversion of HOAc is observed. It is noted that an increase in rectifying stages required more reboiler heat duty to obtain BuOAc of 99.5 wt.%. However, for 30 wt.% of HOAc, an increase in a number of rectifying stages results in the slight decrease of conversion of HOAc and the increase of reboiler heat duty. From the results, it is indicated that no further separation stages in the rectifying section are required because the decanter ensures a sufficient separation of water from the organic compounds because of the low solubility of BuOH and BuOAc in water. Considering the influence of the number of stripping stages (not shown in the figure), it is found that increasing the number of stripping stages has no significant effect on the conversion of HOAc and reboiler duty for all the values of feed HOAc concentration.

3.4 Effect of Reboiler Duty

Fig. 5 shows the conversion of HOAc and the mass fraction of BuOAc in the bottom stream as a function of reboiler heat duty at different acid concentration. Considering for case in which 30 wt.% acetic acid is fed to the column, it is observed that increasing the reboiler duty increases the BuOAc purity in the bottoms. It is even possible to get higher conversion of HOAc with an increase in reboiler duty. For other cases, the conversion of HOAc and the mass fraction of BuOAc in the bottom stream show a similar trend. This is expected because an increase of the heat duty increases the temperature in the reactive section, resulting in the increased conversion of HOAc. It should be noted that as the concentration of HOAc in feed stream decreases from 100 to 30 wt.%, higher reboiler duty is required due to the presence of higher amount of water in fresh feed.

3.5 Suitable Configuration of Reactive Distillation Column

From the above studies on the influence of HOAc concentration and key design and operating variables, it is found that the HOAc concentration in feed stream is very important variable to design a reactive distillation column. It has an impact on design parameters, i.e., feed location, reboiler duty and total stages of column. As HOAc concentration is decreased from 100 wt.% to 30 wt.%, more energy consumption is required for the production of BuOAc with the purity of 99.5 wt.%. For example, with 30 wt.% and 50 wt.% HOAc, reboiler heat duty of 9400 and 4800 kW is required. Considering the required heat duty, the use of 80 wt.% HOAc as a reactant directly for the synthesis of BuOAc in a reactive distillation column seems to be practical. Fig. 6 shows temperature and composition profiles within the column fed by BuOH and 80 wt.% HOAc at the stoichiometric ratio. At the top of the column, a heterogeneous azeotropic mixture between water, BuOH and BuOAc is formed and then separated into the aqueous and organic phases in the decanter. The results in Table 3 show that the distillate stream contains mostly water (94.9 wt.%) whereas the major component of the bottom stream is BuOAc (99.5 wt.%). Table 4 presents a suitable configuration of the reactive distillation column fed by 80 wt.% HOAc and pure BuOH which is used for further control study.

4. Control of Reactive Distillation

Based on the optimal configuration of a reactive distillation column for butyl acetate production from dilute acetic acid (80 wt.%), the control system of the reactive distillation is studied with the objective to maintain the BuOAc purity of 99.5 wt.% at the bottom product stream. Since the aqueous phase consisting of mainly water is moved from the overhead decanter as distillation and water composition is determined by the liquid-liquid equilibrium, only the composition of BuOAc at the bottom stream is controlled.

Three alternative control structures are studied for controlling the reactive distillation column with a single mixed feed of dilute HOAc and pure BuOH introduced at the 8th stage from the top of the column. The first and the second schemes are based on tray temperature control for regulating the product at a desired specification. This control strategy is known as an inferential control technique and is widely used in industries because the cost of on-line composition analyzer and maintenance is expensive. The third control scheme uses a composition analyzer to direct control the product quality. Even though additional investment is required for the analytical equipment, a great improvement of process operation can be achieved (Liptak, 2003). It should be noted that all the control loops in the proposed control schemes are single-input single-output structures based on proportional-integral-derivative (PID) controllers. According to the actual applications in industries, the P controller is used in level control loop, the PI controllers are used in flow and pressure control loops and the PID controller is used in temperature control loop. The controllers are tuned based on the Tyreus-Luyben tuning method. All valves are designed to be half open at steady state. As a disturbance can causes output variables to move away from their desired set point, the control structure should account for all potential disturbances having a significant effect on the process. In this study, we assume the disturbances consisting of step changes in the fresh feed flow rate (± 10 % of HOAc and BuOH feed flow rate) and the feed composition of HOAc and BuOH.

4.1 Selection of Tray Location for Temperature Control

Since column temperature is closely related to the product quality, the indirect control of product compositions by controlling the temperature of distillation column is commonly found in industrial applications. A typical procedure for selecting a tray location for temperature control is applied in this work (Tang et al., 2005). This procedure attempts to obtain high steady-state gain (relation of manipulated and controlled variables) and to avoid problems with nonlinearity by selecting the control tray where both positive and negative changes in a manipulated variable produce large and equal changes in a controlled variable. Fig. 7 shows the steady state temperature profile when reboiler heat duty as a manipulated variable is changed. Based on the criterion mentioned earlier, the temperature at the 24th stage is selected as the controlled variable of the reactive distillation.

4.2 Control structure 1 (CS1)

The typical control structure of reactive distillation is show in Fig. 8. The fresh feeds of HOAc and BuOH are flow-controlled. The column pressure is controlled by manipulating the condenser heat removal. The base level and reflux drum level are controlled by bottom product flow rate and distillate flow rate, respectively. The organic reflux flow is flow-controlled; it is kept constant at the nominal steady state condition. Temperature control of the 24th stage is implemented by manipulating the reboiler duty.

When the flow rate of HOAc is increased by 10%, it can be seen from Fig. 9 that CS1 is able to maintain temperature at the desired conditions; the controlled stage temperature can quickly be settled at its setpoint value. However, CS1 cannot control the column pressure; the pressure is moved from the desired value (1 atm) to a new steady state (1.105 atm). This can be explained by the limitation of the condenser in which the maximum removal of heat is limited at 3500 kW. It can be seen that the condenser level increases to 72.01 % and the purity of BuOAc at the bottom decreases to 98.48 wt.%. For case of 10 % decrease in HOAc feed rate (Fig. 9), both the temperature and pressure are controlled at the desired set point in 15 and 10 h, respectively. The BuOAc purity at bottom is 99.38 wt.% at bottom rate of 38.12 kmol/h.

Fig. 10 shows the responses of the process disturbed by ± 10 % BuOH feed rate. It is found that CS1 can handle with these changes. With 10 % increase of BuOH feed flow, the product purity of BuOAc at 99.28 wt.% and product rate at 42.38 kmol/h are obtained whereas with 10 % decrease of BuOH feed flow rate, the purity of BuOAc and the product flow are 99.56 wt.% and 35.19 kmol/h, respectively.

Fig. 11 shows the control response of CS1 for case of the step changes in feed composition (±5 wt.% of HOAc and -5 wt.% BuOH in fresh feed). It can be seen that when decreasing the concentration of HOAc from 80 wt.% to 76 wt.%, the results show that the purity of BuOAc at 99.30 wt.% is obtained at the flow rate of 36.69 kmol/h. In this case, both of the column temperature and pressure can immediately be controlled back to the their setpoint. However, when the concentration of HOAc in feed stream is increased from 80 wt.% to 84 wt.%, CS1 is not able to maintain the column pressure due to the limited capability of the condenser whereas it can control the temperature at the setpoint. For case of a decrease in the concentration of BuOH (95 wt.% BuOH in fresh feed), it is found that CS1 cannot handle this disturbance; the system becomes unstable.

From the control responses in Figs. 9 to 11, it can be concluded that CS1 cannot handle two unmeasured disturbances in the increase of HOAc feed rate and the decrease of BuOH feed composition. It is also observed that the condenser level is increased in all disturbances. Since the column temperature is controlled by reboiler duty, the increase of reboiler heat duty results in high vapor flow rate at the top of column leading to the increased pressure at the top of the column. To maintain the column pressure at the desired value, higher condenser heat duty is needed to condense more overhead vapors, resulting in high liquid level in the reflux drum. However, since the organic reflux flow is fixed, the increase in distillate rate is only the way to maintain condenser liquid level. As a result, this control structure cannot cope with the liquid level in reflux drum.

4.3 Control structure 2 (CS2)

Fig. 12 shows the schematic diagram of CS2. In this control structure, the fresh feeds of HOAc and BuOH are still flow-controlled and the column pressure is controlled by manipulating the heat removal of the condenser. Product stream flowrate at the bottom is employed to control the base level. As in CS1, the product composition is indirectly controlled by the control of the temperature at the 24th stage using reboiler duty as a control variable. However, the difference between CS1 and CS2 is in organic reflux flow and condenser level controlled-loops; the reflux drum level is controlled by manipulating the reflux flow and a constant reflux ratio (equal to the steady state value) is maintained by adjusting the distillate flowrate. As a result, in CS2, the reflux ratio can be controlled at a desired value.

The response of the column under the change in ± 10 % HOAc feed rate is shown in Fig. 13. From the figure, the 24th stage temperature and pressure can be controlled at the desired set point while the liquid level in reflux drum is not higher than 50 %. However, it is observed that the BuOAc product purity is lower than its specification (< 99.5 wt.%). When the step change in BuOH feed rate (± 10 %) is introduced, the PID controllers can manage this disturbance quit well; the temperature is controlled at the set point with shorter settling time (12 h) (Fig. 14). However, the column pressure takes a long operating time to reach the desired target (1 atm). Under the disturbance in +10 % and –10 % of BuOH feed flowrate, the BuOAC products obtained are 99.21 and 99.54 wt.%, respectively.

The control performance of CS2 for case of the step changes in feed composition is shown in Fig. 15. The CS2 can handle with these changes. The controllers are able to maintain the temperature and pressure at its desired set point and the condenser liquid level is not higher than 51 %. However, the product purity of BuOAc at the bottom stream is still lower than the desired value.

From Figs. 13 to 15, it can be seen that in CS2, since the change in the organic reflux rate is allowed, the condenser level can be maintained within the specified value (< 55 %). In addition, CS2 is able to control the temperature and pressure at desired set point in all case studies. Considering the product specification of BuOAc, it is found that although CS2 can accurately control the temperature of the 24th stage, the product composition is changed from the design value, indicating the limitation of CS2. Therefore, CS3 is designed for the control of reactive distillation with respect to the BuOAc purity at 99.5 wt.% as a desired target.

4.4 Control structure 3 (CS3)

In this control scheme, all important control loops are the same as in CS2 except the composition control loop. Instead of using indirect composition control approach, the direct composition control is selected (Fig. 16). In CS3, the composition of the bottom product is assumed to be measurable and is controlled by manipulating the vapor boilup. It is noted that several types of instruments are available for composition measurement. Among of these, a gas chromatograph is the most widely used. Although the time required for composition analysis is a major problem, the equipment has presently been enhanced and can be used for automatic control (Liptak, 2003).

Figs. 17 and 18 show the control response when the flow rate of HOAc and BuOH are increased and decreased by 10 % whereas Fig. 19 demonstrate the response for the step changes in feeds composition. It can be seen that the CS3 is able to maintain the composition and pressure at the desired set point in all simulations. However, the oscillation in the process response is observed at the early period time. It is noted that the dynamic response of the composition control loops in CS3 are slower than the others because of the lag time in the bottom composition to the reboiler duty control loop.

5. Conclusion

This study concentrates on the direct use of dilute acetic acid for the synthesis of butyl acetate from esterification with butanol in a reactive distillation. The influence of important design parameters on the conversion of acetic acid is evaluated at different concentration of feed acetic acid. The results show that the maximum conversion of acetic acid and purity of butyl acetate at bottom stream can be achieved when both acetic acid and butanol feeds are introduced to the column at the top stage of the reactive section. Changing a number of stages in the reactive section and non-reactive section has slight effect on both the performance of the reactive distillation under the studied conditions. It is observed that when acetic acid with lower concentration is used, higher reboiler heat duty is required in order to obtain butyl acetate at 99.5 wt.% purity. Regarding to the required heat duty, the use of 80 wt.% acetic acid as a reactant for the synthesis of butyl acetate in a reactive distillation column seems to be practical and the optimal design of the column consists of 7 rectifying, 13 reactive, and 7 stripping stages.

Based on the optimum configuration of a reactive distillation column for the production of butyl acetate from dilute acetic acid (80 wt.%) and the obtained steady state conditions, three alternative control structures are studied for controlling the reactive distillation column at desired steady state conditions under unmeasured disturbances in feed flow rate and concentration of acetic acid and butanol. The first two control structures (CS1 and CS2) employ the indirect control of bottom product composition with fixed reflux flow rate and reflux ratio, respectively. Tray temperature is used to infer product composition. The third control structure uses the direct control of the purity of butyl acetate based on an internal composition measurement. The results show that the use of the composition measurement is required to achieve the product with desired specification.

Nomenclature

a_i	activity of component i	[-]
BuOAc	butyl acetate	[-]
BuOH	butanol	[-]
H_2O	water	[-]
HOAc	acetic acid	[-]
k_f	the forward rate constant	[mol/(g s]
K_{eq}	the reaction equilibrium constant	[-]
T	temperature	[K]

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Table 1. Specifications of reactive distillation column

Feed conditions		
	HOAc	BuOH
Flow rate (kmol/h)	100	100
Temperature (°C)	25	25
Pressure (atm)	1.2	1.2
Column specifications		
Number of rectifying stages		11
Numver of reactive stages		13
Number of stripping stages		15
Overhead pressure (atm)		1
Column pressure drop (atm)		0.134

Table 2. Comparison of experimental data and simulation results

	Experimental Data (Steinigeweg and Gmehling, 2002)	Simulation Results (HYSYS)
Bottom flow (mol/h)	42	41.9
Distillate flow (mol/h)	27	27.1
x_B (HOAc)	0.171	0.172
x_B (BuOH)	0.287	0.298
x_B (BuOAc)	0.517	0.527
x_B (H_2O)	0.025	0.003
x_D (HOAc)	0.143	0.1586
x_D (BuOH)	0	0
x_D (BuOAc)	0.008	0.0154
x_D (H_2O)	0.849	0.826
Reboiler Duty (Watt)	1070	950
X_{BuOH} (%)	64.58	64.31

Table 3. Optimal steady-state operating conditions for the reactive distillation fed by 80 wt % HOAc

	Bottom	Distillate
Flowrate (kmol/h)	49.5113	92.1637
Composition (Mass Fraction)		
H_2O	0	0.9490
HOAc	0.0017	0.0183
BuOH	0.0031	0.0190
BuOAc	0.9953	0.0137

Table 4. Compositions and flow rate of distillate and bottom streams

Feed conditions at 80 wt % HOAc		
Feed	HOAc	BuOH
Temperature (°C)	25	25
Pressure (atm)	1.259	1.259
Feed flow (kmol/h)	91.67	50
Feed stage	8	8
Column specifications		
Number of rectifying stages		7
Numver of reactive stages		13
Number of stripping stages		7
Overhead pressure (atm)		1
Column pressure drop (atm)		0.248

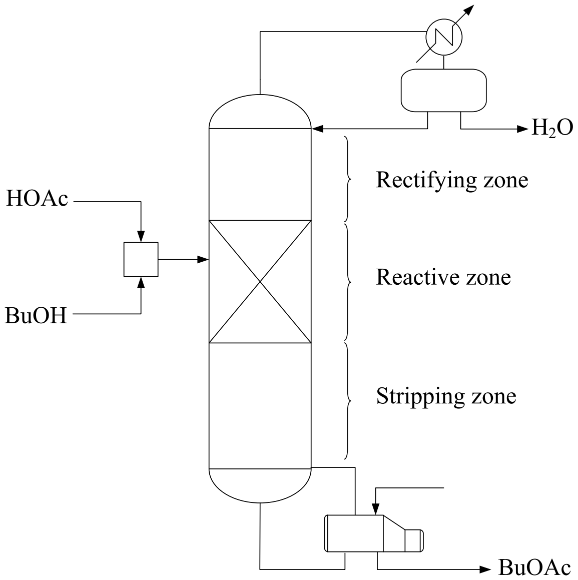

Fig. 1 Configuration of a reactive distillation column for butyl acetate process.

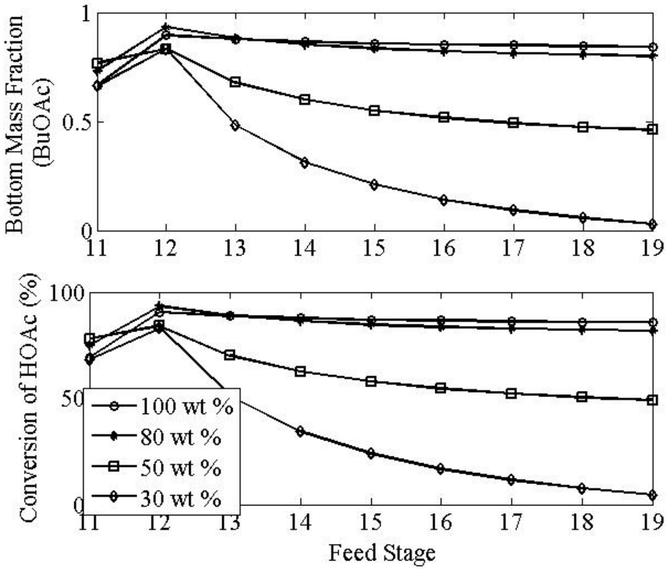

Fig. 2 Effect of feed location at different acid concentrations.

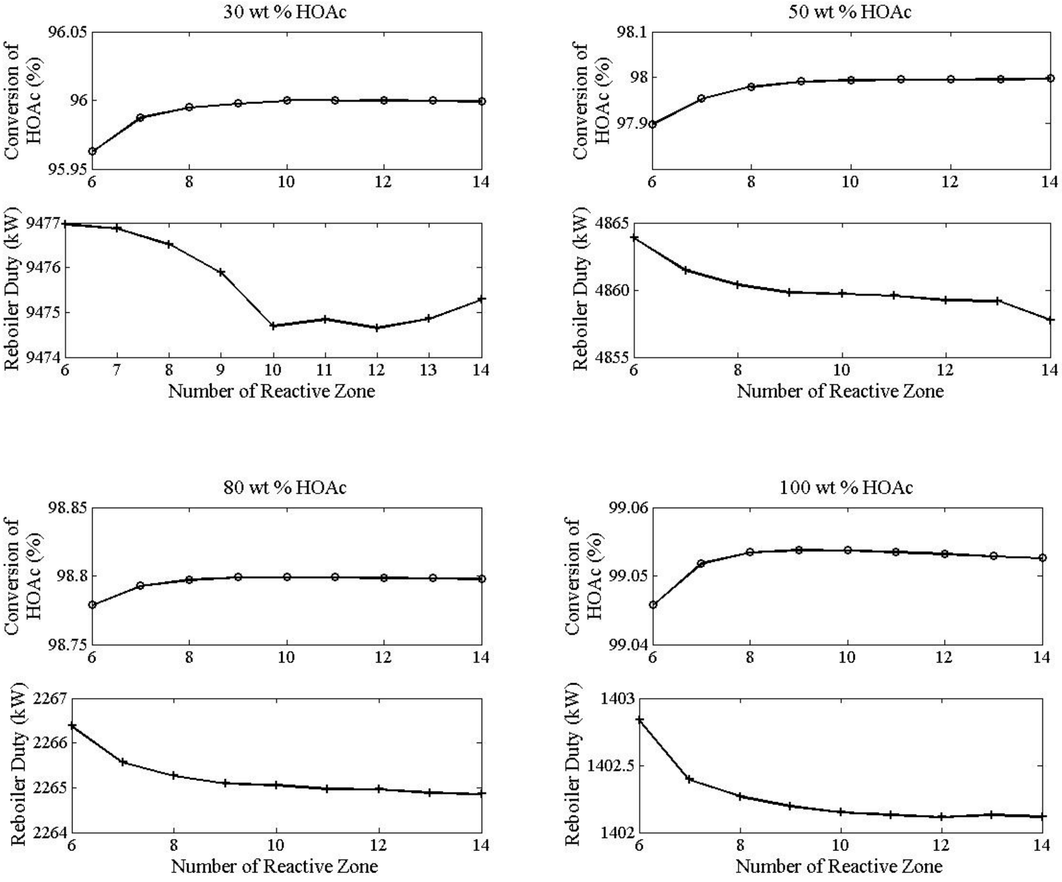

Fig. 3 Effect of the number of reactive stages at different acid concentration.

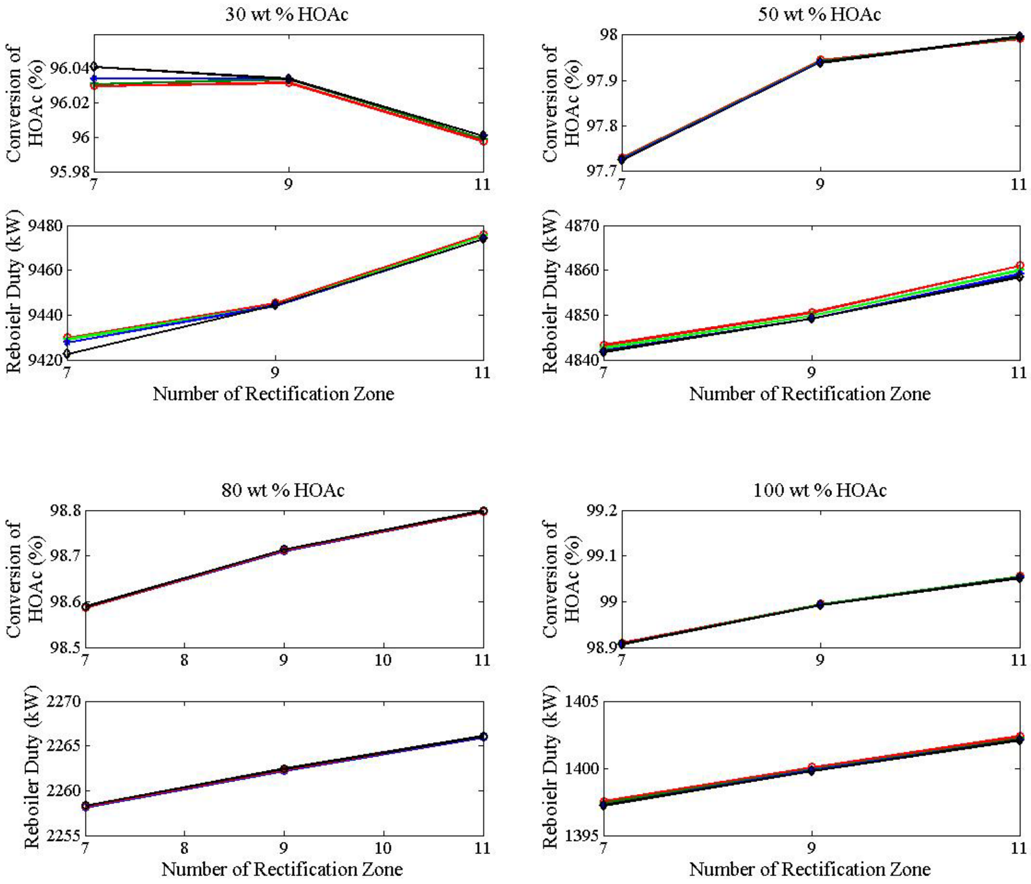

Fig. 4 Effect of the number of non-reactive stages at different acid concentration.

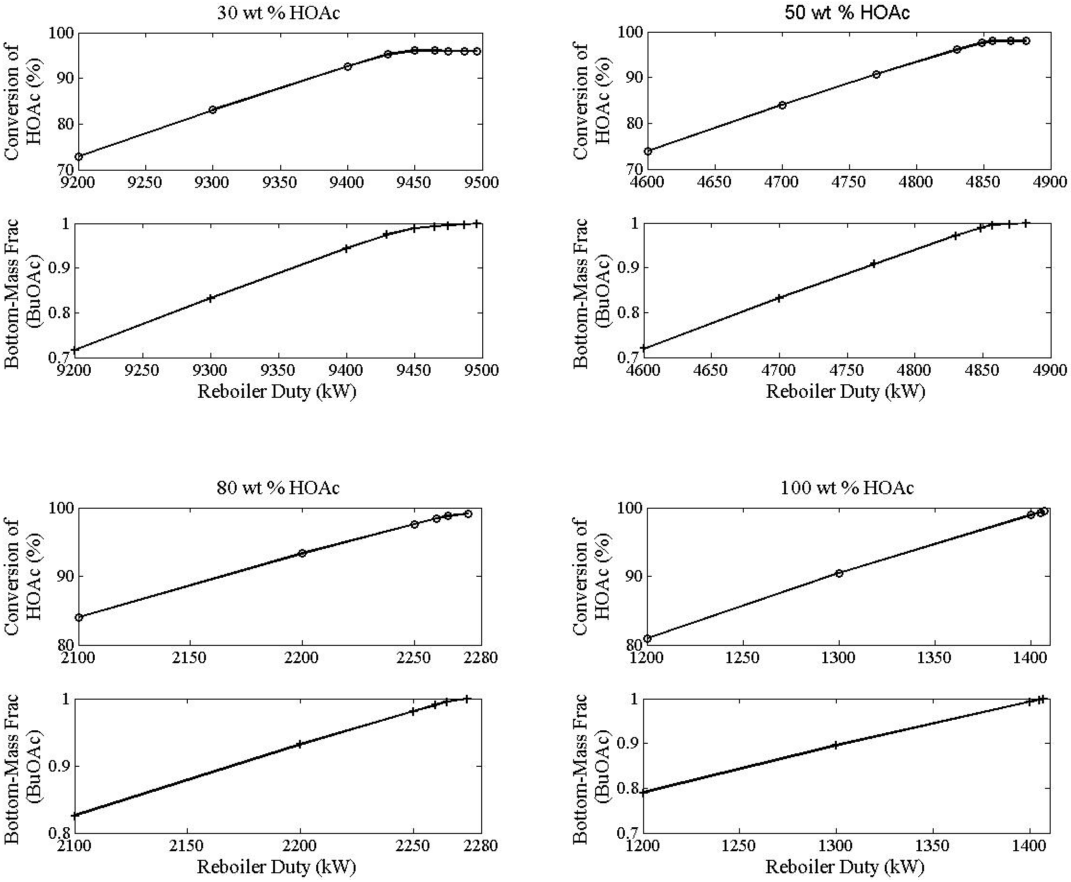

Fig. 5 Effect of reboiler duty at different acid concentration.

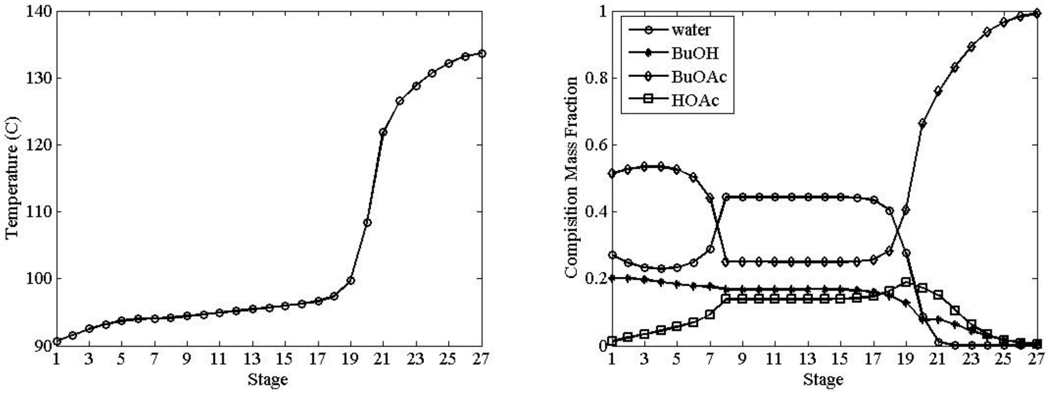

Fig. 6 Temperature and composition profiles at nominal operating condition.

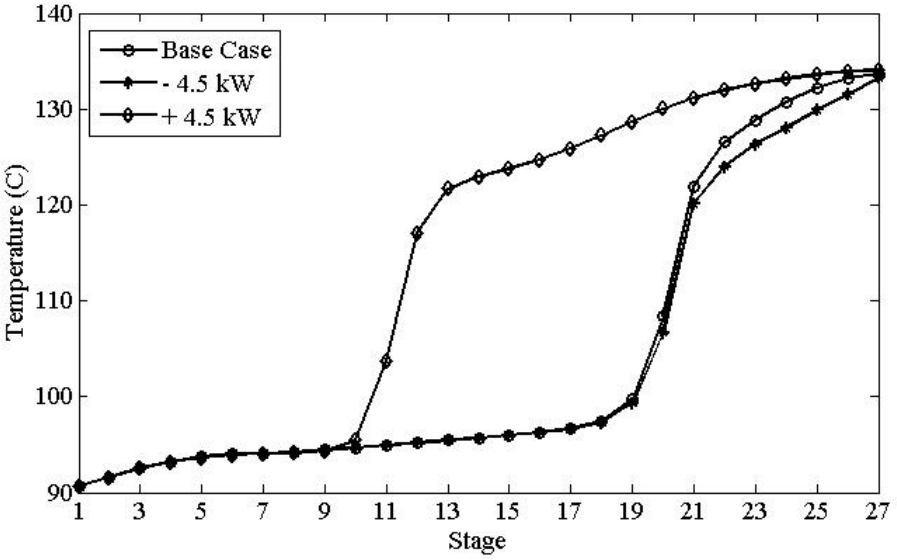

Fig. 7 Effect of reboiler heat duty on column temperature profiles.

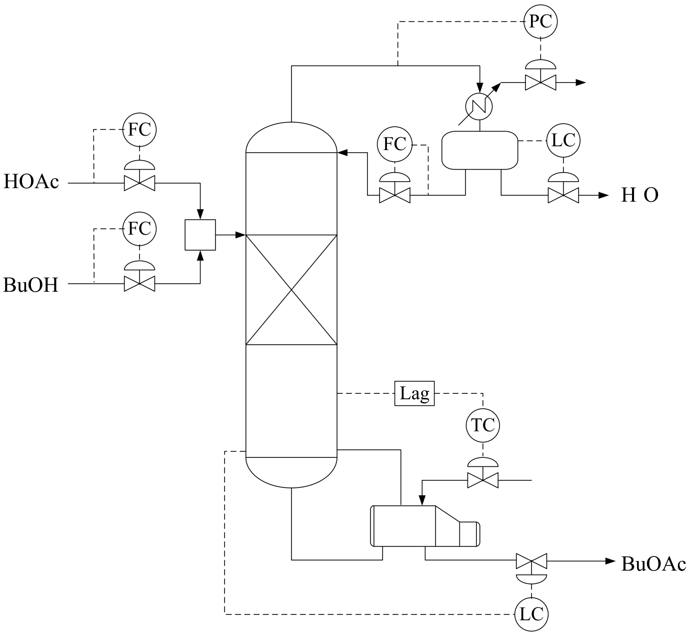

Fig. 8 Control structure 1: constant reflux flow.

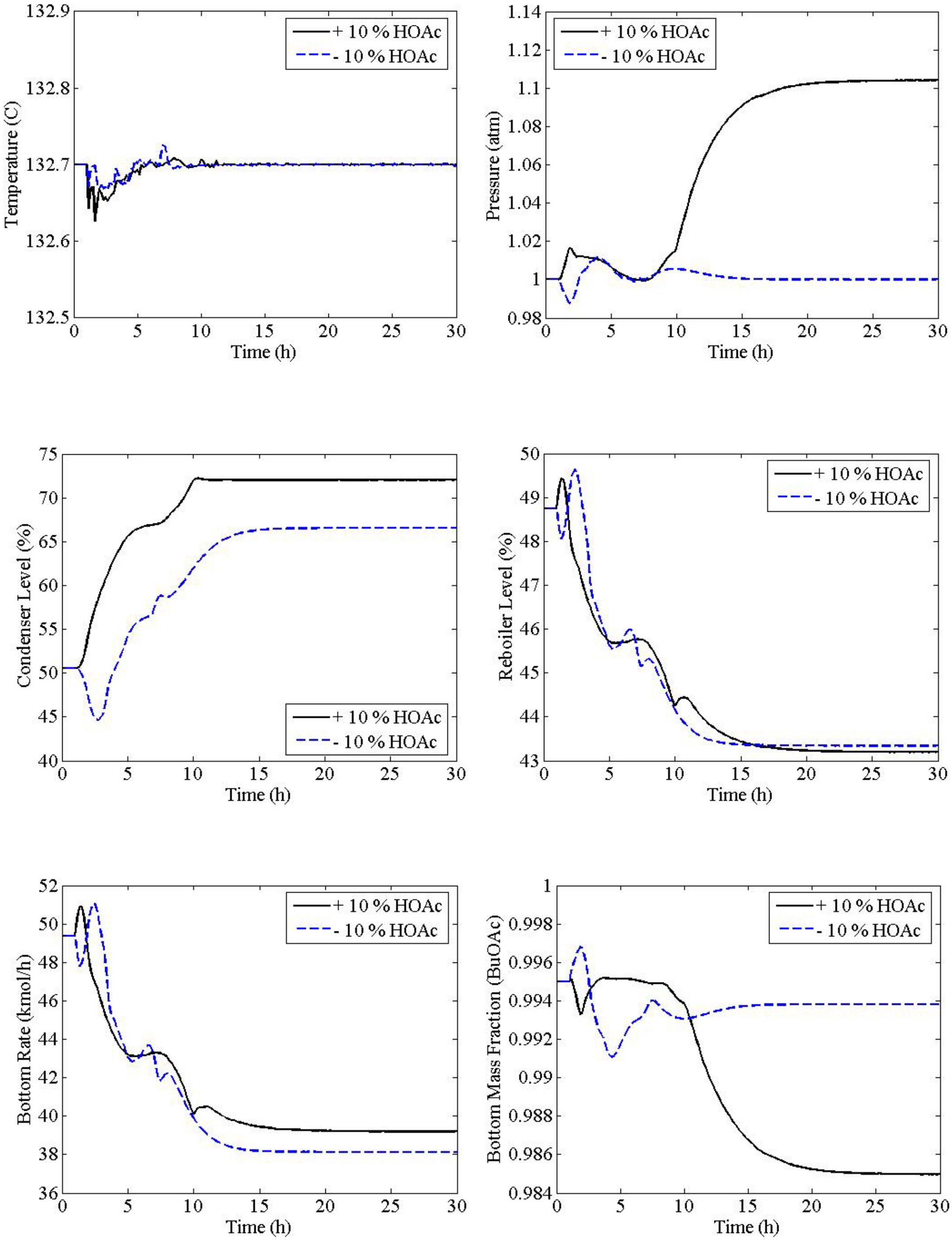

Fig. 9 Control responses of CS1 with ±10 % HOAc feed rate.

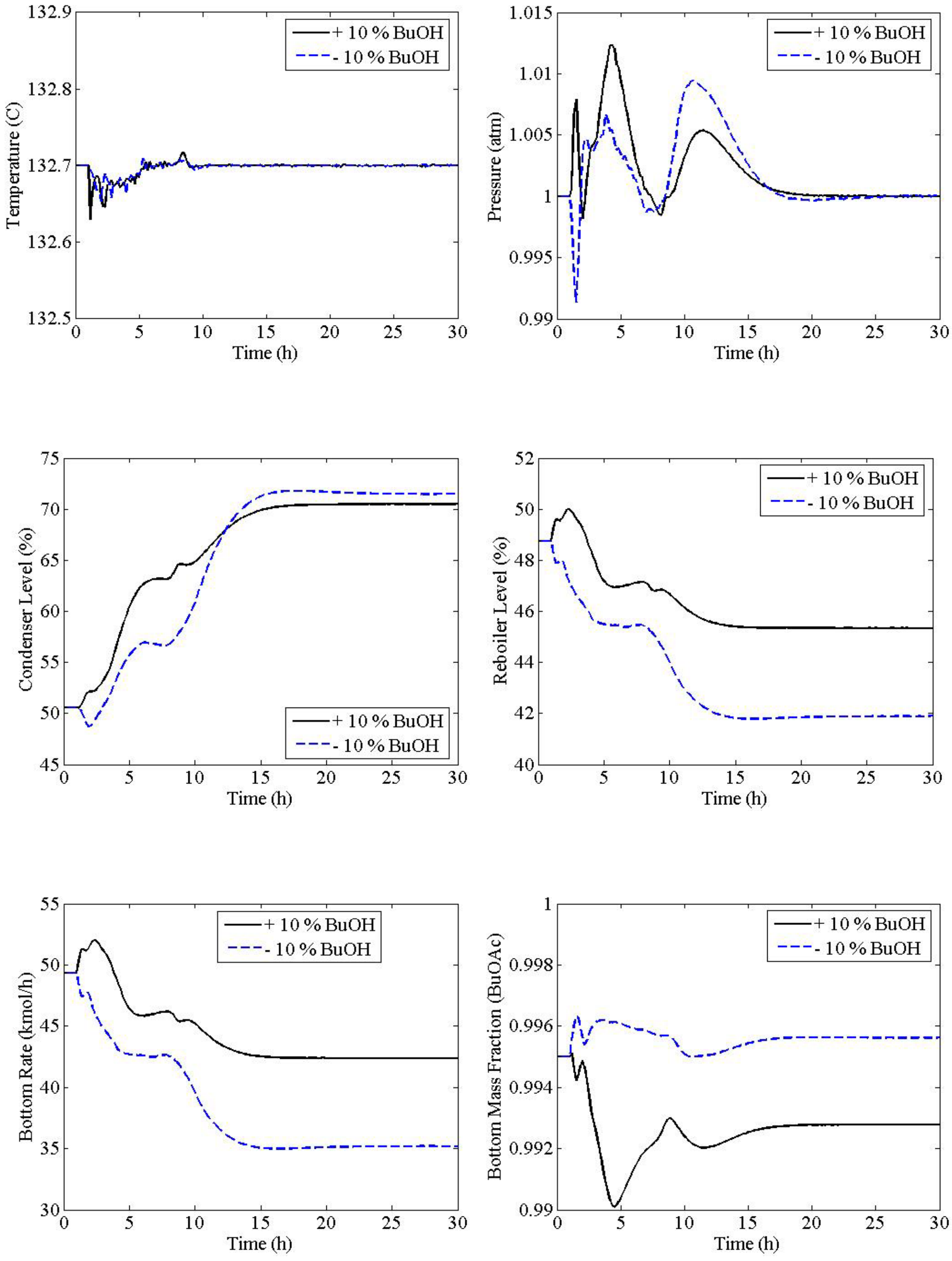

Fig. 10 Control responses of CS1 with ±10 % BuOH feed rate.

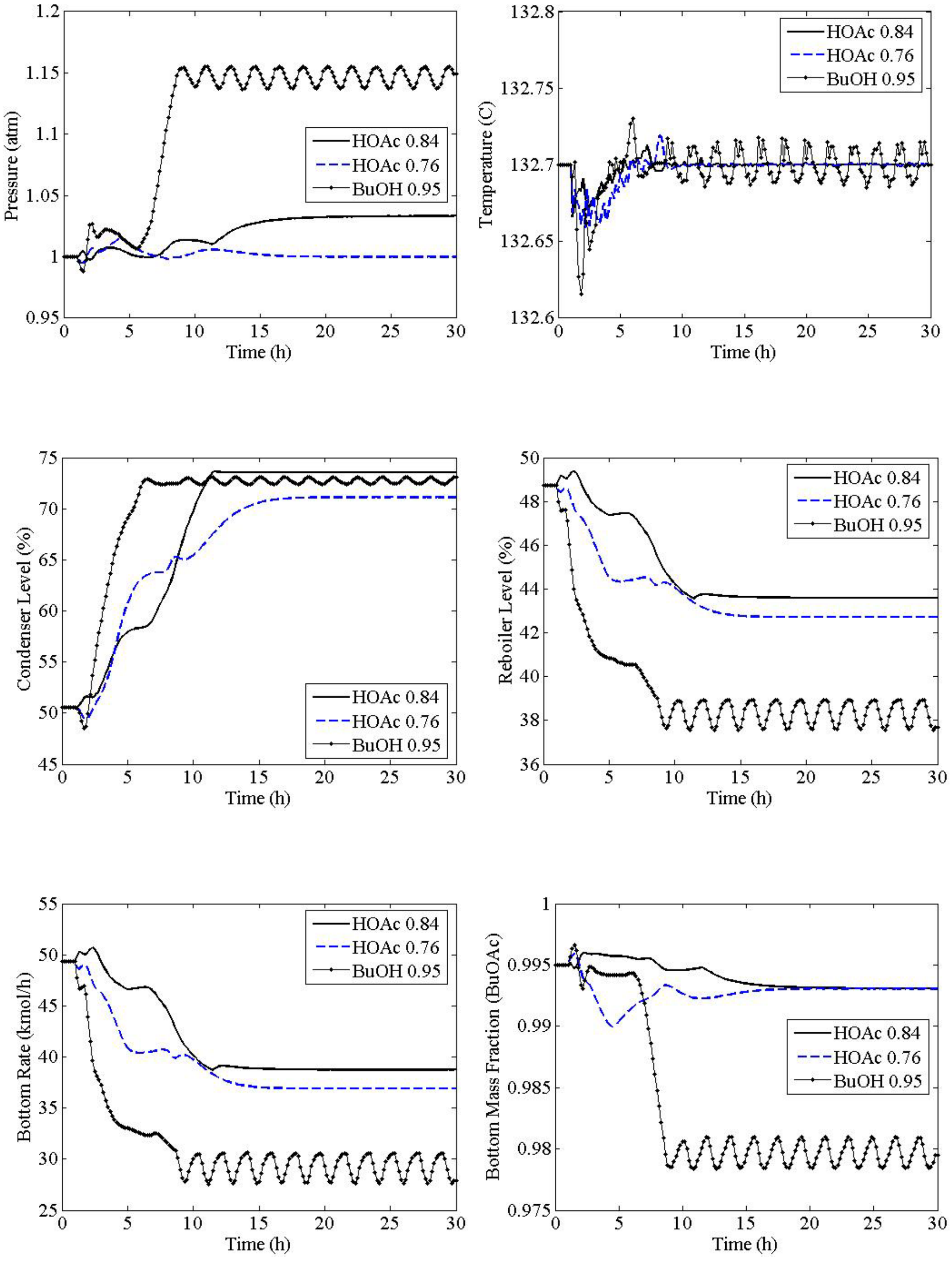

Fig. 11 Control responses of CS1 with step change in composition of feeds stream.

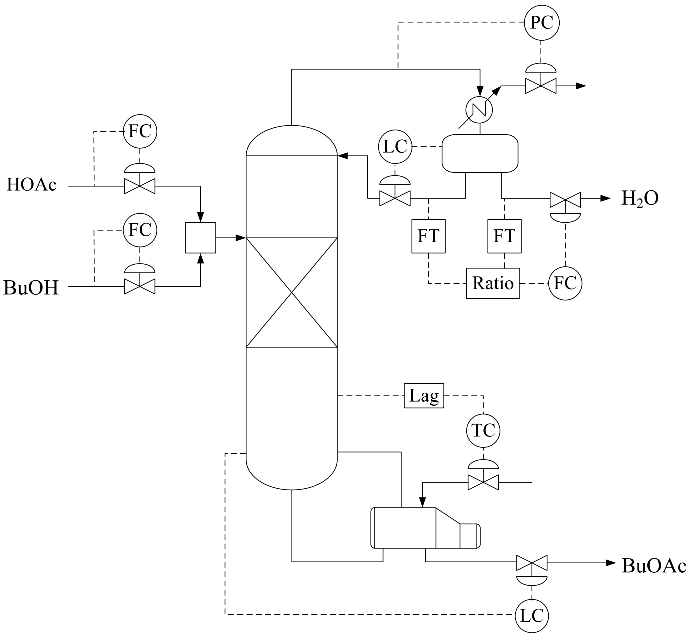

Fig. 12 Control structure 2: constant reflux ratio.