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DESIGN OF A REACTIVE DISTILLATION COLUMN FOR GLYCEROL ETHER PRODUCTION

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A Thesis Submitted in Partial Fulfillment of the Requirements
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น้ำมันไบโอดีเซลเป็นพลังงานทางเลือกที่สำคัญ ไบโอดีเซลถูกผลิตจากปฏิกิริยาทรานเอสเทอริฟิเคชันระหว่างน้ำมันพืชและแอลกอฮอล์ซึ่งจะได้ผลิตภัณฑ์ร่วมเป็นกลีเซอรอลดิบเสมอ การนำกลีเซอรอลดิบมาผลิตเป็นกลีเซอรอลอีเทอร์จะช่วยเพิ่มมูลค่าให้แก่กลีเซอรอลดิบอีกทั้งยังเพิ่มความสามารถในการแข่งขันของผู้ผลิตไบโอดีเซล งานวิจัยนี้จะสนใจการผลิตกลีเซอรอลอีเทอร์จากปฏิกิริยาอีเทอร์ริฟิเคชั่นระหว่างกลีเซอรอลบริสุทธิ์และเทอร์บิวทิวแอลกอฮอล์โดยใช้หอกลั่นแบบมีปฏิกิริยา เนื่องจากธรรมชาติของปฏิกิริยาอีเทอร์ริฟิเคชั่นถูกจำกัดด้วยสมดุลเคมีดังนั้นหอกลั่นแบบมีปฏิกิริยาซึ่งเกิดปฏิกิริยาเคมีและการแยกสารในเวลาเดียวกันจึงถูกใช้ในการปรับปรุงประสิทธิภาพการผลิตกลีเซอรอลอีเทอร์ อย่างไรก็ตามในกลีเซอรอลดิบจะมีเมทานอลผสมเสมอ และเมทานอลสามารถนำไปผลิตเป็นไดเมทิลอีเทอร์ ซึ่งไดเมทิลอีเทอร์เป็นพลังงานทางเลือกที่นำไปใช้แทนน้ำมันดีเซลหรือแก๊สแอลพีจีได้ การวิจัยนี้ได้แบ่งการศึกษาออกเป็น 3 ส่วน ส่วนแรกเป็นการศึกษาตัวแปรของหอกลั่นแบบมีปฏิกิริยาต่อประสิทธิภาพการผลิตกลีเซอรอลอีเทอร์ จากผลการศึกษาพบว่าหอกลั่นแบบมีปฏิกิริยาสามารถเพิ่มค่าการเปลี่ยนของกลีเซอรอลเป็นกลีเซอรอลอีเทอร์ได้ถึง 99% และจากการวิเคราะห์ค่าใช้จ่ายรวมต่อปีพบว่าโครงสร้างหอกลั่นแบบมีปฏิกิริยาที่เหมาะสมมีจำนวนชั้นเท่ากับ 11 ส่วนที่สองเป็นการศึกษาตัวแปรของหอกลั่นแบบมีปฏิกิริยาต่อประสิทธิภาพการผลิตไดเมทิลอีเทอร์จากเมทานอลในกลีเซอรอลดิบ จากผลการศึกษาพบว่าหอกลั่นแบบมีปฏิกิริยาสามารถเพิ่มค่าการเปลี่ยนของเมทานอลได้ถึง 99% และจากการวิเคราะห์ค่าใช้จ่ายรวมต่อปีพบว่าโครงสร้างหอกลั่นแบบมีปฏิกิริยาที่เหมาะสมมีจำนวนชั้นเท่ากับ 12 ส่วนสุดท้ายเป็นการศึกษาตัวทำละลายสำหรับการแยกของผสมอะซีโอโตรประหว่างเทอร์บิวทิวแอลกอฮอร์และน้ำออกจากกันโดยตัวทำละลายที่ใช้ศึกษาประกอบด้วย เฮกซิลอะซีเตท 2-เฮปทาโนน และ 3-ออกทาโนน โดยตัวทำละลายเหล่านี้จะถูกเปรียบเทียบกันโดยใช้เกณฑ์ค่าใช้จ่ายรวมต่อปีและผลกระทบต่อสิ่งแวดล้อม จากผลการศึกษาพบว่าเฮกซิลอะซีเตทเป็นตัวทำละลายที่เหมาะสมที่สุด

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต ....
สาขาวิชา วิศวกรรมเคมี ลายมือชื่อ อ.ที่ปรึกษาหลัก ....
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KEYWORDS: GLYCEROL ETHER / DIMETHYL ETHER / REACTIVE DISTILLATION

PUNJAWAT KAEWWISETKUL: DESIGN OF A REACTIVE DISTILLATION COLUMN FOR GLYCEROL ETHER PRODUCTION. ADVISOR: ASST. PROF. AMORNCHAI ARPORNWICHANOP, D.Eng., 120 pp.

Biodiesel, an important alternative energy, is generally produced from a transesterification reaction of vegetable oils and alcohol. This reaction always generates crude glycerol as by-product. As a result, the utilization of crude glycerol to produce higher value-added products can increase the competitive potential of biodiesel producers. In this research, the production of di and tri tert-butyl ether of glycerol (known as glycerol ether) from etherification of glycerol and tert-butyl alcohol is studied. Due to the nature of the reversible etherification reaction, a reactive distillation in which chemical reaction and separation can occur at the same time in single unit is considered to improve the glycerol ether production. Furthermore, since methanol is always present in crude glycerol, it is considered to be used for the production of dimethyl ether, a promising alternative fuel to replace diesel fuel and liquefied petroleum gas. This study is divided into three parts. In the first part, the effects of key design and operating parameters of the reactive distillation on the performance of glycerol ether production are studied. The results show that the use of the reactive distillation can increase the conversion of glycerol to glycerol ether into 99%. Based on a total annual cost analysis, the optimal configuration of reactive distillation column consists of 2 rectifying stages, 8 reactive stages and 1 stripping stages. In the second part, the application of a reactive distillation to the dimethyl ether production is investigated and the analysis of a total annual cost is used to design the reactive distillation column. The simulation results show that the reactive distillation can increase the conversion of methanol in crude glycerol to dimethyl ether into 99% and the optimal configuration of the reactive distillation column consists of 2 rectifying stages, 8 reactive stages and 2 stripping stages. As a separation of tert-butyl alcohol and water, which forms a azeotrope mixture is a difficult task, in the final part of the study, the use of a extractive distillation using different solvents, which are hexyl acetate, 2-heptanone and 3-octanone, for recovery of tert-butyl alcohol in the production process of glycerol ether is studied and compared in terms of the total annual cost and potential environmental impact as criteria. The results show that hexyl acetate is the most appropriate solvent.

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Student's Signature ....
Advisor's Signature ....

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CHAPTER I
INTRODUCTION

1.1 Introduction

Nowadays, the growing fuel crisis has been a major problem that many countries are facing. This crisis is mainly attributed to the increasing energy demand from the growing population and limiting reserve of conventional fossil fuels. For this reason, searching for alternative fuel with environmental friendliness becomes very important. Among the various renewable fuels, biodiesel has been received considerable attention as it is clean and can be produced from vegetable oils (Nanda et al., 2011).

Generally, a transesterification reaction is most commonly used to produce biodiesel from alcohol and vegetable oils, such as rapeseed oil and soybean oil or animal fats. It is known that in this biodiesel production process, 10% by weight of vegetable oils or animal fats are converted to crude glycerol. As a result of the large demand of biodiesel in many countries, a large amount of crude glycerol is generated. However, crude glycerol contains many impurities, such as methanol, remaining catalyst, water, soap, salt and esters, which are generated during the reaction step (Kongjao et al, 2010, Tan et al, 2013). The composition of crude glycerol, in general, depends on a biodiesel production process, type of catalyst, used raw materials (i.e., type of vegetable oil) and level of post-treatments for each biodiesel process. Crude glycerol and refined crude glycerol will go through filtration, chemical addition and fractional vacuum distillation before it is sent to suppliers. Distillation of crude glycerol is a high energy demand process due to the high specific heat capacity of glycerol that leads to a high energy input requirement for vaporization. The pharmaceutical, cosmetic and food industries require higher purity grade of glycerol which the purification process to be more complex and cost more (Kongjao et al, 2010). However, the market prices of glycerol and crude glycerol are gradually lower because of the oversupply of glycerol caused by the increasing biodiesel production. For this reason, the use of glycerol to produce high value-added products would reduce the biodiesel production cost and increase the competitive potential of biodiesel producers (Singhabhandhu and Tezuka, 2010).

Glycerol ($C_3H_8O_3$) is the simplest trihydric alcohol which has the IUPAC name of propane-1,2,3-triol. It is also commercially known as glycerin, 1,2,3-trihydroxypropane, glyceride or glycol alcohol. Pure glycerol is colorless, non-toxic, biodegradable, biocompatible, odorless, viscous liquid with syrupy and sweet taste (Hunsom et al., 2013). It has three hydrophilic hydroxyl groups that are responsible for its solubility in water and its hygroscopic nature (Rahmat et al., 2010). Glycerol is known to be a versatile chemical that can be converted into numerous chemicals or bio-based products, such as drugs, personal products, oral care products, food and beverages, polyether, alkyd resins, triacetin, etc. However, a crude glycerol from biodiesel production is unlike pure glycerol. For example, color of crude glycerol from biodiesel production is brown or black as a result of vegetable color in crude glycerol (Tan et al., 2013).

Alternatively, glycerol can be used to produce various fuel additives (i.e., di and tri tert-butyl ether of glycerol), which increase a cetane number in diesel fuels and decrease an emission of pollutants, such as smoke, dust, carbon dioxide, hydrocarbon compound and aldehydes. Moreover, the fuel additive can reduce a cloud point and increases the performance and volume of diesel or bio-diesel product (Rahmat et al., 2010).

Methanol is always present in crude glycerol from biodiesel production because most industrial biodiesel processes utilize high molar ratio of methanol to vegetable oils to drive the transesterification reaction to completion (Tan et al., 2013). Methanol in crude glycerol is considered a valuable reactant to produce other value-added products, such as dimethyl ether, which is widely used as a promising alternative fuel to replace conventional diesel and liquefied petroleum gas (LPG). The advantages of dimethyl ether, compared to conventional diesel and liquefied petroleum gas (LPG), are lower incomplete combustion, lower carbon monoxide emission, lower nitrogen oxides emission, higher thermal efficiency, near zero aromatic emission and sulfur free (Su et al., 2013).

In earlier studies, many researchers used isobutene and glycerol to produce fuel additive, but isobutene is costly and needs additional process of purification, i.e., sulfuric acid extraction or molecular sieves to separate the fuel additive from the by-product (C_8–C_{16}) produced from oligomerisation reaction between glycerol and isobutene (Viswanadham and Saxena, 2011). There were a few studies focusing on using butylene instead of isobutene; however, butylene has a problem about unstable catalyst used in the process. Then, bio-alcohols, such as ethanol and butanol, were also employed to synthesis the fuel additive. The main disadvantage was to obtain mono tert-butyl ether of glycerol (by-product) more than di and tri tert-butyl ether of glycerol, which is the desired product (fuel additive). Presently, the tert-butyl alcohol and glycerol preferred to be used for producing the fuel additive as tert-butyl alcohol is cheaper than isobutene and tert-butyl alcohol can be produced from biomass such as starch, lignocellulosic and straw but isobutene is produced by catalytic cracking and steam cracking fractions of refining petroleum. In addition, tert-butyl alcohol is also a by-product from propylene oxide production (Viswanadham and Saxena, 2011). Moreover, the use of tert-butyl alcohol can prevent oligomerisation reaction (C_8-C_{16} hydrocarbon) and it can be dissolved in glycerol whereas isobutene needs to use solvents or be operated at high pressures. However, etherification reaction of glycerol with tert-butyl and alcohol has lower conversion and selectivity than etherification reaction between glycerol and isobutene because the catalyst is deactivated by water as a by-product. (Viswanadham and Saxena, 2011)

There are a number of studies concerning the production of fuel additives from tert-butyl alcohol and glycerol. Ozbay et al. (2010) compared various solid acid catalysts for the etherification reaction, such as Amberlyst-15, Amberlyst-16, Amberlyst-35, Nafion-SAC-13, and gamma-alumina. The result showed that Amberlyst-15 was the highest activity at temperature of 110°C, but Amberlyst-16 gave higher di tert-butyl ether of glycerol selectivity values. Frusteri et al. (2009) found that water as a by-product can inhibit the etherification reaction. Thus, separation water from the reactor can improve the conversion of glycerol. Kiatkittipong et al. (2011) determined the kinetic models of the etherification reaction of tert-butyl alcohol and glycerol in an autoclave reactor. The developed kinetic model was used to predict the performance of a reactive distillation which was used to enhance the etherification reaction. However, the purification of the product stream and the utilization of unreacted reactants were not mentioned in their study. Elena et al. (2012) designed the production process of fuel additive in the plug flow reactor. The process included separation and recycle systems. However, it was found that high amount of mono tert-butyl ether of glycerol (MTBG) was generated up to 60 wt%. as a by-product. Thus, high energy demand and large distillation column were required to recycle mono tert-butyl ether of glycerol (MTBG) to the reactor. The developed process generated massive water and used high tert-butyl alcohol to glycerol ratio. For this reason, after the etherification of tert-butyl alcohol and glycerol is complete, excess of tert-butyl alcohol is available for recovery. However, this excess tert-butyl alcohol is form azeotrope with water as by-product of etherification reaction of tert-butyl alcohol and glycerol. Binary mixtures which form azeotrope are characterized like a pure component when they are sent to a distillation column. For this reason, the separation of binary mixtures which form azeotropes is not possible separation by conventional distillation (de Figueirêdo et al., 2011).

To enhance the production process of fuel additive, a reactive distillation is regarded as a potential alternative as it offers some advantages over a conventional process. For example, both the reaction and separation tasks can be performed in single unit, so capital and operating costs can be reduced. Moreover, the reactive distillation provides high conversion, improves yield of products, and reduces energy consumptions (Harmsen, 2011). However, design of the reactive distillation is hardy design and involves many design variables, such as number of rectifying stage, number of reactive stage, number of stripping stage. For this reason, use of process flowsheet simulator, which has an integrated set of product and process design tools in order to synthesis and optimize the entire innovation and engineering workflow process throughout the plant, such as sensitivity analysis, design spec and calculator block, can facilitate a design process of complicated system like a reactive distillation.

The purpose of this study was to design a reactive distillation for etherification reaction of glycerol and tert-butyl alcohol for fuel additive production. Use of pure glycerol and crude glycerol were considered. A total annual cost was used as criteria to determine a suitable design of the reactive distillation. The simulation studies of the reactive distillation were performed using Aspen Plus simulator. Effects of primary design operating parameters, such as number of reactive, rectifying and stripping stages, reflux ratio, distillate to feed ratio, and molar ratio of reactants, on fuel additive production were analyzed. In this study, both glycerol and crude glycerol were used to produce the fuel additive. To enhance the reactive distillation-based process, the concept of using a reaction heat from the dehydration reaction of methanol into dimethyl ether to reduce energy consumption for glycerol separation from methanol in crude glycerol was also investigated.

1.2 Objectives

This work aimed design the reactive distillation for glycerol ether production from etherification reaction of pure glycerol and tert-butyl alcohol and dimethyl ether production from dehydration reaction of methanol in crude glycerol

1.3 Scopes of work

1. To study and simulate the reactive distillation for glycerol ether product (di and tri tert-butyl ether of glycerol) from etherification reaction of pure tert-butyl alcohol and pure glycerol by using Aspen Plus simulator. The kinetic rate for etherification reaction of tert-butyl alcohol and glycerol proposed by Kiatkittipong et al. (2011) was used in this study.
2. To study parameters of the reactive distillation for glycerol ether production, such as feed stage location, the number of reactive stages, reflux ratio and reboiler duty on conversion of glycerol and yield of glycerol ether.
3. To determine optimal operating parameters of the reactive distillation for glycerol ether production based on a total annual cost analysis.
4. To study and simulation the reactive distillation for dimethyl ether from dehydration reaction of methanol in crude glycerol by using Aspen Plus simulator. The kinetic rate of dehydration reaction proposed by Lei et al. (2011) was used in this study.

5. To study parameters of the reactive distillation for dimethyl ether production, such as feed stage location, the number of reactive stages, reflux ratio and reboiler duty on conversion of methanol.

6. To determine the optimal operating parameters of the reactive distillation for dimethyl ether production based on a total annual cost analysis.

CHAPTER II

LITERATURE REVIEWS

2.1 Crude glycerol from biodiesel production

Glycerol ($C_3H_8O_3$), also known as glycerine or propane-1,2,3-triol, is a by-product of biodiesel production by transesterification reaction from methanol and vegetable oil, such as rapeseed oil, soybean oil, and animal fat. In this process, 10% by weight of vegetable oil is converted into the crude glycerol. The purity of glycerol from biodiesel production is poor because the impurities, such as methanol, remaining catalyst, water, soap, salts and ester are formed during the reaction. This fact makes the price of crude glycerol low. Thus, glycerol from biodiesel production is called crude glycerol (Tan et al., 2013).

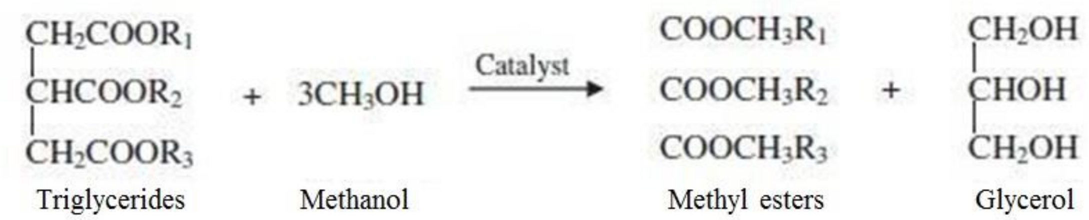

Figure 2.1 Transesterification reaction

Because the worldwide biodiesel industries have rapidly grown due to the increasing energy demand, the limiting reserve of conventional fossil fuels and the growing population, a large surplus of crude glycerol has been generated (Posada,2012).

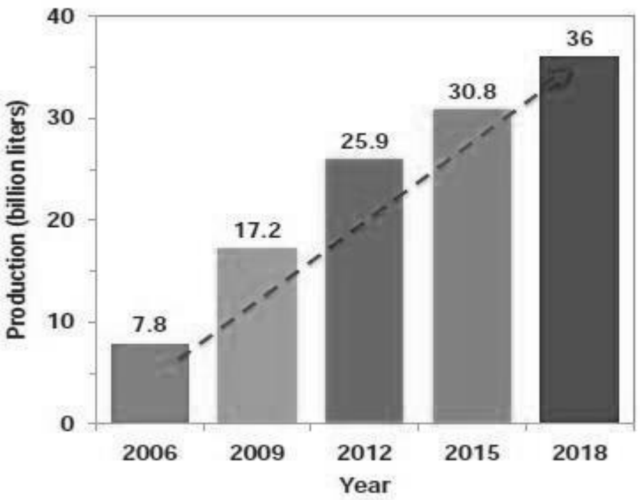

Figure 2.2 World's scenario of crude glycerol
(Nanda et al., 2011)

The trend of large surplus of glycerol will continue in the future (Ayoub and Abdullah, 2012). The rapid growth of the biodiesel industries has generated a surplus glycerol and oversupply in the market that has resulted in decreasing glycerol price and environmental concern about disposal of contaminated glycerol. Moreover, the demand of current market is not enough for the excess amount of glycerol which is generated from biodiesel production. Therefore, the new use for the glycerol or new applications of glycerol, for example, the conversion of glycerol into value-added products, must be explored. Some simple applications for the usage of glycerol have been investigated, such as acrolein (application in the synthesis between acrylic acid ester and acylic acid), 1,3-propanediol (application in the productions of polymer, cosmetic, food, lubricant and medicine) and hydrogen (Tan et al., 2013).

2.1.1 Composition of crude glycerol from biodiesel production

Crude glycerol from biodiesel production does not have only glycerol. For this reason, the price of crude glycerol is very low. Most biodiesel processes utilize 6 to 1 molar ratio of methanol and vegetable oil blend to drive the reaction to the completion. Thus, the methanol is always in the crude glycerol from biodiesel production (Tan et al., 2013).

Moreover, the composition of crude glycerol depends on the process of biodiesel production, type of catalyst, raw material such as type of vegetable oil and level of post-treatment for each biodiesel process. The physical and chemical properties of crude glycerol are important to their applications. Therefore, it is necessary to characterize the crude glycerol on its physical, chemical, and nutritional properties before the crude glycerol can be considered for possible value-added utilization (Thompson and He, 2006).

Many researchers had studied the composition of crude glycerol from biodiesel production. For example, Thompson and He (2006) studied the physical, chemical composition, and nutritional properties of crude glycerol from many biodiesel feedstocks such as rapeseed oil, soybean oil, mustard oil, canola oil, crambe oil, and waste cooking oil. Crude glycerol was produced from a batch reactor with transesterification reaction between methanol and vegetable oil. They found that glycerol in crude glycerol from any feedstocks was generally between 60 and 70 wt % of crude glycerol. Their results showed that the composition in crude glycerol from any feedstocks was not different significantly from the others. The viscosity of the crude glycerol ranged from 8.46 to 8.80 cPs, but the waste vegetable oil was 26.5 cPs. The heat of combustion of the crude glycerol ranged from 1.86×10^3 to 20.5×10^3 kJ/kg but the waste vegetable oil was 25.2×10^3 kJ/kg. For elements, the average amount of carbon content was approximately 25 wt%. The carbon, potassium, magnesium, sodium, phosphorus, and sulphur in small quantities ranged from 4 to 163 ppm but the sodium was 1 wt%. For nutrition, proteins content ranged from 0.06 to 0.44 wt%, fat content ranged from 1 to 13 wt% and carbohydrates ranged from 75 to 83 wt%, while waste vegetable oil had 60 wt% of fats and 27 wt% of carbohydrates.

Asad-ur-Rehman et al. (2008) studied the crude glycerol from biodiesel production by the transesterification reaction between sunflower oil and methanol. The crude glycerol consisted of 30 wt% of glycerol, 50 wt% of methanol, 13 wt% of soap, 2 wt% of moisture, approximately 2 to 3 wt% of salt (from primarily sodium and potassium salt), and 2 to 3 wt% of other impurities (non-glycerol organic matters).

Hansen et al. (2009) studied the chemical composition of crude glycerol from eleven Australian biodiesel manufacturers and found a large significant variation in the chemical composition collected from each manufacturer. Glycerol content in crude glycerol ranged between 38 and 96 wt%. The pH ranged between 2 and 10. In conclusion, the work from Thompson and He (2006), Asad-ur-Rehman et al. (2008) and Hensen et al. (2009) showed that the composition of crude glycerol was depended on the process of biodiesel production more than the raw material such as types of vegetable oil.

2.1.2 Purification of crude glycerol from biodiesel

The quality of crude glycerol from biodiesel production is low and unsuitable to be used as the feedstocks for further application because the crude glycerol has many impurities such as water, organic and inorganic salts, soap, methanol and vegetable color. Therefore, the purification of crude glycerol is required to convert the crude glycerol into a usable state (Tan et al., 2013). The high-purity glycerol is still required for pharmaceutical, cosmetic and food industries. However, the purification of crude glycerol is costly, especially for medium and small sized biodiesel plants (Rahmat et al., 2010).

Presently, many methods have been invented to purify the crude glycerol such as simple distillation, filtration, chemical treatment, adsorption (using activated carbon), ion-exchange (using resin), extraction, and crystallization (Kongjao et al, 2010). Two or more purification methods are integrated in the process in order to purify the crude glycerol. However, most of these purification processes are integrated with the simple distillation or vacuum distillation methods because the distillation and vacuum distillation are simple and generate high purity of glycerol.

For example, vacuum distillation has been found to be capable of recovering glycerol from crude glycerol in the presence of methanol, water, high concentration of salt and matter organic non glycerol (MONG) (Yong et al., 2001).

Yong et al. (2001) reported that the purification of crude glycerol by simple distillation at 120–126°C yielded glycerol purity at 96.6 vol%. However, the distillation of crude glycerol was a high energy demand process due to the high specific heat capacity of glycerol that led to a high energy input requirement for vaporization (Manosak et al., 2011).

In addition, the crude glycerol could be purified by ion-exchange method which was used for the removal of impurities such as color and odour. This technique did not require the vaporization of glycerol. For example, Isahak et al. (2010) studied the ion exchange resin method by using Amberlite IRN-78 and Amberlite 200 to purify crude glycerol. The resins were placed in the vertical column and formed a bed. These results showed that the impurities such as inorganic salts and free fatty acid salts had been removed when the ion-exchange resin method was used.

Hájek and Skopal (2010) studied the neutralization of soaps to free fatty acids and carbonates to carbon dioxide by adding phosphoric acid. The purity of glycerol was achieved at approximately 86 wt%. The by-product of neutralization was the potash phosphate fertilizer (KH_2PO_4). The process of this work was easy and environmentally-friendly because no special chemicals or equipment were required and all products can be utilized. Moreover, this work did not require distillation column to purify crude glycerol.

2.2 Glycerol ether production

Glycerol ether (di and tri tert-butyl ether of glycerol) is a fuel additive for diesel and biodiesel fuels. These chemicals are essential for diesel and biodiesel fuels. The benefits of added additive in diesel or biodiesel fuel include the increase of cetane number and the decrease of smoke, dust, CO_2, SO_x, NO_x, hydrocarbon and aldehyde compounds emission (Rahmat et al., 2010). Moreover, it can reduce cloud point, increasing performance and volume of diesel or biodiesel. In addition, the etherification reaction of glycerol with tert-butyl alcohol is a promising process which can convert glycerol to add more valuable products.

Generally, glycerol ether is produced by etherification reaction between isobutene and glycerol. Karinen and Krause (2006) studied the production of glycerol ether from glycerol and isobutene on Amberlyst-35 (ion-exchange resin catalyst) by varying the conditions of reaction such as temperature, feed ratio of isobutene to glycerol into batch reactor. The pressure in the reactor was operated at 1.5 MPa in order to dissolve isobutene into glycerol (at atmosphere pressure isobutene dissolved in glycerol only 3 mol%). The result showed that the ether product distribution could be controlled by adjusting feed ratio of isobutene to glycerol. Increasing feed ratio of isobutene to glycerol could improve the selectivity of the reaction of di and tri tert-butyl ether of glycerol. However, the excess isobutene increased the oligomerisation reaction which produced by-product (C_8–C_{16} hydrocarbons). If the feed ratio of isobutene to glycerol molar ratio was too low, major product was the mono tert-butyl ether of glycerol.

Klepáčová et al. (2005) compared etherification reaction of glycerol and isobutene with etherification reaction of glycerol and tert butyl alcohol. Etherification reaction of glycerol with tert-butyl alcohol was toward lower conversion and selectivity than etherification reaction of glycerol with isobutene because water, a by-product, deactivated the catalyst (Amberlys-15). However, isobutene was more high-priced than tert butyl alcohol and needed additional process to separate fuel additives from the C_8–C_{16} hydrocarbons which was a by-product from the oligomerisation reaction. Tert-butyl alcohol was a by-product from propylene oxide production and could be produced from biomass such as starch, lignocellulosic and straw while isobutene was produced by catalytic cracking and steam cracking fractions of refining petroleum. In addition, tert-butyl alcohol could be dissolved in glycerol at atmosphere pressure, therefore tert-butyl alcohol did not require high pressure or solvent for dissolving in glycerol (Viswanadham and Saxena, 2013; Frusteri et al., 2009). Many researchers studied etherification reaction of glycerol with tert-butyl alcohol. For example, Ozbay et al. (2010) compared types of solid acid catalysts for etherification reaction such as Amberlyst-15, Amberlyst-16, Amberlyst-35, Nafion-SAC-13, and gamma-alumina. The reaction was carried out in a continuous flow reactor. The result showed that Amberlyst-15 had the highest activity at about 110°C. However, Amberlyst-16 gave higher di tert-butyl ether of glycerol selectivity values. Viswanadham and Saxena (2013) developed Nano-crystalline BEA catalyst, which had an intercrystalline meso-pores structure, for etherification reaction between glycerol and tert-butyl alcohol to improve conversion and selectivity of etherification reaction. Nano-crystalline BEA catalyst of their studies could improve conversion and selectivity of di and tri tert-butyl ether of glycerol up to 99 mol% which was higher than conversion and selectivity of Amberlyst-15. The presence of water as a by-product could inhibit etherification reaction. Therefore, it was necessary to separate water from a reactor to increase the rate of reaction.

The kinetic rate constant of the etherification reaction of glycerol with tert- butyl alcohol are important information for process simulation. Kiatkittipong et al. (2011) determined kinetic models for the etherification reaction of tert-butyl alcohol and glycerol with Amberlyst-15 as a catalyst by regressing measured data from an autoclave reactor. Moreover, they used these kinetic to study the effects of operating parameters in the reactive distillation column such as reflux ratio, reboiler duty and number of stage by Aspen Plus simulator. However, purification of product and recycle system were not included in this study.

Elena et al. (2012) designed glycerol ether production process including product purification and recycling system for production of fuel additive by Aspen Plus simulator. These processes used conventional plug flow reactor for production of glycerol ether. The optimal operating parameters were determined to minimize total annual cost. However, this process produced mono tert-butyl ether of glycerol as a by-product up to 60 wt%. of product and demanded high tert-butyl alcohol to glycerol molar ratio to improve selectivity of di and tri tert-butyl ether of glycerol, so it required high energy and many distillation columns to recycle mono tert-butyl ether of glycerol and tert-butyl alcohol to reactor.

2.3 Dimethyl ether production

Dimethyl ether can be produced from natural gas, coal, biomass or coal. Moreover, Dimethyl ether is a sulfur-free, near-zero aromatics synthetic fuel. Currently, many researchers have studied catalysts to improve the conversion of dimethyl production. For example, Mollavali et al. (2009) developed grammar-alumina catalyst with different silica supports. The result indicated that the amorphous silica-modified catalysts showed better performance than the conventional alumina catalyst.

Hosseini et al. (2012) studied series of H-ZSM-5 zeolites catalyst, which were synthesized from the hydrothermal crystallization method, for the methanol dehydration process using a fixed-bed flow reactor in order to study the effects of different synthesis parameters such as hydrothermal crystallization temperature and the Si to Al molar ratio. The results found that the optimized catalyst prepared at 170 °C with the Si to Al molar ratio at 100 showed the best catalytic performance among the tested H-ZSM-5 zeolite.

Ladera et al. (2014) found that solid catalyst for the dehydration reaction of methanol such as gamma-Al_2O_3, silica modified alumina, TiO_2ZrO_2, and zeolite materials (HZSM-5, HY, $AlPO_4$, SAPOs, etc.) required high operating temperature (523 – 633 K). The high operating temperature led to catalyst deactivation. For this reason, Ladera et al. (2014) developed TiO_2-supported heteropoly acids catalyst (the heteropoly acids was the $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$) in order to reduce the operating temperature. The result showed that TiO_2-supported heteropoly acids catalyst could reduce operating temperature to 413 - 453 K. Moreover, TiO_2-supported heteropoly acids catalyst could provide more conversion than conventional catalyst.

The kinetic rate constant of the dehydration reactions of methanol into dimethyl ether was the necessary information for process simulation. Lei et al. (2011) determined kinetic models for the dehydration reactions of methanol into dimethyl ether by fitting the experimental data from the fixed bed micro reactor with macro porous sulfonic as a catalyst. Moreover, three processes for improved dimethyl ether production were developed from this kinetic. Process A consisted of a fixed-bed reactor and a reactive distillation column for the production of dimethyl ether. Process B consisted of a fixed-bed reactor and two conventional distillation columns. In addition, Process C consisted of a reactive distillation column and a conventional distillation column. The result found that process A consumed less energy when compared with other processes. Moreover, the total number of stage in reactive distillation for process A was less than process C.

2.4 Multiobjective optimization

Historically, the process design was intended to reduce the operating and capital costs. However, environmental problems have been a major topic of discussion. For this reason, many researchers considered both economic and environmental impacts into process design (Shadiya et al., 2010).

Quintero et al. (2008) compared sugarcane and corn as raw material for ethanol production in Colombia. Economic impact as net present value and potential environmental impact were used as criteria for choosing appropriate raw material. These results from criteria were normalized and converted to quantitative scores. The result showed that sugarcane was chosen to be material for ethanol production. Although the ethanol yield from corn was higher than that from sugarcane, the lower annual yield of corn per cultivated area makes it necessary to use more cropping areas. For this reason, when using corn as raw material, net present value was lower. Moreover, potential environmental impact of ethanol production process by using corn as raw material was higher. Consequently, sugarcane was more appropriate raw material for ethanol production in Colombian than corn.

Morais et al. (2010) compared the two alternative processes for biodiesel production from waste vegetable oils. These processes were alkali-catalyzed transesterification process with and without free fatty acids pre-treatment. Potential environmental impacts such as human toxicity potential by either inhalation or dermal exposure and economic potentials and economic impacts as net present value were used as criteria. The result showed that the process with free fatty acids with pre-treatment caused higher environmental impact. However, it was more advantageous in economic impact up to 1.8 times. This was due to the fact that alkali-catalyzed transesterification process with free fatty acids pre-treatment can increase conversion of triglycerides and fatty acids to biodiesel. For this reason, when considering the trade-offs between environmental impacts and economic impacts, transesterification process with free fatty acids pre-treatment was more suitable than transesterification process without free fatty acids pre-treatment.

Sandra et al. (2011) studied effects of residence time of triglycerides in reactor for biodiesel production on potential environmental impacts and economic impacts as net present value. The result showed that increasing residence time of triglycerides in the reactor can reduce potential environmental impacts. This was due to the fact that increasing residence time of triglycerides in the reactor resulted in more conversion of triglycerides to fatty acid methyl esters which was low on potential environmental impacts than triglycerides. However, residence time did not affect the potential environmental impacts when residence time was higher than 120 minutes. For the effects of economic impact, residence time of triglycerides at 120 minutes gave the highest net present value. For these reasons, optimum operating residence time of triglycerides in the reactor was chosen to be 120 minutes.

Olamide et al. (2012) compared the plug flow reactor and continuous stirred-tank reactor for acrylonitrile process by using potential environmental impacts such as human toxicity potential by either inhalation or dermal exposure and economic impact as net present value method as criteria. The objectives of their work were to gain the maximum profit and to reduce the waste generated. The result showed that using plug flow provided the net present value 69% of more than using continuous stirred-tank reactor. Moreover, it can reduce waste up to 38%. For this reason, using plug flow reactor for acrylonitrile process gave benefits in both environmental impact and economic impact.

CHAPTER III

THEORY

3.1 Glycerol Ether

Glycerol ethers are the mono, di, and tri tert-butyl ether of glycerol that can be produced from etherification reaction of glycerol and tert-butyl alcohol or isobutene.

Etherification reaction of glycerol and tert-butyl alcohol;

$$C_3H_8O_3 + C_4H_{10}O \leftrightarrow C_7H_{16}O_3 + H_2O \tag{3-1}$$

$$C_7H_{16}O_3 + C_4H_{10}O \leftrightarrow C_{11}H_{24}O_3 + H_2O \tag{3-2}$$

$$C_{11}H_{24}O_3 + C_4H_{10}O \leftrightarrow C_{15}H_{32}O + H_2O \tag{3-3}$$

Etherification reaction of glycerol and isobutene;

$$C_3H_8O_3 + C_4H_8 \leftrightarrow C_7H_{16}O_3 \tag{3-4}$$

$$C_7H_{16}O_3 + C_4H_8 \leftrightarrow C_{11}H_{24}O_3 \tag{3-5}$$

$$C_{11}H_{24}O_3 + C_4H_8 \leftrightarrow C_{15}H_{32}O \tag{3-6}$$

Where

$C_3H_8O_3$ is the glycerol, $C_4H_{10}O$ is the tert-butyl alcohol, C_4H_8 is the isobutene, $C_7H_{16}O_3$ is the mono tert-butyl ether of glycerol, $C_{11}H_{24}O_3$ is the di tert-butyl ether of glycerol, $C_{15}H_{32}O$ is the tri tert-butyl ether of glycerol and H_2O is the water and. (Kiatkittipong et al., 2011)

However, isobutene is more expensive than tert-butyl alcohol (Viswanadham & Saxena, 2013). Moreover, tert-butyl alcohol is major by-product from propylene production and can be produced from biomass such as starch, lignocellulosic and straw. Therefore, it can provide cheaper alternative raw material for glycerol ether production. Because di and tri tert-butyl ether of glycerol have more solubility in diesel fuel than mono tert-butyl ethers of glycerol and directly blend to diesel fuel, the etherification reaction of glycerol and tert-butyl alcohol must be directed to the maximum di, and tri tert-butyl ether of glycerol yield.

Glycerol ether is a fuel additive for diesel and biodiesel. The benefits for added glycerol ether in diesel or biodiesel are increasing cetane number, preventing incomplete combustion, decreasing emitted pollution such as smoke, dust, carbon dioxide, hydrocarbon compound and aldehydes. Moreover, it can reduce cloud point, which the value for diesel fuel is –16 °C and around 0°C for biodiesel, reduce viscosity, increase performance and volume of diesel or biodiesel. Moreover, it can help decrease SO_x and NO_x emission. Glycerol ether has been proved that it can replace the controversial tertiary alkyl ether (MTBE and ETBE) (Rahmat et al., 2010).

3.1.1 Kinetic model

Kinetic rate constants of the etherification reactions of glycerol with tert- butyl alcohol are necessary information for process simulation because this work focuses on the production of glycerol ether from the etherification of glycerol and tert-butyl alcohol. Kiatkittipong et al. (2011) determined the kinetic model for etherification reaction of glycerol with tert-butyl alcohol by regressing measured data from an autoclave reactor. The etherification reaction of glycerol and tert-butyl alcohol with Amberlyst-15 as a catalyst consists of three stepwise reversible reactions. Lists of the rate constants and equilibrium constants for etherification reactions of glycerol with tert-butyl alcohol are given in Table 3-1.The etherification reaction of glycerol and tert-butyl alcohol is shown as follows:

$$C_3H_8O_3 + C_4H_{10}O \xleftrightarrow[k_{-1}]{k_1} C_7H_{16}O_3 + H_2O \qquad (3\text{-}7)$$

$$C_7H_{16}O_3 + C_4H_{10}O \xleftrightarrow[k_{-2}]{k_2} C_{11}H_{24}O_3 + H_2O \qquad (3\text{-}8)$$

$$C_{11}H_{24}O_3 + C_4H_{10}O \xleftrightarrow[k_{-3}]{k_3} C_{15}H_{32}O + H_2O \qquad (3\text{-}9)$$

Where

$C_3H_8O_3$ is the glycerol, $C_4H_{10}O$ is the tert-butyl alcohol, $C_7H_{16}O_3$ is the mono tert-butyl ether of glycerol, $C_{11}H_{24}O_3$ is the di tert-butyl ether of glycerol, $C_{15}H_{32}O$ is the tri tert-butyl ether of glycerol and H_2O is the water (Kiatkittipong et al., 2011).

The rate expressions of each reaction step are shown as follows:

$$r_1 = k_1(a_{C_3H_8O_3}a_{C_4H_{10}O} - \frac{1}{K_{eq1}}a_{C_7H_{16}O_3}a_{H_2O}) \quad (3\text{-}10)$$

$$r_2 = k_2(a_{C_7H_{16}O_3}a_{C_4H_{10}O} - \frac{1}{K_{eq2}}a_{C_{11}H_{24}O_3}a_{H_2O}) \quad (3\text{-}11)$$

$$r_3 = k_3(a_{C_{11}H_{24}O_3}a_{C_4H_{10}O} - \frac{1}{K_{eq3}}a_{C_{15}H_{32}O}a_{H_2O}) \quad (3\text{-}12)$$

Abbreviations:

$a_{C_3H_8O_3}$ is the activity of glycerol; $a_{C_4H_{10}O}$ is the activity of tert-butyl alcohol; $a_{C_7H_{16}O_3}$ is the activity of mono tert-butyl ether of glycerol; $a_{C_{11}H_{24}O_3}$ is the activity of di tert-butyl ether of glycerol; $a_{C_{15}H_{32}O}$ is the activity of tri tert-butyl ether of glycerol, a_{H_2O} is the activity of water.

Table 3.1 Lists of the rate constants and equilibrium constants for etherification reactions of glycerol with tert-butyl alcohol (Kiatkittipong et al., 2011).

Equilibrium constant	Rate constant
K_{eq1}=exp(2.534-1005.5/T)	k_1=exp(16.114-6641.5/T)
K_{eq2}=exp(2.087-1051.1/T)	k_2=exp(26.511-10305/T)
K_{eq3}=exp(0.978-2212/T)	k_3=exp(5.462-3715/T)

3.2 Dimethyl ether

Presently, the synthetic energy sources have become interesting alternatives to conventional petroleum based energy sourced because the synthetic energy have many benefits over conventional petroleum based energy such as environmental friendly, high energy density, and potential for commercialization. Dimethyl ether is widely considered as a promising alternative fuel that can be used instead of conventional diesel. The benefits of using dimethyl ether instead of conventional diesel are lower incomplete combustion, lower carbon monoxide emission, lower nitrogen oxides emission, higher thermal efficiency, approximately near zero aromatic emission and sulfur free (Su et al., 2013). For this reason, dimethyl ether is widely used as the alternative fuel for diesel engines in many countries to meet the stringent emission regulations (such as EURO 5, US 2010, 2009 Japan, etc.) Moreover, the characteristics of dimethyl ether are similar to liquefied petroleum gas (LPG) and its combustion is cleaner than liquefied petroleum gas. Therefore, dimethyl ether can be used instead of liquefied petroleum gas. Dimethyl ether can be produced from synthesis gas produced from many sources such as renewable materials (biomass, waste and agricultural products) and fossil fuels (natural gas and coal). Dimethyl ether is priced lower than the conventional diesel fuel and liquefied petroleum gas (5.5 - 6.5 US$/MMBtu for production in Japan in 2005 and 4.1 US$/MMBtu for production in Middle East in 2005 comparing with LPG average price in Japan at 7 US$/MMBtu in 2005). Presently, various commercial projects are actively developed by major industries especially in Asia. For example, Japan developed prototype dimethyl ether vehicles and established 4 dimethyl ether gas stations at many places. In the European Union, Volvo, Buckshow, and others have already finished the development and tests of dimethyl ether trucks (Yoon and Han, 2009). Mixture of dimethyl ether and liquefied petroleum gas is used as fuel in China. Moreover, demand of dimethyl ether in China has increased because of popularization of civil LPG and development of alternatively fuelled vehicles. The annual consumption of dimethyl ether increased in a stable aspect. It can be predicted that the annual demand for dimethyl ether will fast continually increase in the future with the development of dimethyl vehicles (Su et al., 2013).

3.2.1 Dimethyl ether production

Dimethyl ether can be produced from two steps.

Step One: hydrocarbons derivations from coal, natural gas, or biomass are converted to synthesis gas (carbon monoxide and hydrogen) by Partial Oxidation Reforming or Steam Reforming (Yoon and Han, 2009).

Partial oxidation reforming:

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \qquad (3\text{-}13)$$

Steam reforming:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad (3\text{-}14)$$

In order to produce more hydrogen, the water gas shift reaction is carried out by adding more steam:

Water gas shift reaction;

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (3\text{-}15)$$

Step two: the conversion of syngas into dimethyl ether has two different ways. Method one: syngas is converted into methanol. Then, the dehydration reaction converts methanol to dimethyl ether (Yoon and Han, 2009).

Methanol synthesis:

$$2CO + 4H_2 \rightarrow 2CH_3OH \qquad (3\text{-}16)$$

$$CO_2 + 3H_2 \rightarrow CH_3OH \qquad (3\text{-}17)$$

Methanol dehydration;

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \qquad (3\text{-}18)$$

Method two: syngas is directly converted into dimethyl ether

$$4H_2 + 2CO \rightarrow CH_3OCH_3 + H_2O \qquad (3\text{-}19)$$

3.2.2 Kinetic model

Kinetic rate constant for the dehydration reaction of methanol into dimethyl ether is necessary information for process simulation. This work focused on the production of dimethyl ether from dehydration reaction of methanol into dimethyl ether. Lei et al. (2011) determined the kinetic model for dehydration reaction of methanol into dimethyl ether by fitting the experimental data from fixed bed micro reactor with macro porous sulfonic as a catalyst. List of the values of the pre-exponential factor and activation energy of etherification reaction is given below.

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \tag{3-20}$$

$$r = kW_{cat}[MeOH]^{1.51}[H_2O]^{-0.51} \tag{3-21}$$

$$k = A\exp\left(\frac{-E_a}{RT}\right) \tag{3-22}$$

Where A is the Arrhenius pre-exponential factor ($A=5.19\times10^9$ $m^3\times kg\text{-}cat^{-1}s^{-1}$) and E_a is the activation energy ($E_a = 133.8$ $kJ\times mol^{-1}$).

The dehydration reaction of methanol into dimethyl ether with macro porous sulfonic acid ion exchange resin as a catalyst is an equilibrium reaction and exothermic reaction.

3.3 Reactive distillation column

Reactive distillation column (RD) has many advantages over conventional sequential processing such as a fixed bed reactor followed by distillation column because reactive distillation can perform both reaction and phase separation in a single unit. Thus, it can reduce both capital cost and operating cost (Tuchlenski et al., 2001). The usage of reactive distillation for reversible chemical reactions such as etherification, esterification, transesterification reaction is the most important advantage of reactive distillation because reactive distillation is continuous removal products from the reaction zone. Moreover, the removal of the product can reduce the side reaction. Thus, the chemical equilibrium constraint on conversion can be overcome and high conversions can be achieved. Moreover, increasing of conversion in reactive distillation gives a benefit in reduced recycle costs (Harmsen, 2007).

In general, exothermic and endothermic reactions can be used in reactive distillation. However, the exothermic reactions are preferable because the heat of reaction released from the exothermic reactions can be used for product separation resulting in a reduced operation cost (Tuchlenski et al., 2001).

The conventional processes of etherification, esterification and transesterification reaction include a reactor followed by a sequential distillation column obtaining purities of products, byproduct and remaining reactants. This usually takes place in several separation devices. Thus, reactive distillation is a good choice for etherification, esterification and transesterification reaction.

Presently, the industrial uses reactive distillation for many different processes with more than 150 commercial operations of the petrochemical and chemical industry such as synthesis of ethyl, butyl, methyl acetates, ethyl tert-butyl ether (ETBE), hydrolysis of methyl acetate, synthesis of methylal, removal of methanol from formaldehyde, formation of fatty acid esters because reactive distillation can show large saving in capital cost and energy over conventional between 15 and 80%. Moreover, reactive distillation generally requires less equipment and less maintenance (Harmsen, 2007).

The major limitation of reactive distillation is the requirement of an equivalent between the temperature of reaction and the temperature of separation because both reaction and distillation are carried out simultaneously within a single vessel operating at some pressure and the temperature. If temperature is too high, it may be generating undesirable side reactions. If temperature is too low, it requires large amount of catalyst. In conclusion, both high temperature and low temperature may not be recommendation in reactive distillation (Tuchlenski, 2001).

3.3.1 Reactive distillation configurations

A conventional configuration for a chemical process usually has two sections; chemical reaction section and subsequent separation section. For example, a conventional processing scheme for reversible reaction sequence A + B ↔ C+D where C and D are both desired products. The boiling point of the component in a process from low boiling points to high boiling points follow as A,C,D and B (Baur, 2000).

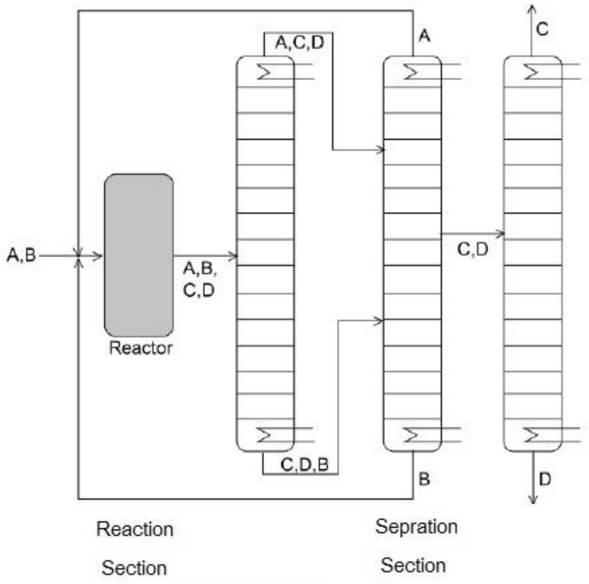

Figure 3.1 Conventional configurations for a conventional chemical process (Baur, 2000)

In the reaction section, reactants A and B are fed into contact with catalysts at optimal process conditions in one or more reactors. The stream leaving from the reactor section goes into separation section. In the separation section, one or more separation steps are separated unconverted A and B reactants from the products C and D. Then, the unreacted components A and B are recycled back into the reaction section. In general, distillation column is chosen in separation section (Baur, 2000).

For the reactive distillation column configuration, the reactive distillation column includes of non-reactive rectifying and stripping sections at the top and bottom with reactive section at the middle of column.

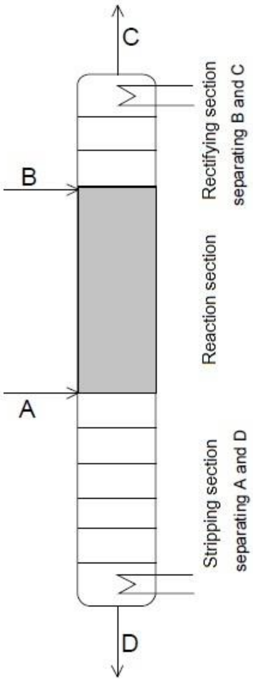

Figure 3.2 Reactive distillation column (Baur, 2000)

From Figure 3.2, reactive distillation column has three sections. The task of each section starts from the top, as follows:

1. The rectifying section separates the heavy reactant B from the light product C in order to recover heavy reactant B into the reaction section.

2. The reaction of reactants A and B occurs in reaction section. Reactants A and B come into the reaction section by counter current flow.

3. The stripping section separates the light reactant A from the heavy product D in order to recover light reactant A into the reaction section.

Other parameters of reactive distillation are shown as below.

Reflux ratio

The reflux ratio is the ratio of the liquid flow rate back to rectifying section to distillate rate. Product purity of distillate stream column is control by reflux ratio. The reflux ratio and the number stages can both be adjusted to get desire distillate purity. However, more reflux requires higher reboiler duty (Norazlinda and Zakaria, 2010)

Reboiler

Generally, Reboiler for distillation columns are usually used the kettle or the vertical thermosyphon type (Seader et al, 2011). The reboiler is heat exchangers used to provide heat to bottom of distillation columns. The vapor from bottom of distillation goes up to column and drives distillation separation

Condenser

The condenser is used to condense the vapor which is leaving from the top of distillation column.

3.3.2 Advantages and limitations of reactive distillation

The benefits for using reactive distillation process compared with the conventional process can be summarized as follows (Tuchlenski et al., 2001).

1. The important benefit of reactive distillation process over conventional process is a reduction in capital cost, because two process sections (reaction section and separation section) can be integrated in reactive distillation. Thus, the reactive distillation leads to lower costs in pumps, piping and instrumentation.

2. If reactive distillation is applied to exothermic reaction. The heat of reaction generated by the reaction can be used for vaporization of liquid. This leads to savings of energy costs by the reduction of rebolier duties.

3. The highest temperature in the reaction section is limited by the boiling point of a reaction mixture. Therefore, the hot spot on the catalyst can be reduced significantly. A simple and reliable temperature control can be achieved.

4. Conversion can be increased due to a fast removal of products from the reaction section. Thus, reactive distillation can improve conversion of reactant approaching to 100% for case of equilibrium-limited reaction due to shifting of the equilibrium to the right. The increasing of conversion gives a benefit in reduced recycle and separation cost.

5. Improved selectivity can be increased because removing one of the products from the reaction mixture or maintaining a low concentration of product in reaction zone can lead to reduction of the side reactions and improved selectivity for the desired products.

6. If the reaction zone in the RD column is placed above the feed position, poisoning of the catalyst can be avoided. This leads to longer lifetime of catalyst compared with the conventional process.

7. Reactive distillation can reduce significantly catalyst requirement compared with conventional process at the same conversion.

8. Reactive distillation is particularly advantageous that the reactor product is a mixture of species that can form azeotropes with other species. Reactive distillation can allow the azeotropes to be reacted away in a single vessel.

However before using the reactive distillation in process, three limitations have to be concerned (Tuchlenski et al., 2001).

1. The temperature range of the separation must correspond to the reaction temperature. The temperature range of separation can be changed by changing the column operating pressure. However, the upper operating temperature and pressure of the distillation column is limited by the thermal stability of the catalyst.

2. The chemical reaction must take place only in the liquid phase.

3. A long lifetime of catalysts is strongly required because it is very expensive to change the catalyst in structured catalytic packing catalysts.

3.4 Estimating Costs

Simulation study can be used to investigate the effects of operating condition and design parameters. This leads to the determination of suitable parameters and conditions for achieving optimal process operation. However, a process design should also consider economic factor. Total annual cost (TAC) analysis is an important tool for preliminary process design by considering both operating and capital costs. The total annual cost is defined as (Douglas, 1988):

$$\text{Total Annual Cost} = \text{Operating cost} + \frac{\text{Capital cost}}{\text{payback period}} \tag{3-23}$$

Operating cost is simple to estimate. When the utility flows, such as fuel, steam, cooling water, power and the flow rate of the raw material streams, are known from simulation, we simply multiply the flow by the monetary value per unit value of that stream. The cost of steam depends on its pressure that generates on the steam. For example, fuel and electricity cost should be more expensive than high pressure steam cost which should be more expensive than low pressure steam. After we determined the operating cost, we can calculate the capital cost. The capital cost consists of installed equipment costs and purchased equipment costs. For example the capital cost of distillation process includes the cost of column, trays, condenser and heat exchanger (Douglas, J. M., 1988).

3.5 Environmental impact assessment tool

Environmental impact assessment can be accomplished by using environmental assessments tools. Many environmental assessments tools were developed, for example waste reduction algorithm, sustainability evaluator to evaluate environmental impact in chemical process design. Using the waste reduction algorithm is less difficult than full life cycle assessment as it only focuses on the production step. Moreover, it requires less data for assessment. Waste reduction algorithm was developed by U.S. EPA. Waste reduction algorithm is calculated from potential environmental impact index. Waste reduction algorithm can be used to compare potential environmental impacts of the two process alternatives. Many potential environmental impacts index are defined (Shadiya qt al., 2012). However, this work focuses on using the human toxicity potential by either inhalation or dermal exposure index (HEPE). The HEPE index is calculated from the time-weighted averages (TWA) of the threshold limit values (TLV). These values can be obtained from Occupational Safety & Health Administration (OSHA) and represent occupational safety exposure limits. Time-weighted average (TWA) is the average exposure on the basis of an 8h/day or 40h/week work schedule (Young and cabezas, 1999). The HEPE index is defined as shown below.

$$\text{Index}_{k,HEPE} = \frac{1}{(TWA)_k} \tag{3-24}$$

3.6 Azeotrope mixture

The azeotrope mean the vapor has the same composition as the liquid and the mixture boils at a temperature (Hilmen E.-K, 2000). Binary mixtures which form azeotrope are characterized like a pure component when they are sent to a distillation column. For this reason, the separation of binary mixtures which form azeotropes is not possible separation by conventional distillation (de Figueirêdo et al., 2011).

3.6.1 General separation azeotrope processes

There are many methods for separation azeotrope mixture. Distillation methods are the common and most used, either by pressure differentiation or the addition solvent in order to alter the phase equilibrium of the azeotrope mixture. Other alternative separation techniques for separation azeotropic mixtures, such as membrane separation, are usually combined with distillation. Pervaporation is most commonly used in membrane technology for separation azeotrope mixture (de Figueirêdo et al., 2011). In pervaporation, the azeotrope mixture is fed in contact with one side of a membrane and product (permeate) is removed as a low pressure vapor from the other side (Figure 3.3). The vapor can be condensed and gathered. The chemical potential gradient between two sides of membrane is the driving force of mass transport. Vacuum pump or inert purge is used to maintain the permeate vapor pressure lower than the partial pressure of the feed liquid. Presently, pervaporation is economic for two applications: one is dehydration of alcohols, and another is removal small amounts of organic compounds from polluted waters (Feng and Huang 1997).

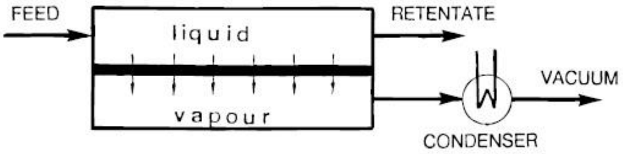

Figure 3.3 Diagram of the pervaporation process (Feng and Huang 1997)

CHAPTER IV
GLYCROL ETHER PRODUCTION BY REACTIVE DISTILLATION

In this chapter, only the production of glycerol ether from etherification reaction of pure glycerol and tert-butyl alcohol in reactive distillation process was analyzed. This chapter considered only reactive distillation for glycerol ether production. The parameters of the reactive distillation on conversion of glycerol and yield of di and tri tert-butyl ether of glycerol were studied in section 4.2. The optimal operating parameters of the reactive distillation for glycerol ether production based on a total annual cost analysis were studied in section 4.3.

4.1 Simulation method of reactive distillation for glycerol ether production

The simulation studies of the reactive distillation were performed by using Aspen Plus simulator. The pressure drop in reactive distillation was neglected. The column was operated at 1 bar. The numbering of the stages is top downward, with stage 1 as the total condenser and stage n as the reboiler. The simulation of a reactive distillation was performed based on RADFRAC module, which is a rigorous equilibrium-stage distillation model for describing a multistage vapor-liquid separation of distillation column, in Aspen Plus commercial software. The NRTL-RK model was employed to predict the thermodynamic properties and the phase equilibrium of substances in the system. The interaction parameters were taken from Aspen Plus database or were estimated using UNIFAC-Dortmund modified method. The kinetic rate for etherification reaction of pure glycerol and tert-butyl alcohol in reactive distillation was from Kiatkittipong et al. (2011). The etherification reaction of glycerol and tert-butyl alcohol is shown below

$$C_3H_8O_3 + C_4H_{10}O \xrightleftharpoons[k_{-1}]{k_1} C_7H_{16}O_3 + H_2O$$

$$C_7H_{16}O_3 + C_4H_{10}O \xrightleftharpoons[k_{-2}]{k_2} C_{11}H_{24}O_3 + H_2O$$

$$C_{11}H_{24}O_3 + C_4H_{10}O \xrightleftharpoons[k_{-3}]{k_3} C_{15}H_{32}O + H_2O$$

Where

$C_3H_8O_3$ is the glycerol, $C_4H_{10}O$ is the tert-butyl alcohol, $C_7H_{16}O_3$ is the mono tert-butyl ether of glycerol, $C_{11}H_{24}O_3$ is the di tert-butyl ether of glycerol, $C_{15}H_{32}O$ is the tri tert-butyl ether of glycerol and H_2O is the water (Kiatkittipong et al., 2011).

The configuration of a reactive distillation column shown in Figure 4-1 was used in this study. The pure glycerol and tert-butyl alcohol are fed into reactive distillation. Mono, di and tri tert-butyl ether of glycerol and water are generated in the reactive stages where the etherification of glycerol and tert-butyl alcohol occurs. Di and tri tert-butyl ether of glycerol are considered as the product of etherification reaction whereas mono tert-butyl ether of glycerol and water are considered as by-products.

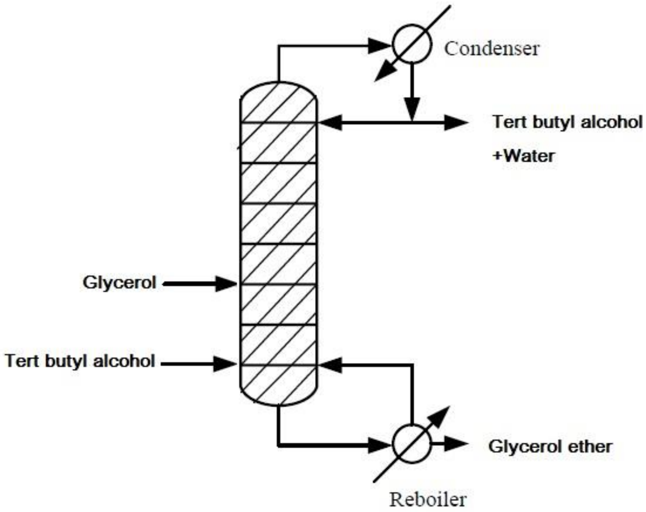

Figure 4.1 Reactive distillation for glycerol ether production

4.1.1 Model validation

In order to use the kinetic model in Aspen Plus for simulation with confidence, the reliability of the kinetic model is tested by comparing the simulated results obtained from Aspen Plus with the experimental data from Kiatkittipong et al. (2011). Results from the simulation comparison to the experimental data are shown in Figure 4.2. At the reactive distillation, feed stream of tert-butyl alcohol and glycerol at temperature 298 ^{o}C and feed ratio of tert-butyl alcohol to glycerol at 4 by volume, are fed to bottom and first stage of reactive stages in reactive distillation. The reactive distillation column is operated at the pressure of 1 bar with reflux ratio at 2. The column specification of reactive distillation is 6 rectifying stages and 6 reactive stages.

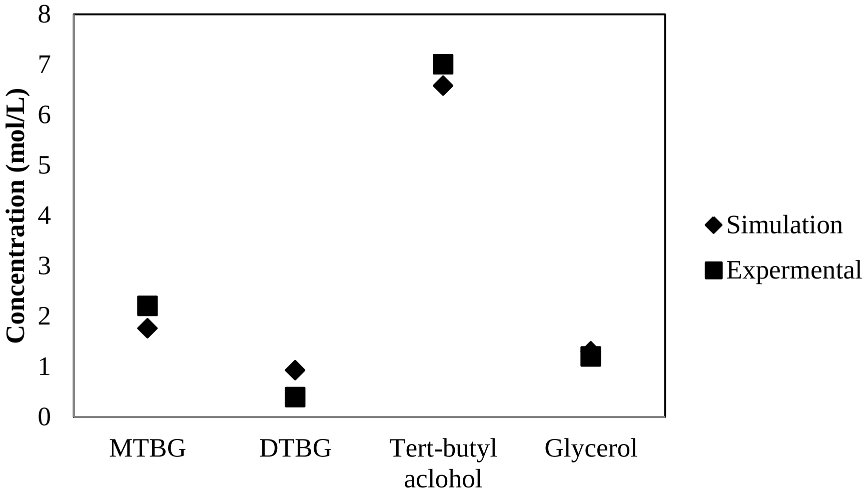

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Figure 4.2 Comparison of simulated results this work and experimental result from Kiatkittipong et al. (2011)

4.2 Standard condition of reactive distillation for glycerol ether production

The reactive distillation column at standard condition consists of 12 stages, including a total reboiler and condenser which is the numbering of the stages is top downward. The column pressur is 1 bar. Feed conditions at standard condition are glycerol of 2 kmol/h and tert-butyl alcohol of 10 kmol/h, reflux ratio at 1, reboiler duty at 80 kW and feed location of glycerol and tert-butyl alcohol at first stage and bottom of reactive stages respectively. The reactive stages are stages 7 to 11. The standard conditions of reactive distillation are given in Table 4.1. The composition profile and temperature profile of the standard condition were shown in Figure 4.3 and 4.4, respectively.

Table 4.1 Standard condition of reactive distillation

Condition of feed		Column specification	
Temperature (K)	298	Rectifying stages	5
Feed flow rate (kmol/hr)		Reaction stages	5
Glycerol	2	Stripping stages	0
Tert-butyl alcohol	10	Reboiler duty (kW)	80
Feed stage		Reflux ratio	1
Glycerol	7		
Tert-butyl alcohol	11		

All system performances of reactive distillation for glycerol ether production were considered in terms of conversion of glycerol, and yield of di and tri tert-butyl ether of glycerol. The conversions of glycerol and yield of di and tri-tert butyl ether of glycerol were defined as follows;

$$\%\ \text{Conversion} = \frac{\text{Difference of glycerol in molar flow rate of inlet and outlet}}{\text{Molar feed flow rate of glycerol to reactive distillation}} \times 100\%$$

$$\%\ \text{Yield} = \frac{\text{Molar flow rate of outlet of di and tri tert-butyl ether of glycerol}}{\text{Difference in molar flow rate of inlet and outlet of glycerol}} \times 100\%$$

Figures 4.3 and 4.4 show the composition profile and temperature profile at standard condition. Figure 4.3 demonstrates that, at the top of the column, the mole fraction of tert-butyl alcohol and water are 64.3% and 35.7% respectively, while the amount of glycerol ether (mono and di tert-butyl ether of glycerol) is not observed. The bottom products consist of tert-butyl alcohol, water and glycerol ether. Figure 4.4 show that temperature in reactive stages is higher than temperature in rectifying stages. This indicates that etherification reaction between tert-butyl alcohol and glycerol is exothermic reaction.

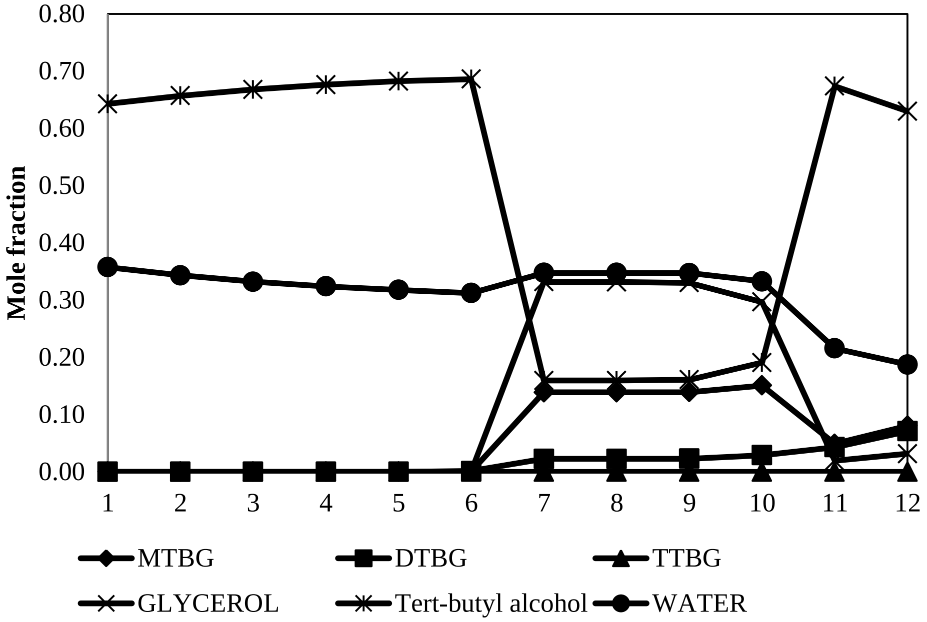

Figure 4.3 Composition profile of reactive distillation at standard condition

Where

MTBG is the mono tert-butyl ether of glycerol, DTBG is the di tert-butyl ether of glycerol, TTBG is the tri tert-butyl ether of glycerol.

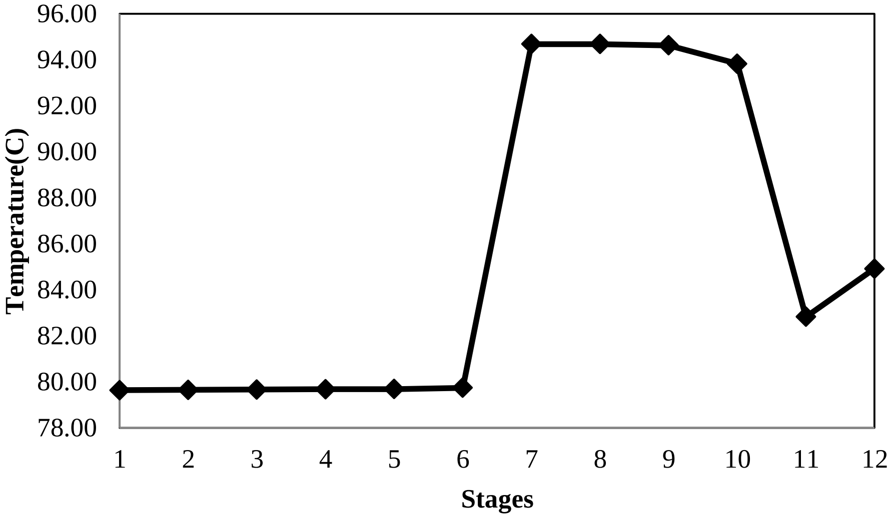

Figure 4.4 Temperature profile of reactive distillation at standard condition

4.2.1 Effects of feed ratio of tert-butyl alcohol to glycerol

The molar feed ratio of tert-butyl alcohol to glycerol is an important key parameter on the performance of the reactive distillation. The mole ratios of tert-butyl alcohol to glycerol are studied at 2:1 to 10:1. Figure 4.5 shows the effects of the feed molar ratio of tert-butyl alcohol to glycerol on the conversion of glycerol and yield of di and tri tert-butyl ether of glycerol. The simulation results show that the conversion of glycerol and yield of di and tri tert-butyl ether of glycerol increases with increasing molar feed ratio of tert-butyl alcohol to glycerol. This is due to the fact that the tert-butyl alcohol is the reactant of three etherification reactions of glycerol and tert-butyl alcohol. For this reason, tert-butyl alcohol forces the etherification to forward.

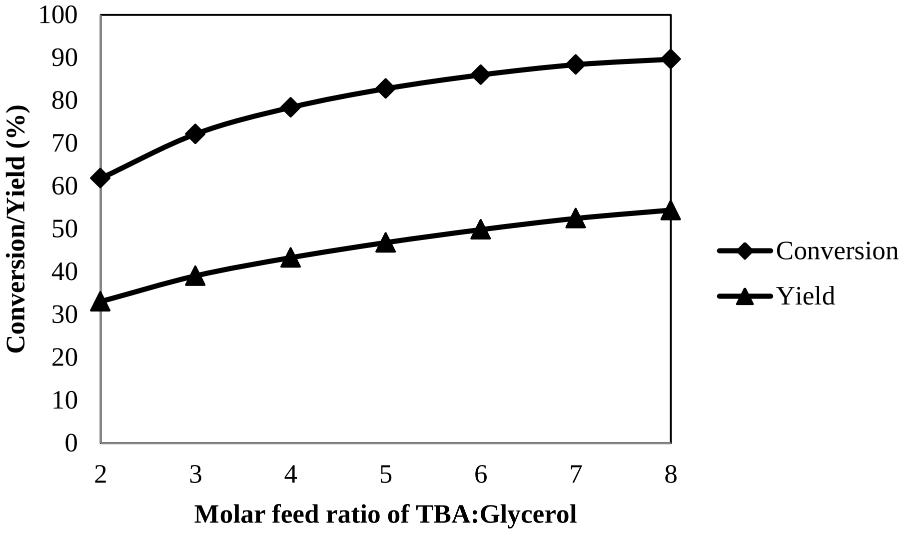

Figure 4.5 Effects of molar feed ratio of tert-butyl alcohol to glycerol on conversion of glycerol and yield of di and tri tert-butyl ether of glycerol

4.2.2 Effects of feed temperature

The effects of feed temperature on the performance of the reactive distillation column in term of conversion of glycerol and yield of di and tri tert-butyl ether of glycerol are investigated. Figure 4.6 indicates that conversion of glycerol and yield of di and tri tert-butyl alcohol are slightly decreased with increasing feed temperature of glycerol. Increasing feed temperature of glycerol results in reducing amount of tert-butyl alcohol as a reactant in reactive stages. For these reasons, conversion of glycerol and yield of di and tri tert-butyl alcohol are decreased by increasing temperature of glycerol feed. Figure 4.7 demonstrates that conversion of glycerol and yield of di and tri tert-butyl alcohol are increased by increasing the feed temperature of tert-butyl alcohol. The increasing feed temperature of tert-butyl alcohol results in increasing temperature in reboiler. As the temperature in the reboiler increasing, more unreacted glycerol and mono tert-butyl ether of glycerol go up to the reactive stages and therefore reacts in reactive stages. For this reason, conversion of glycerol and yield of di and tri tert-butyl ether of glycerol are increasing. In addition, when feed temperature of tert-butyl alcohol more than 82.42 ^{o}C both conversion and yield of di and tri tert-butyl ether of glycerol are rapid increased. This is due to the fact that tert-butyl alcohol becomes to vapor at 82.42 ^{o}C thus more amount of heat in tert-butyl alcohol transfers to reboiler. For this reason, more unreacted glycerol and mono tert-butyl ether of glycerol go up to the reactive stages and therefore reacts in reactive stages.

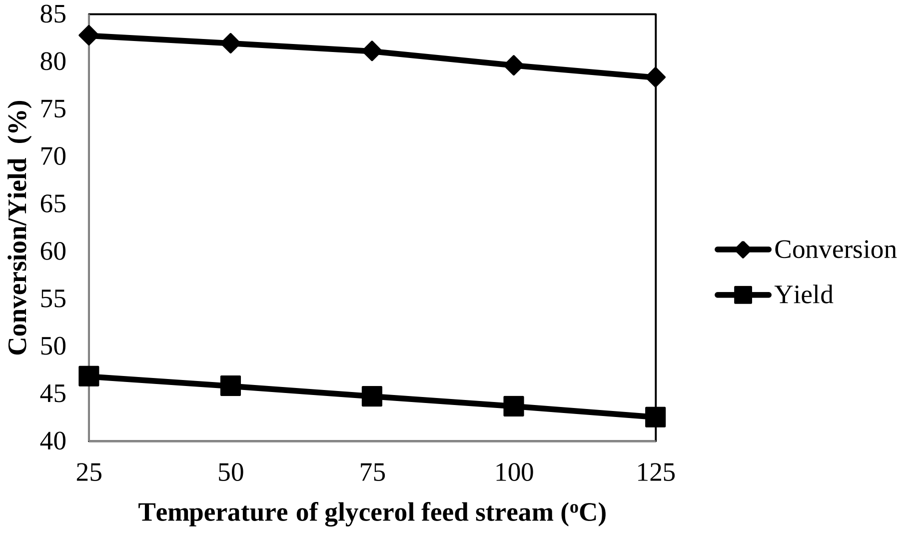

Figure 4.6 Effects of glycerol feed temperature on conversion of glycerol and yield of di and tri tert-butyl alcohol

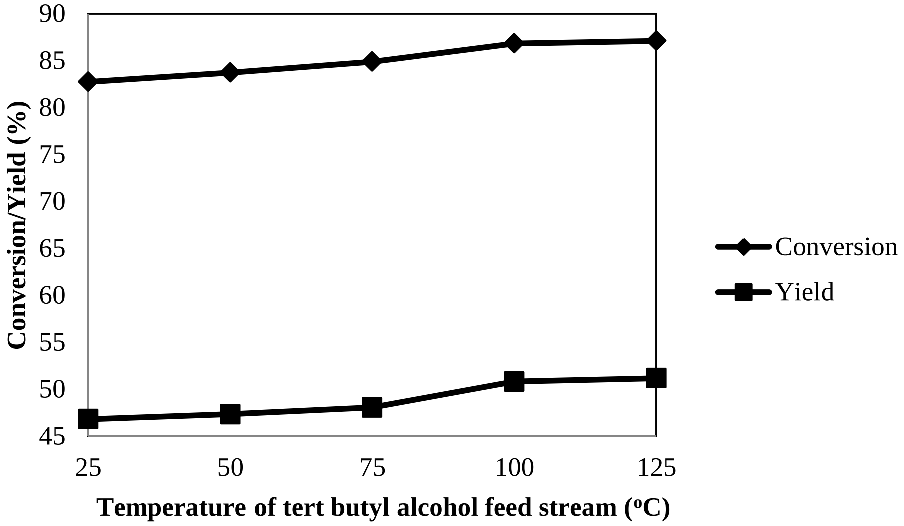

Figure 4.7 Effects of tert-butyl alcohol feed temperature on conversion of glycerol and yield of di and tri tert-butyl alcohol

4.2.3 Effects of reboiler heat duty

Figure 4.8 shows the effects of reboiler duty on the conversion of glycerol and yield of di and tri tert-butyl ether of glycerol within range of 60 to 160 kW. As the heat duty increases, more unreacted reactants such as glycerol and mono tert-butyl ether of glycerol go up to the reactive stages and therefore react in reactive stages. For this reason, both conversion of glycerol and yield of di and tri tert-butyl ether of glycerol are increased by increase reboiler duty.

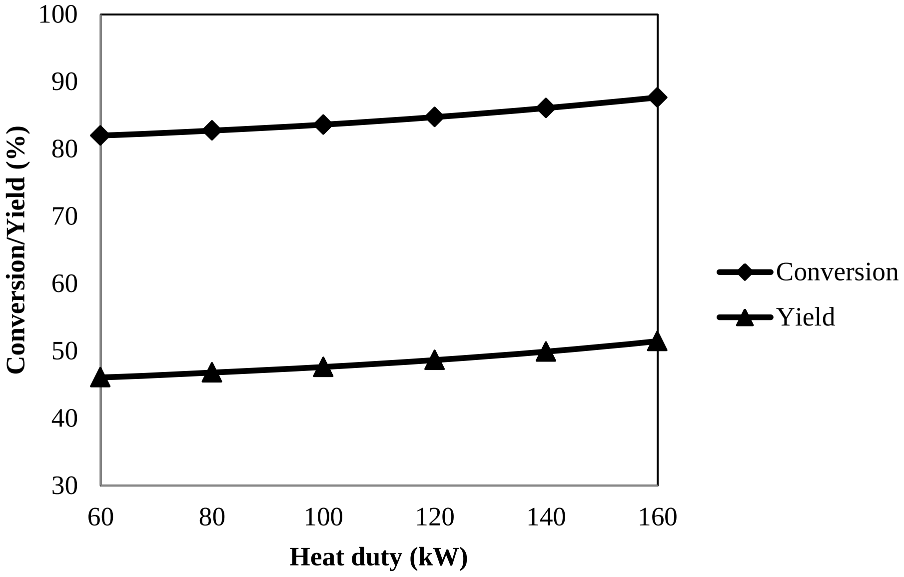

Figure 4.8 Effects of reboiler duty on conversion of glycerol and yield of di and tri tert-butyl alcohol

4.2.4 Effects of feed stage location

The location of the two feed locations is also important design variable. The locations of feed stage are adjusted to make the best performance of reactive distillation in term of conversion of glycerol and yield of di and tri tert-butyl ether of glycerol. It was found that feeding tert-butyl alcohol (lighter reactant) at bottom of reactive stages and feeding glycerol (heavier reactant) at top of reactive stages give the best reactive reaction performance. The amount of glycerol in reactive stages is decreasing, when feed location of glycerol is changes from top to bottom of reactive stages. On the other hand, amount of tert-butyl alcohol is decreasing, when feed location of methanol is changed from bottom to top of reactive stages. For this reason, tert-butyl alcohol (lighter reactant) and glycerol (heavier reactant) must be fed at bottom and top of reaction stages respectively. The effects of feed stage location of glycerol and tert-butyl alcohol on the conversion of glycerol and yield of di and tri tert-butyl ether of glycerol in the reactive distillation are shown in Figure 4.9 and 4.10.

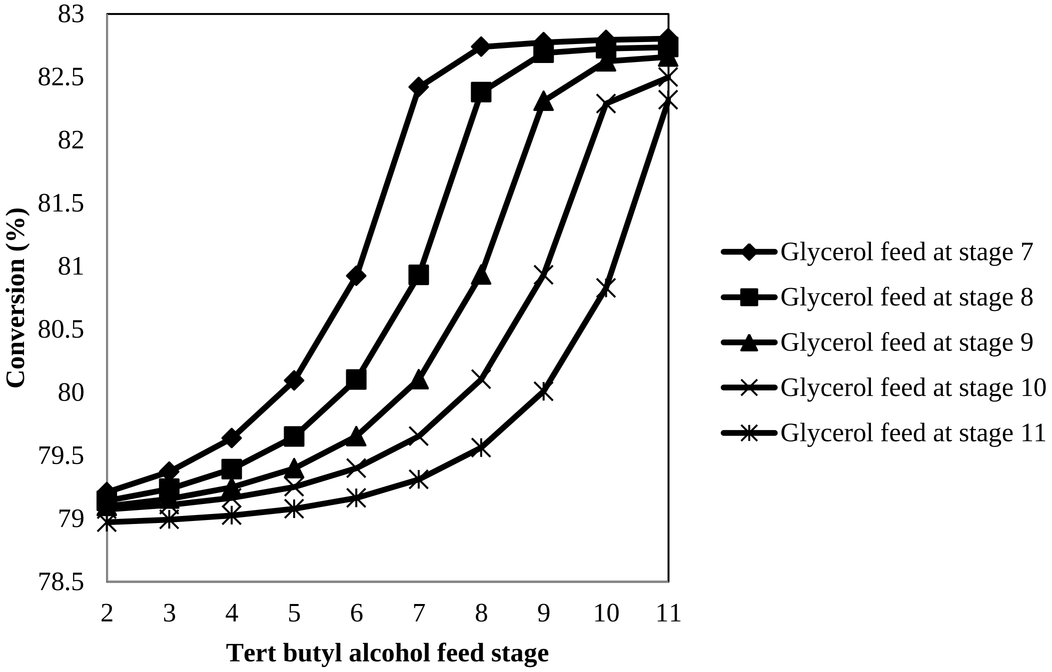

Figure 4.9 Effects of tert-butyl alcohol feed stages location on conversion of glycerol at various glycerol feed stage location

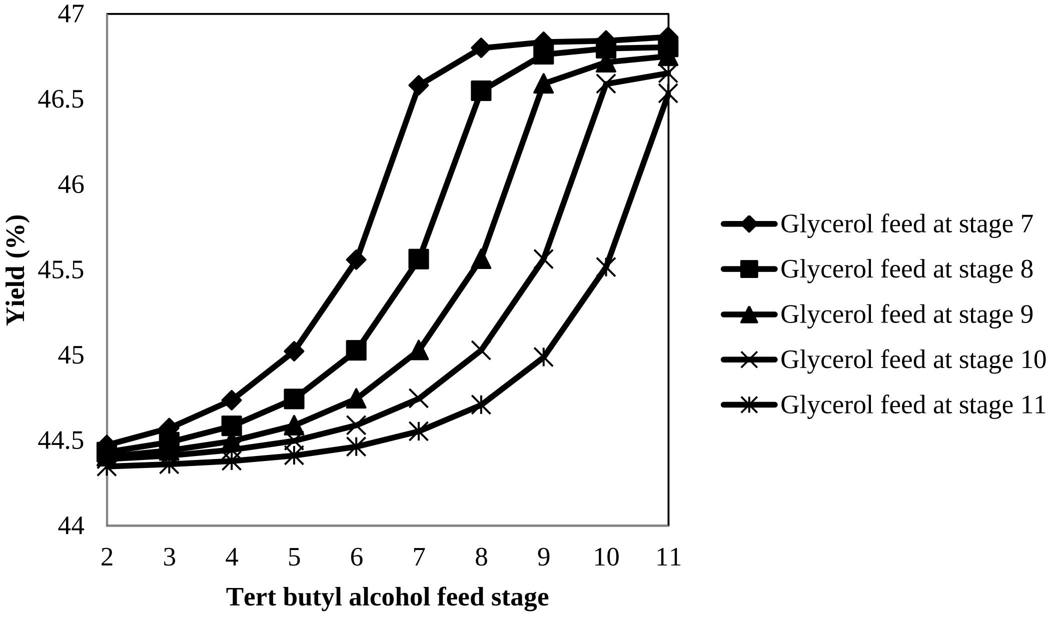

Figure 4.10 Effects of tert-butyl alcohol feed stages location on yield of di and tri tert-butyl ether of glycerol at various glycerol feed stage location

4.2.5 Effects of the number of reactive stages

Figure 4.11 and 4.12 demonstrate the effects of changing the number of reactive stages in term of conversion of glycerol and yield of di and tri tert-butyl ether of glycerol at standard condition. The numbers of reactive stages are varied from 1 to 8. The conversion of glycerol and yield of di and tri tert-butyl ether of glycerol increases when increases the number of reactive stages from 1 to 8 because increasing number of reactive stages can be increased space time of reactant in reactive stages. Figure 4.12 shows that yield of di and tri tert-butyl ether of glycerol is increased by increasing number of reactive stages. This is due to the fact that increasing number of reactive stages can be increased space time of reactant as tert-butyl alcohol and intermediate as mono tert-butyl ether of glycerol in reactive stages. For this reason, tert-butyl alcohol and mono-tert butyl ether of glycerol are reacted and converted to di and tri tert-butyl ether of glycerol.

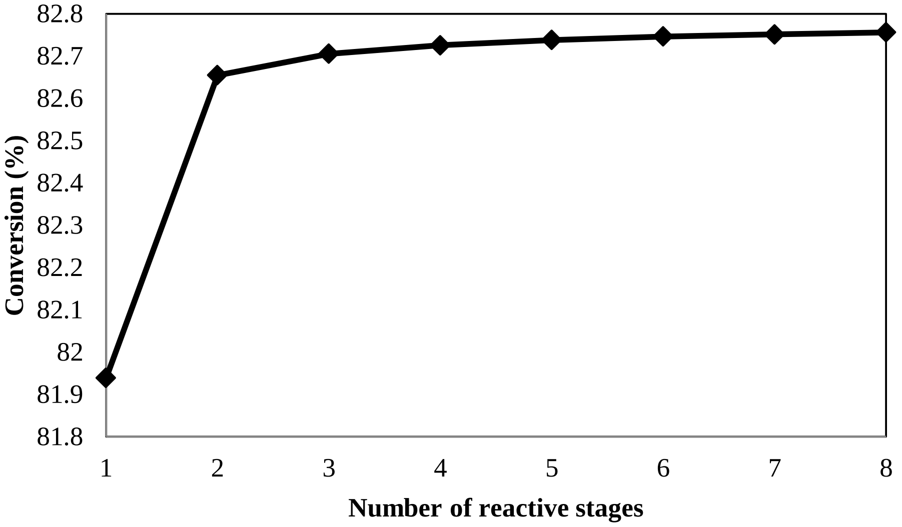

Figure 4.11 Effects of number of reactive stages on conversion of glycerol

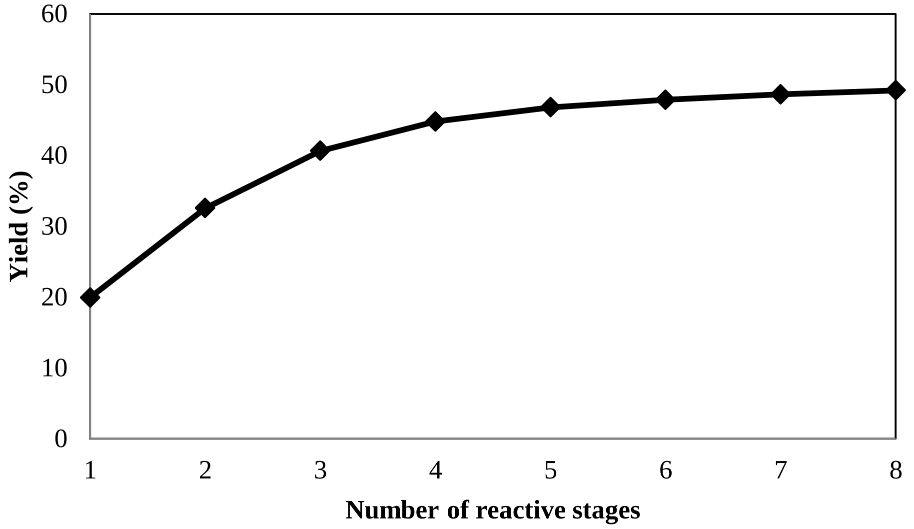

Figure 4.12 Effects of reactive stages on yield of di and tri tert-butyl alcohol

4.2.6 Effects of the number of rectifying stages

Figure 4.13 and 4.14 demonstrate that impact of a number of the number of rectifying stages on the performance of reactive distillation is investigated at standard condition**.** The numbers of rectifying stages are varied from 1 to 10. Increasing number of rectifying stage can help separation water as inhibitor of etherification reaction of tert-butyl alcohol and glycerol out from reactive stages, so conversion of glycerol and yield of di and tri tert-butyl ether of glycerol is increasing.

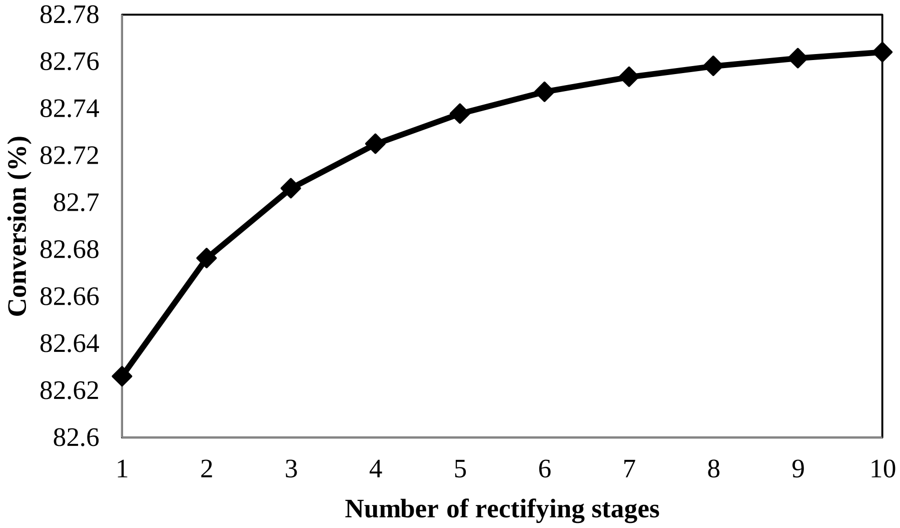

Figure 4.13 Effects of the number of rectifying stages on conversion of glycerol

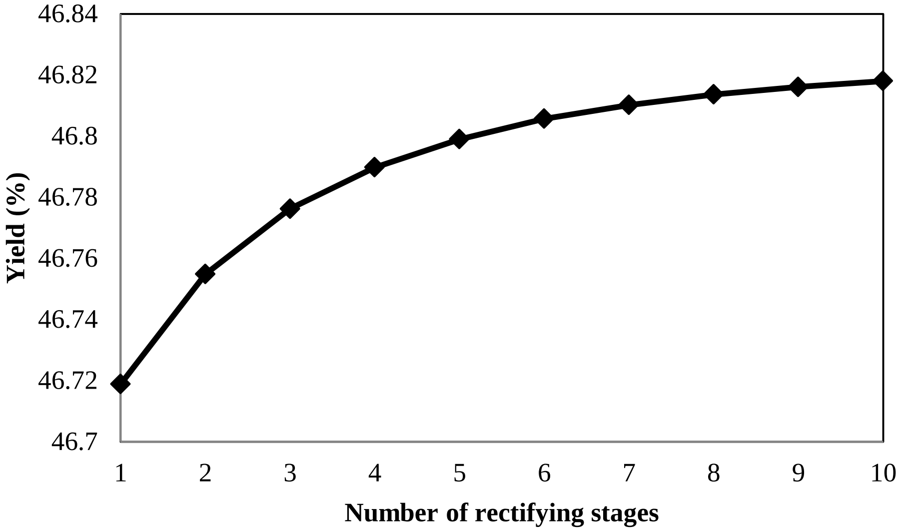

Figure 4.14 Effects of the number of rectifying stages on yield of di and tri tert-butyl alcohol

4.2.7 Effects of the number of stripping stages

From Figure 4.15 and 4.16 show that the impact of the number of the stripping stages on the performance of reactive distillation is investigated at standard condition. The numbers of stripping stages are varied from 0 to 8. When the number of stages in the stripping section is increased, more unreacted glycerol and mono tert-butyl ether of glycerol cannot separate from the bottom of reactive distillation and does not return to the reactive stages. For this reason, conversion of glycerol and yield of di and tri tert-butyl ether of glycerol are decreased.

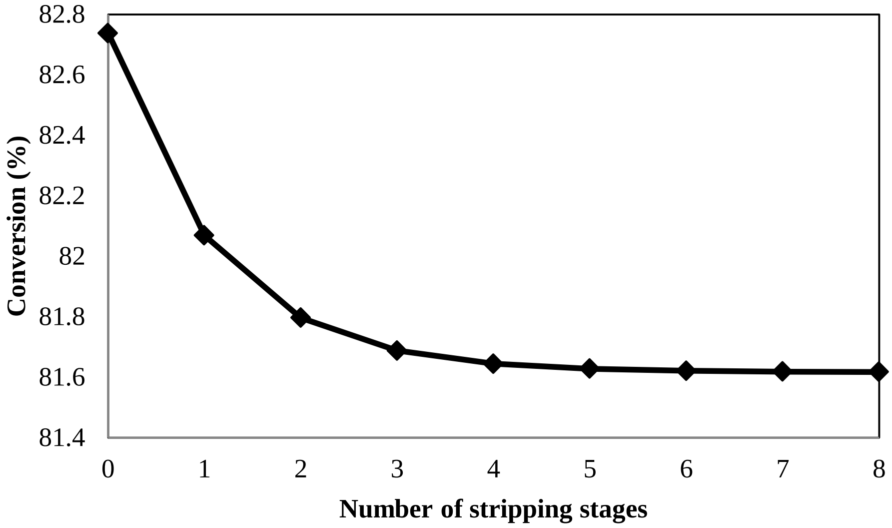

Figure 4.15 Effects of number of stripping stages on conversion of glycerol

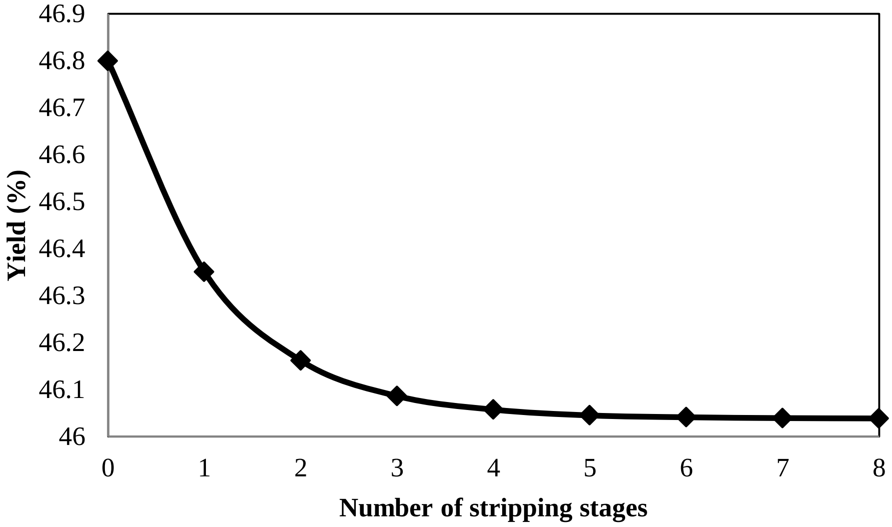

Figure 4.16 Effects of number of stripping on yield of di and tri tert-butyl alcohol

4.2.8 Effects of reflux ratio

Figure 4.17 and 4.18 show the effects of reflux ratio of reactive distillation on conversion of glycerol and yield of di and tri tert-butyl ether of glycerol. Figure 4.17 and 4.18 indicate that conversion of glycerol and yield of di and tri tert-butyl ether of glycerol are decreased by increasing reflux ratio. This is due to the fact that increasing reflux ratio results in increasing amount of water in reactive stages. Because water can inhibit the etherification reaction of tert-butyl alcohol and glycerol, the reflux ratio should be operating at lowest possible.

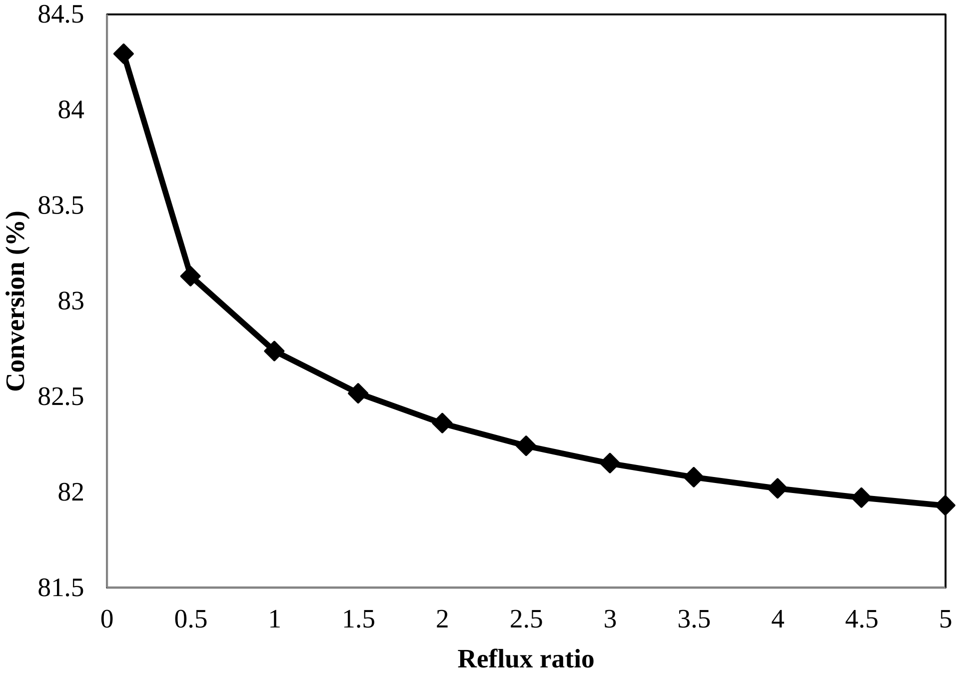

Figure 4.17 Effects of reflux on conversion of conversion of glycerol

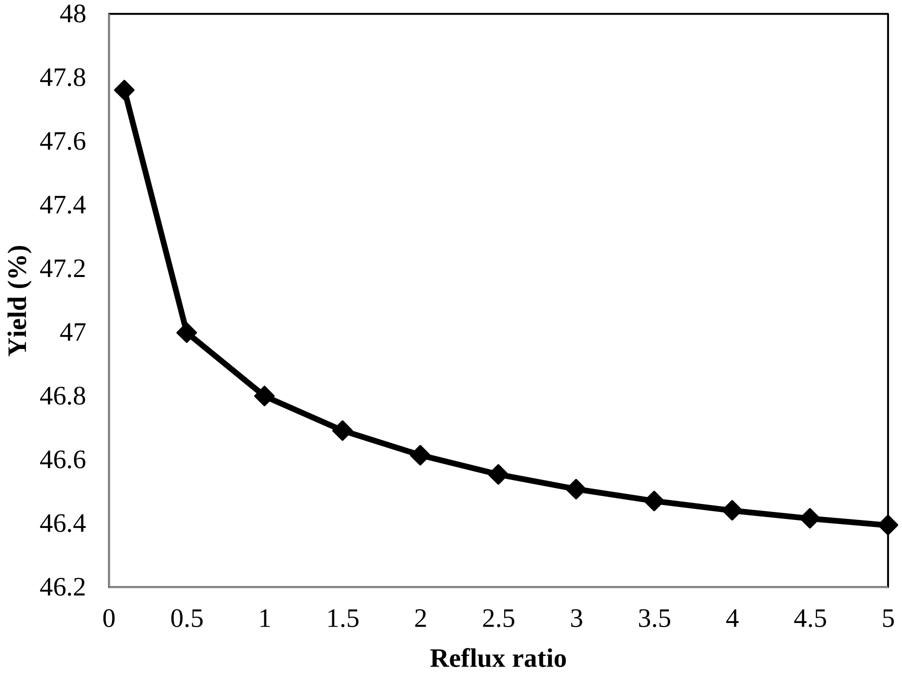

Figure 4.18 Effects of reflux ratio on yield of di and tri tert-butyl alcohol

4.3 Economic assessment of reactive distillation for glycerol ether production

This section is to study the steady-state economic of reactive distillation for glycerol ether (di and tri tert-butyl ether of glycerol) production. An optimum single reactive distillation for glycerol ether production by using the total annual cost as the criteria was investigated. The total annual cost includes operating cost and annualized capital cost. The tray sizing function in aspen plus simulation was used to estimate diameter of reactive distillation. The distance between trays is kept at 2 ft. The annualized capital cost was calculated with the payback period of 3 years and using the cost data from Appendix B of Douglas (1988) book. The total annual cost (TAC) is defined as shown below.

$$\mathrm{TAC} = \mathrm{TAC}_{\mathrm{ope}} + \frac{\mathrm{TAC}_{\mathrm{cap}}}{\text{Payback Period}}$$

The calculation of capital cost includes the cost of reactive distillation. The calculation of operating cost includes cooling water and streaming cost. All cases in this study, the molar ratio of tert-butyl alcohol to glycerol is 6:1.

4.3.1 Assumptions and specifications for glycerol ether stream and reactive distillation design

The annualized capital cost is calculated with the payback period of 3 years and using the cost data from Appendix B of Douglas (1988) book.

Assumption and specification for reactive distillation design and glycerol ether stream

1. The design objective is to obtain 99 mol% conversion of glycerol.
2. The design objective is to obtain 99 mol% yield of fuel additive (di and tri tert-butyl ether of glycerol).
3. The design specification is to obtain 2.124 kmol/hr of fuel additive (di and tri tert-butyl ether of glycerol) at glycerol ether stream.
4. Purity of product stream is 98 mol%
5. Feed stages location of glycerol and tert-butyl alcohol is fixed at top and bottom of reactive stages respectively.
6. The molar ratio of tert-butyl alcohol to glycerol is fixed at 6:1.

Based on these assumption and specification, there are five variables to optimize, the designs are as follows:

1. Number of rectifying stages
2. Number of stripping stages
3. Number of reactive stages
4. Reflux ratio
5. Reboiler duty

The design procedure of reactive distillation design is the following:

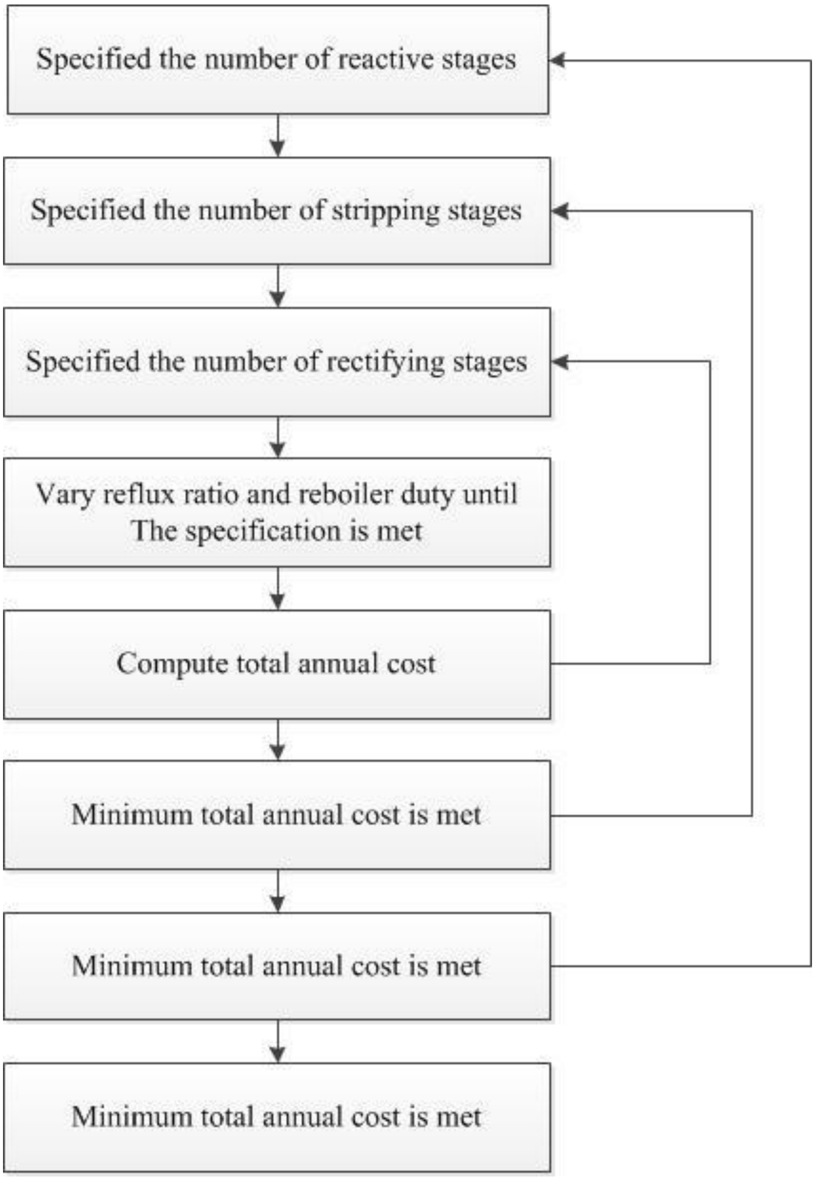

Figure 4.19 Design procedure of reactive distillation for glycerol ether production

4.3.2 Result

From Figure 4.20, it shows that the numbers of reactive stages is important parameter. Increasing the number of reactive stages provides many benefits. First, increasing number of reactive stages results in increasing space time of reactant in reactive stages, thus the conversion of glycerol and yield of fuel additive are increasing. Second, increasing numbers of reactive stages give benefit in better separation performance such as separation heavy product from light unreacted reactant and by-product. For this reasons, operating cost and capital cost of reboiler can be reduced by increasing number of reactive stages. However, increasing numbers of reactive stages more than 8 stages result in higher capital cost. We concluded that the optimum number of reactive stage is 8 stages.

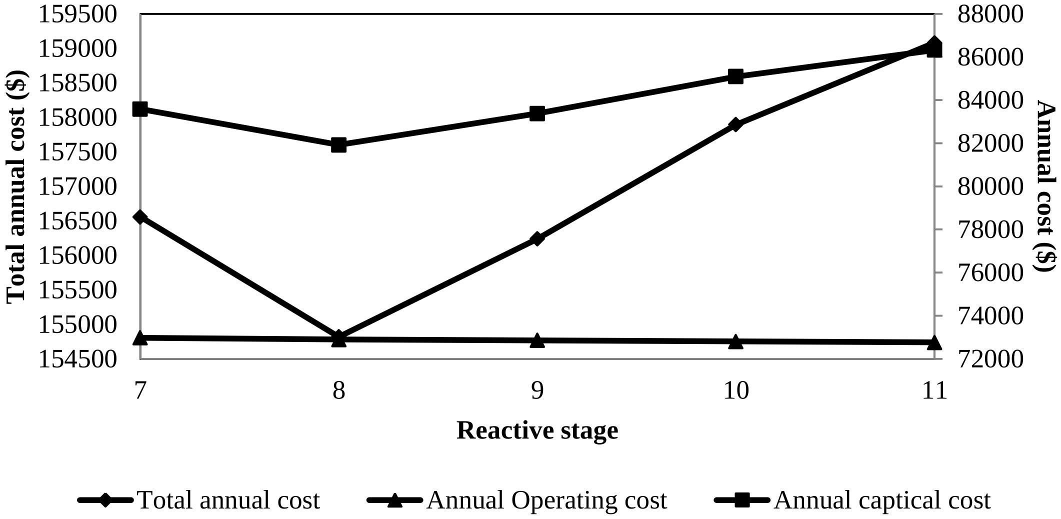

Figure 4.20 Effects of reactive stages on total annual cost

The effects of reactive stages, rectifying stage and stripping stage on total annual cost of reactive distillation are demonstrated in Figure 4.21, 4.22 and 4.23. Because glycerol and mono-tert butyl ether of glycerol are completely used in reactive stage, all remaining components in rectifying stages and stripping stages are fuel additive (di and tri tert butyl ether of glycerol), tert-butyl alcohol and water. Boiling point of glycerol ether is much higher than that of tert-butyl alcohol and water, so separation fuel additive from tert-butyl alcohol and water requires a few rectifying and stripping stages to achieve purity specification.

Increasing number of rectifying stage provides many benefits. First, increasing number of rectifying stages can help separation water out from reactive stages, so it can reduce reboiler duty. Second, increasing numbers of rectifying stages result in increasing both conversion of glycerol and yield of di and tri tert-butyl ether of glycerol. However, increasing the number of rectifying stage requires more capital cost.

Increasing the number of stripping stages can help separation tert-butyl alcohol from glycerol ether to meet purity specification of product. However, increasing the numbers of stripping stages requires more capital cost and reduce both conversion of glycerol and yield of di and tri tert-butyl ether of glycerol. However, purity of product cannot increase to 99% without stripping stages. For this reason, stripping stages are one of essential part of reactive distillation due to specification of contamination of product. From Figures 4.21, 4-22 and 4.23, they show that the optimum rectifying stages are 2 stages and optimum stripping stage is 1 stage.

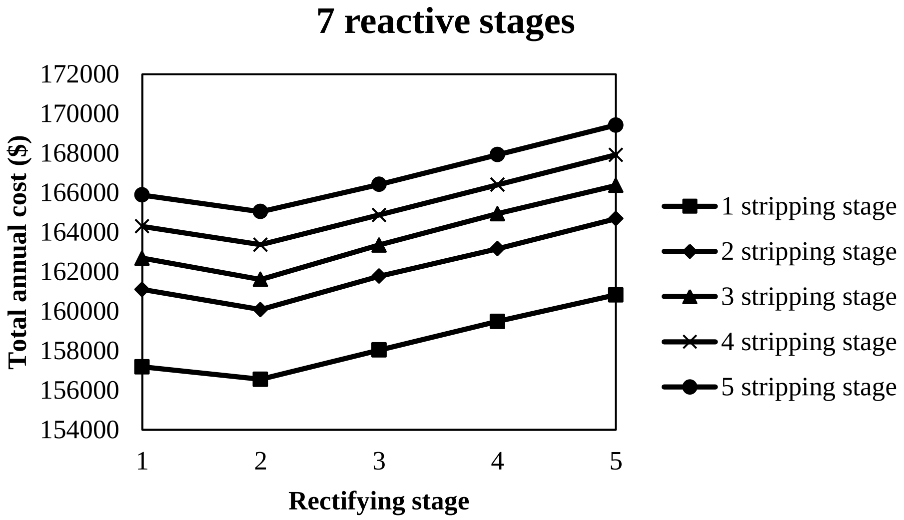

Figure 4.21 The effects of rectifying and stripping stage on total annual cost of reactive distillation by fix reactive stage at 7 stages

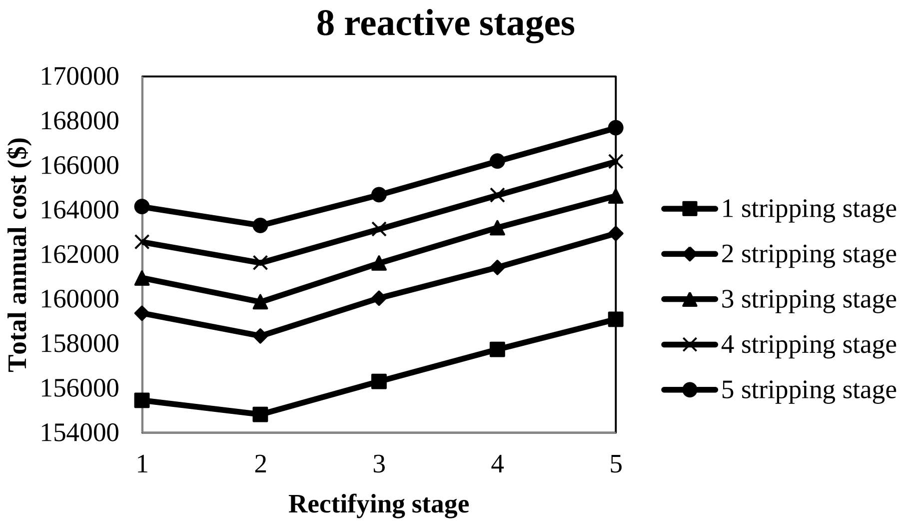

Figure 4.22 The effects of rectifying and stripping stage on total annual cost of reactive distillation by fix reactive stage at 8 stages

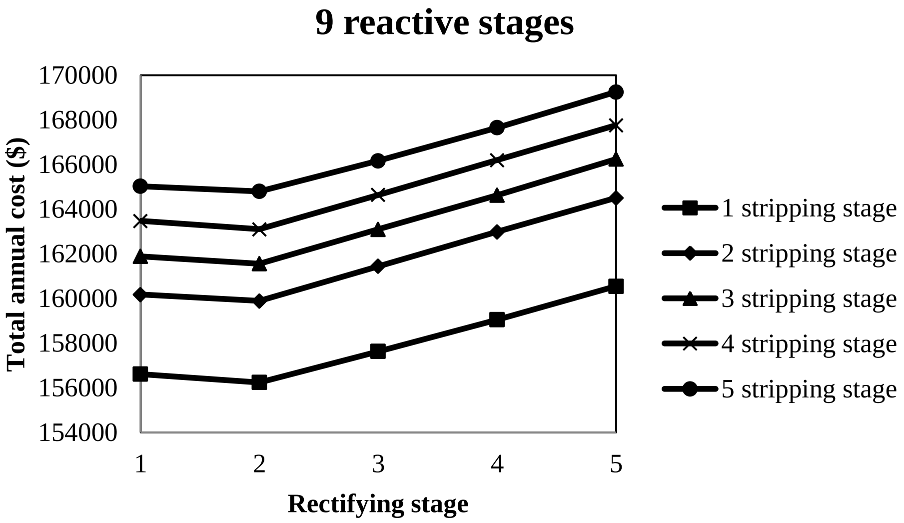

Figure 4.23 The effects of rectifying and stripping stage on total annual cost of reactive distillation by fix reactive stage at 9 stages

For effects of reboiler duty, increasing reboiler duty can increase conversion and selectivity of di and tri tert-butyl alcohol because unreacted glycerol goes up to the reactive stages and therefore reacts in reactive stages. The reboiler duty must operate highly enough to separate all of unreacted glycerol in bottom of reactive distillation going up to the reactive stages and separates all of water as by product and excess tert-butyl alcohol from product (di and tri tert-butyl ether of alcohol).

However, higher reboiler requires higher operating cost. The optimal operating reboiler duty is 260.1 kW.

For effects of reflux ratio, increasing reflux ratio results in decreases of both conversion of glycerol and yield of di and tri tert-butyl ether of glycerol. This is due to the fact that increasing reflux ratio results in increasing amount of water as inhibiter of etherification reaction of tert-butyl alcohol and glycerol in reactive stages. Furthermore, increasing reflux ratio requires higher total annual cost. For this reason, reflux ratio must be operated as low value as possible. The optimal operating parameters of reactive distillation are summarized in table 4.2.

Table 4.2 Optimal operating parameters of reactive distillation for glycerol ether production

Condition of feed		Column specification	
Temperature (K)	298	Rectifying stages	2
Feed flow rate (kmol/hr)		Reaction stages	8
Glycerol	2.15	Stripping stages	1
Tert-butyl alcohol	12.9	Reboiler duty (kW)	260.1
Feed stage		Reflux ratio	0.05
Glycerol	4		
Tert-butyl alcohol	11		

CHAPTER V

DIMETHYL ETHER PRODUCTION BY REACTIVE DISTILLATION

In this chapter, crude glycerol is considered for production of glycerol ether. However, it is always found that there is contamination of methanol in crude glycerol from biodiesel production because most industrial biodiesel processes utilize high molar ratio of methanol to vegetable oil in order to drive the transesterification reaction to completion (Tan et al., 2013). Methanol in crude glycerol can cause etherification reaction with tert-butyl alcohol and then produces methyl tertiary butyl ether (MTBE) (Preston, 1998). The MTBE is a fuel additive. However, it often contaminates water supply aquifers due to leaking underground storage tanks or spilling onto the ground of gasoline containing MTBE (Naddafi et al., 2008). For this reason, contamination of methanol in crude glycerol must be eliminated before being used as reactant for glycerol ether production. However, distillation of crude glycerol is high energy demand process due to the high specific heat capacity of glycerol that leads to a high energy input requirement for vaporization. For this reason, the use of methanol to produce high value-added products would reduce the biodiesel production cost and increase the competitive potential of biodiesel producers. Methanol in crude glycerol is considered a valuable reactant to produce other value-added products such as dimethyl ether, which is widely used as a promising alternative fuel to replace convectional diesel and liquefied petroleum gas (LPG). The advantages of dimethyl ether, compared to conventional diesel and liquefied petroleum gas (LPG), are lower incomplete combustion, lower carbon monoxide emission, lower nitrogen oxides emission, higher thermal efficiency, near zero aromatic emission and sulfur free (Su et al., 2013).

To enhance the production process of dimethyl ether, a reactive distillation is regarded as a potential alternative as it offers some advantages over a conventional process. For example, both the reaction and separation tasks can be performed in single unit, so capital and operating costs can be reduced. Moreover, the reactive distillation provides high conversion, improves yield of products, and reduces energy consumptions (Harmsen, 2011). Generally, dimethyl ether is produced from dehydration reaction of methanol (Yoon and Han, 2009). The dehydration reaction of methanol into dimethyl ether is exothermic reaction, so reactive distillation can use heat of dehydration reaction of methanol to reduce reboiler duty. Moreover, the pure glycerol from this process pure enough can be used for glycerol ether production. In this chapter considers reactive distillation for dimethyl ether production and distillation column for separation water out from glycerol. The parameters of the reactive distillation on conversion of methanol are studied in section 5.3 while the parameters of distillation column on purity of glycerol are studied in section 5.4. The optimal operating parameters of the reactive distillation based on a total annual cost analysis are studied in section 5.6 while the optimal operating parameters of distillation column based on a total annual cost analysis are studied in section 5.7.

5.1 Process flow sheet description

In this work, the design of reactive distillation for production dimethyl ether is developed. Methanol in crude glycerol is used to produce dimethyl ether in reactive distillation. The design plant flow sheet of this work is presented in Figure 5.1. In this plant, flow sheet contains two units as follows: reactive distillation and distillation column. The pressure drop in both reactive distillation and distillation column is negligible. Reactive distillation which can incorporate both phase separation and chemical reaction in a single unit is used to produce dimethyl ether by dehydration reaction of methanol in crude glycerol and separates dimethyl ether from glycerol and water. The methanol is completely used in reactive distillation. The distillation column is used to separate glycerol out from water and produces pure glycerol. First, feed stream of crude glycerol is sent to reactive distillation. The composition of crude glycerol feed stream is adapt from Hansen et al. (2009). The composition of crude glycerol is assumed that consist of glycerol 70% mol and methanol 30% mol. Dimethyl ether is separated to top of reactive distillation while glycerol and water are sent to bottom of reactive distillation. For reaction in reactive distillation, reaction distillation can improve conversion of methanol to 99% in order to eliminate methanol recycle section. Second, the glycerol and water from bottom of reactive distillation are sent into distillation column in order to separate glycerol from water. Water is sent to top of distillation column in waste water stream while pure glycerol is sent into bottom of distillation column in glycerol stream.

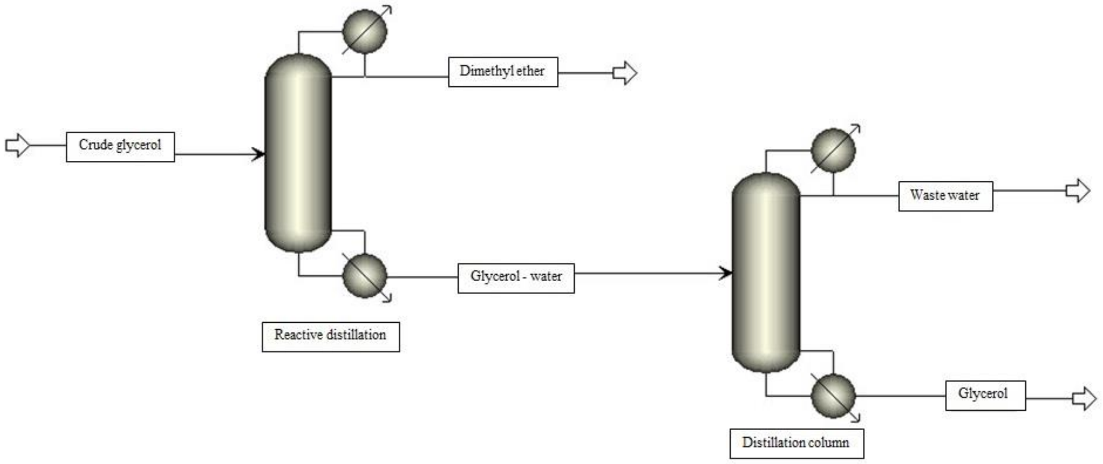

Figure 5.1 Process flow sheet of dimethyl ether production

5.2 Simulation method of reactive distillation column for dimethyl ether production

The simulation studies of the reactive distillation were performed by using Aspen Plus simulator. The pressure drop in both reactive distillation and distillation column is negligible. The numbering of the stages is top downward, with stage 1 as total condenser and stage n as reboiler. The simulation of a reactive distillation was performed based on RADFRAC module, which is a rigorous equilibrium-stage distillation model to describe a multistage vapor-liquid separation of distillation column, in Aspen Plus commercial software. The NRTL-RK model was employed to predict thermodynamic properties and phase equilibrium of substances in the system. The interaction parameters were taken from Aspen Plus database or were estimated using UNIFAC-Dortmund modified method. The kinetic rate for dehydration reaction of methanol in reactive distillation was used from Lei et al. (2011). The dehydration reaction of methanol is show below.

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$$

Figure 5.2 showing the configuration of a reactive distillation column was used in this study. In this work, methanol in crude glycerol was used as reactant for dehydration reaction of methanol. Dimethyl ether and water are generated in the reactive stages where the dehydration reaction of methanol is occurred. Dimethyl ether was considered as the product of dehydration reaction of methanol whereas water was considered as a by-product.

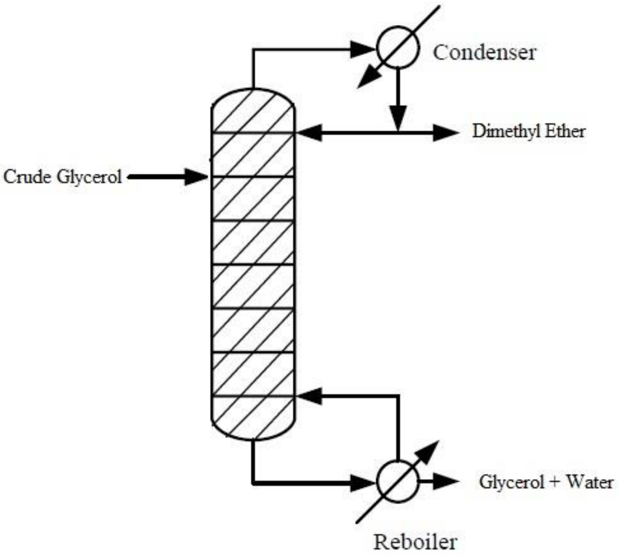

Figure 5.2 Reactive distillation for dimethyl ether production

5.2.1 Model validation

In order to use the kinetic model in Aspen Plus for simulating with confidence, the reliability of the kinetic model is tested by comparing the simulated results obtained from Aspen Plus with the experimental data from Lei et al. (2011). With same condition of experiment of fixed-bed reactor from in their study, results of the simulation comparison to the experimental data are shown in Figure 5.3. At the condition of fixed-bed reactor in their study, feed stream of mixture of methanol and water is sent into fixed-bed reactor with a volumetric flow rate of 0.20 ml/min. Initial mole fraction of methanol varied from 0.85 to 1.00 in feed stream. The conditions of fixed-bed reactor are 10 mm in inner diameter, 420 mm in length and 2 g of catalyst. The temperature in fixed-bed reactor is fixed at 423, 415 and 407 K. Moreover, the simulation results of reactive distillation are compared to their simulation results. The condition of reactive distillation in their paper, feed stream of methanol at temperature 298 ^{o}C and flow rate 2.5 mol/s is fed into first stages of reactive stages in reactive distillation. The reactive distillation column is operated at the pressure of 9 bar with reflux ratio 2 and reboiler duty 75 kW. The column specification of reactive distillation is 7 rectifying stages, 17 reactive stages and 5 stripping stages. Results of the simulation in this work run in comparison to simulation data are shown in Table 5.1.

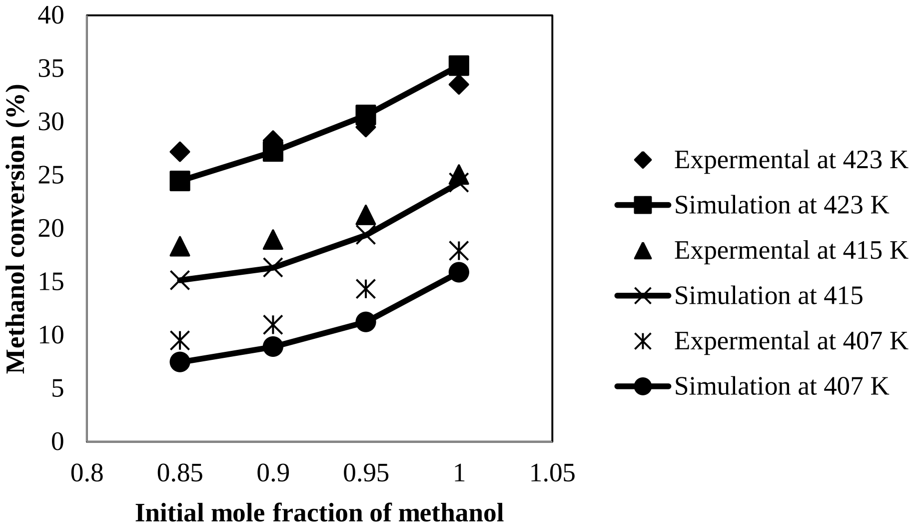

Figure 5.3 Comparison of simulated results and experimental result from Lei et al. (2011)

Table 5. 1 Comparison of simulated in this work and simulation result from Lei et al. (2011)

	Lei et al. model	Validated model
Dimethyl ether purity (%)	99.55	99.99
Dimethyl ether mass flow rate (kg/h)	102.96	103.425
Conversion	49.66	50.11

5.3 Standard condition of reactive distillation for dimethyl ether production

The reactive distillation column at standard condition consists of 13 stages. The numbering of the stages is top downward, with stage 1 as total condenser and stage n as reboiler. Feed stream of crude glycerol at feed flow rate of 3.078 kmol/hr is sent into reactive distillation at first stage of reactive stages. The reactive distillation is operated at 8 bar. The reactive stages are stages 5 to 9. The composition profile and temperature profile of the standard condition are showed in Figure 5.4 and 5.5, respectively. The standard conditions of distillation column are given at Table 5.2.

Table 5.2 Standard conditions of reactive distillation for dimethyl ether production

Condition of feed		Column specification	
Temperature (K)	298	Rectifying stages	3
Feed flow rate (kmol/hr)		Reaction stages	5
Crude glycerol	3.0786	Stripping stages	3
Feed stage		Reboiler duty (kW)	50
Crude glycerol	5	Reflux ratio	1.2
		Composition of crude glycerol feed (mol%)	
		Glycerol	70%
		Methanol	30%

All system performances of reactive distillation for dimethyl ether production were considered in terms of conversion of methanol. The conversion of methanol was defined as follows;

$$\% \text{ Conversion} = \frac{\text{Difference in molar flow rate of inlet and outlet of methanol}}{\text{Molar feed flow rate of methanol in crude glycerol to reactive distillation}} \times 100\%$$

Figure 5.4 and 5.5 show the composition profile and temperature profile at standard condition. Figure 5.4 demonstrates that, at the top of the column, the mole fraction of dimethyl ether and methanol are 79% and 21% respectively, while not amount of glycerol and water are observed. The bottom products consist of glycerol and water.

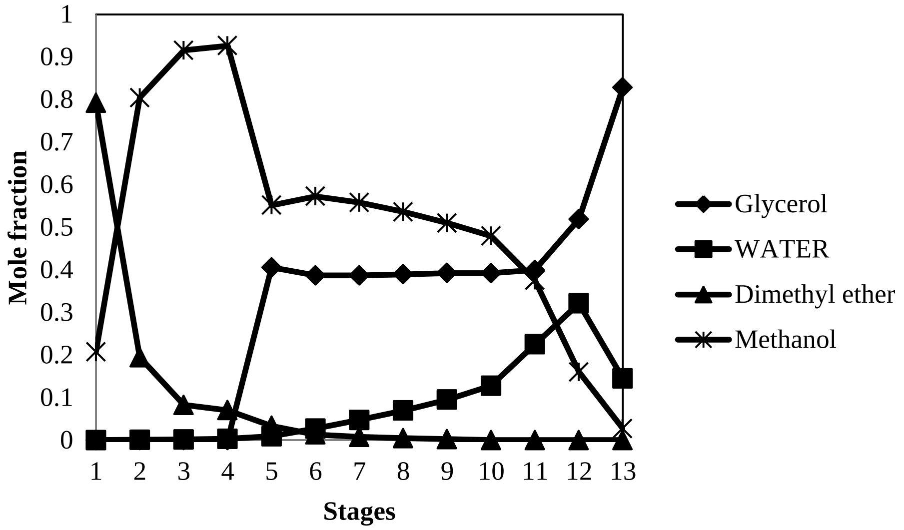

Figure 5.4 Composition profile at standard condition

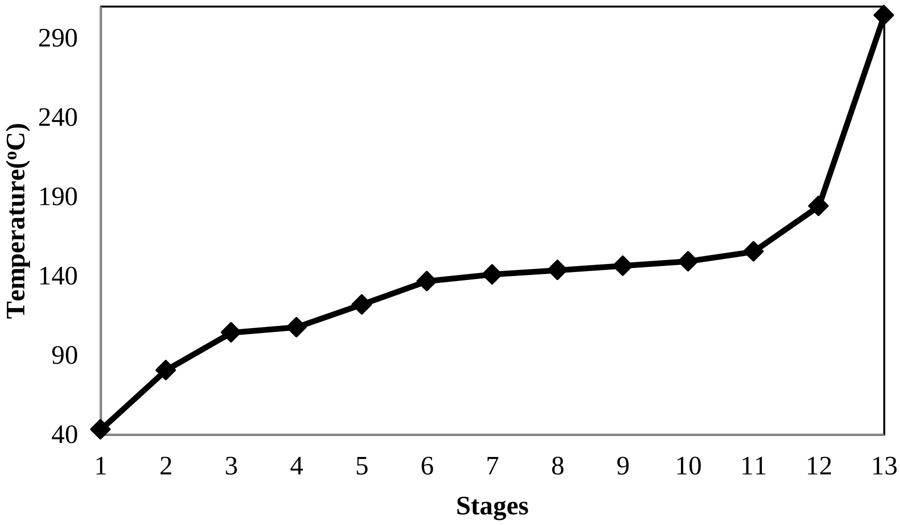

Figure 5.5 Temperature profile at standard condition

5.3.1 Effect of feed temperature

Figure 5.6 demonstrates effect of feed temperature of crude glycerol on conversion of methanol. It is found that conversion of methanol is decreasing when increasing feed temperature of crude glycerol. This is due to the fact that temperature of reactive stages is increasing from increasing feed temperature of crude glycerol.

The increasing temperature in reactive stages results in decreasing amount of methanol which is reactant of dimethyl ether in reactive stages.

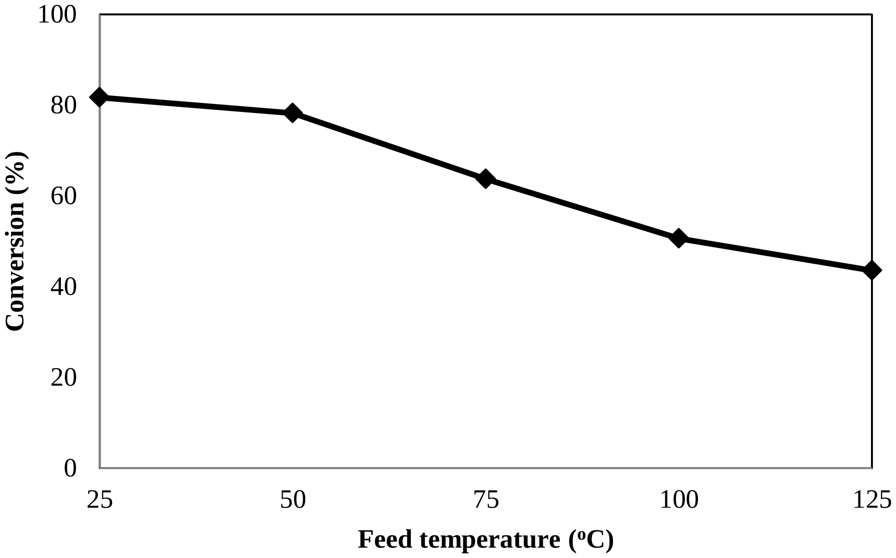

Figure 5.6 Effect of feed temperature of crude glycerol on conversion of methanol

5.3.2 Effect of reboiler heat duty

Figure 5.7 shows the effect of reboiler duty on conversion of methanol within range of 20 to 70 kW. It can be seen that increasing the reboiler heat duty results in decreasing of the conversion of methanol. As heat duty increases, water from reboiler comes to reactive stages. Because water is inhibitor of dehydration reaction of methanol, conversion of methanol in reactive stages is decreased by increasing reboiler duty.

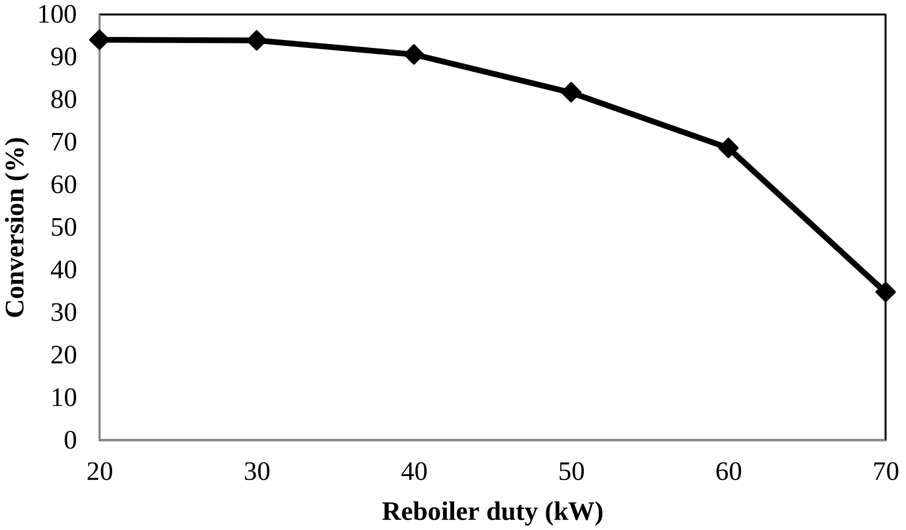

Figure 5.7 Effect of reboiler duty on conversion of methanol

5.3.3 Effect of feed stage location

Figure 5.8 shows effect of feed stage location on conversion of methanol. It is found that feeding crude glycerol at top of reactive stages gives best conversion of methanol. This is due to the fact that amount of methanol in reactive stages is decreased when the location feed of crude glycerol in the reactive distillation is below top of reactive stages. This is because temperature of reactive stages increases from top to bottom. For this reason, when feed crude glycerol lower top of reactive stages, more amount methanol is converted to vapor. In case of crude glycerol is fed at above reactive stages, conversion of methanol decreases because more amount methanol out from reactive distillation to top product (dimethyl ether). Moreover, purity of dimethyl ether decreases because methanol comes from feeding crude glycerol above reactive stages.

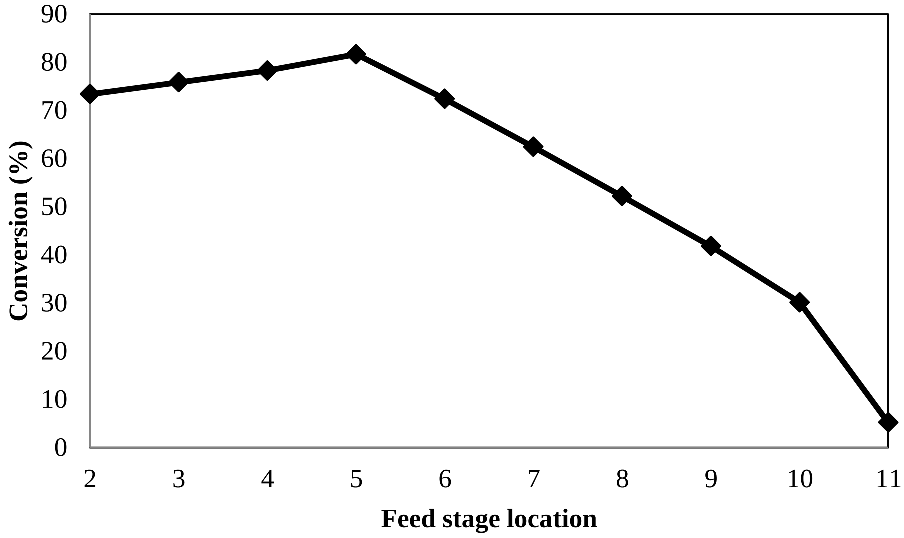

Figure 5.8 Effect of feed stages location on conversion of methanol

5.3.4 Effect of the number of reactive stages

Figure 5.9 shows that the number of reactive stages is most important parameter in term of conversion of methanol. Conversion of methanol rapidly increases when the number of reactive stages is varied from 1 to 6. This is beacuse increaseing the number of reactive stages results in increaseing space time of reactant as methanol in reactive stages.

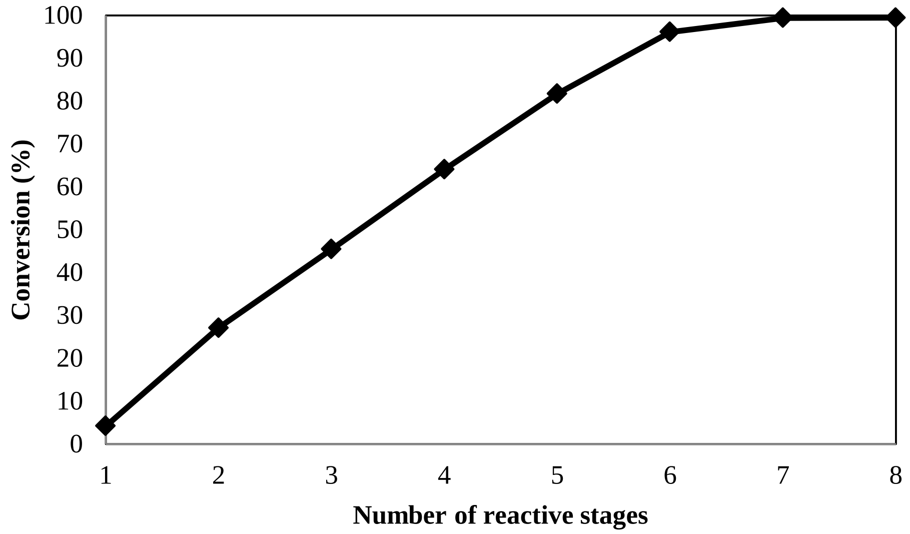

Figure 5.9 Effect of number of reactive stages on conversion of methanol

5.3.5 Effect of the number of rectifying stages

Figure 5.10 indicates that increasing the number of rectifying stages results in increasing amount of methanol in reactive stages. Moreover, amount of dimethyl ether in reactive stages is slightly decreasing. This result enhances a conversion of methanol.

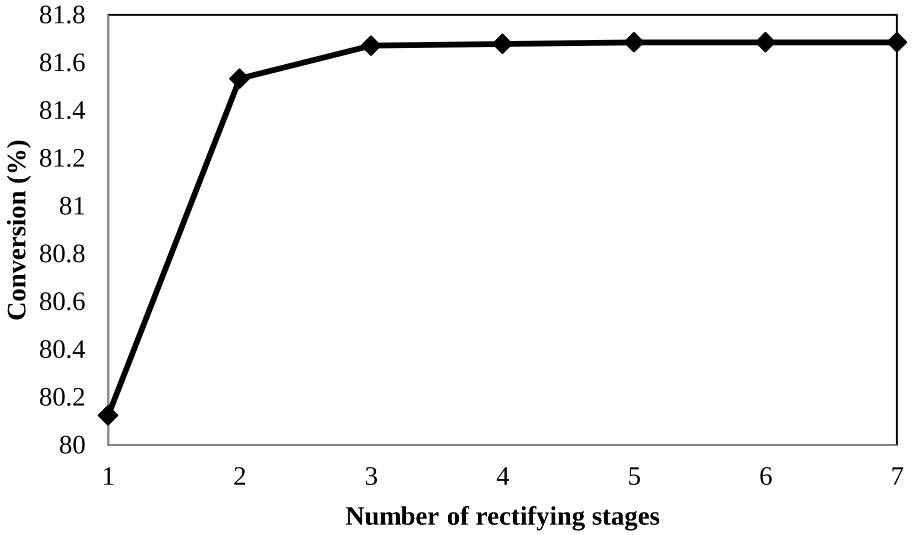

Figure 5.10 Effect of number of rectifying stages on conversion of methanol

5.3.6 Effect of the number of stripping stages

The influence of stripping stage is examined. The effect of stripping stages on conversion of methanol is shown in Figure 5.11. Figure 5.11 demonstrates that conversion of methanol can be increased by increasing the number of stripping stages. This is due to the fact that increasing the number of stripping stages results in increasing amount of methanol as a reactant.

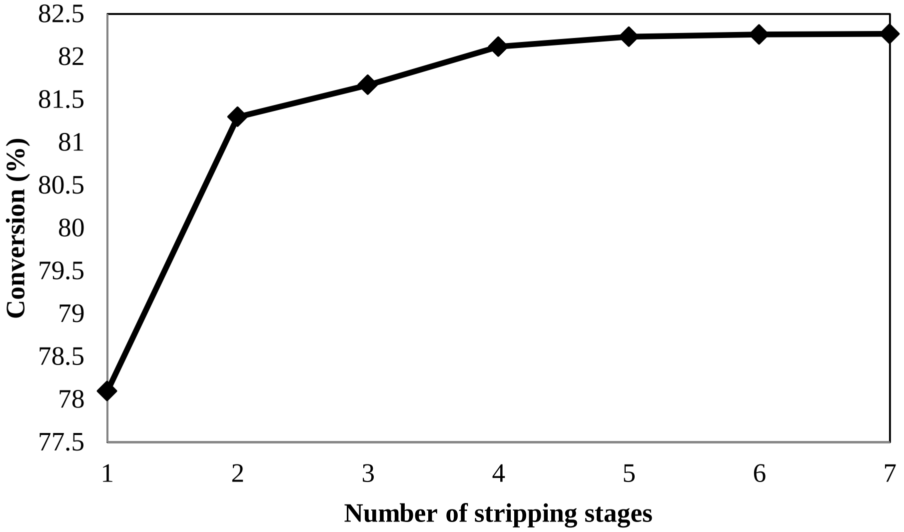

Figure 5.11 Effect of number of stripping stages on conversion of methanol

5.3.7 Effect of reflux ratio

Figure 5.12 shows the influent of reflux ratio on conversion of methanol. Increasing of reflux ratio results in the methanol that not reacts is fed back to the column. For this reason, conversion of methanol can be increased by increasing reflux ratio.

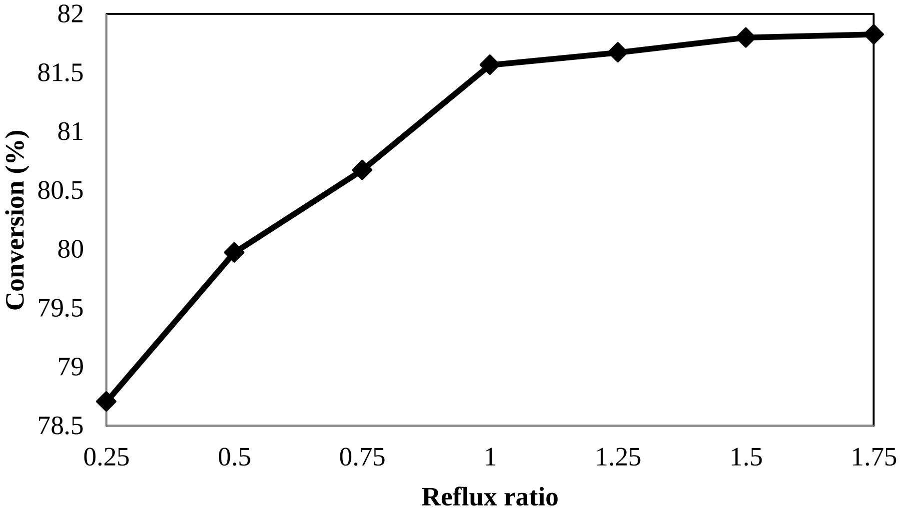

Figure 5.12 Effect of reflux ratio at varying number of reactive stages

5.4 Standard condition of distillation column

The distillation column at standard condition consists of 11 stages. The numbering of the stages is top downward, with stage 1 as total condenser and stage n as reboiler. Feed stream of glycerol-water at feed flow rate of 2.62 kmol/hr is sent into distillation at stage 5. The distillation column is operated at 1 bar. The standard conditions of distillation column are given at Table 5.3.

Table 5.3 Standard condition of distillation column for purify glycerol

Condition of feed		Column specification	
Temperature (K)		Total stages	11
Glycerol-water	600	Reboiler duty (kW)	6.02
Feed flow rate (kmol/hr)		Reflux ratio	1.9
Glycerol-water	2.62	Composition of glycerol-water feed (mol%)	
Feed stage		Glycerol	82.3%
Glycerol-water	5	Water	17.7%

5.4.1 Effect of reboiler heat duty

Figure 5.13 shows that increasing reboiler duty results in increasing of glycerol purity in glycerol stream by decreasing m of water at bottom of distillation column. However, molar flow rate of glycerol stream slightly decreases at reboiler duty more than 5 kW.

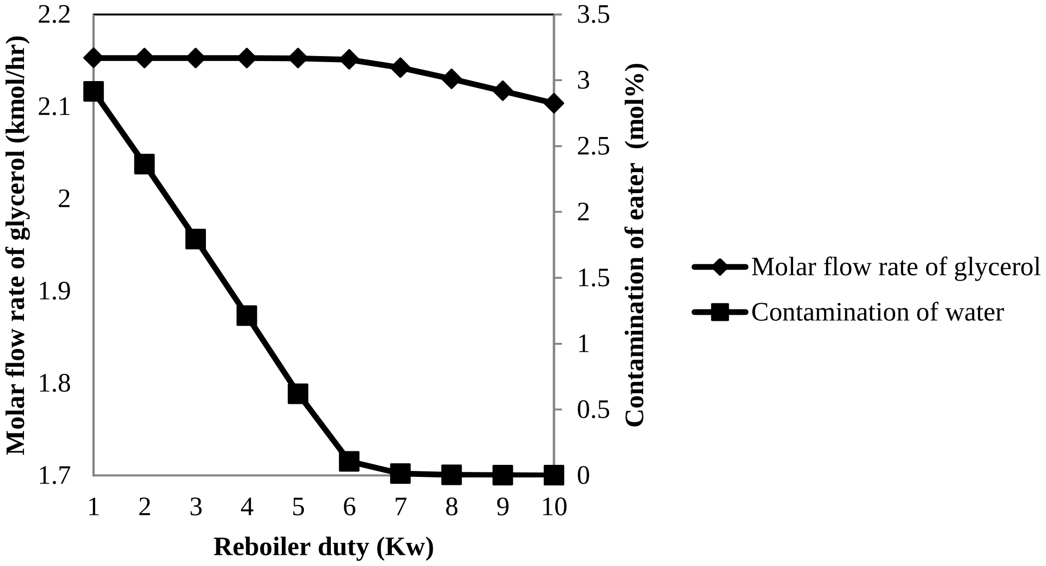

Figure 5.13 Effect of reboiler on molar flow rate of glycerol and mole fraction of water in pure glycerol stream

5.4.2 Effect of the number of stages

Figure 5.14 demonstrates that extending the number of stages while the other operating parameters are same as standard condition. The result shows that purity of glycerol stream is increasing by increasing number of reactive stages.

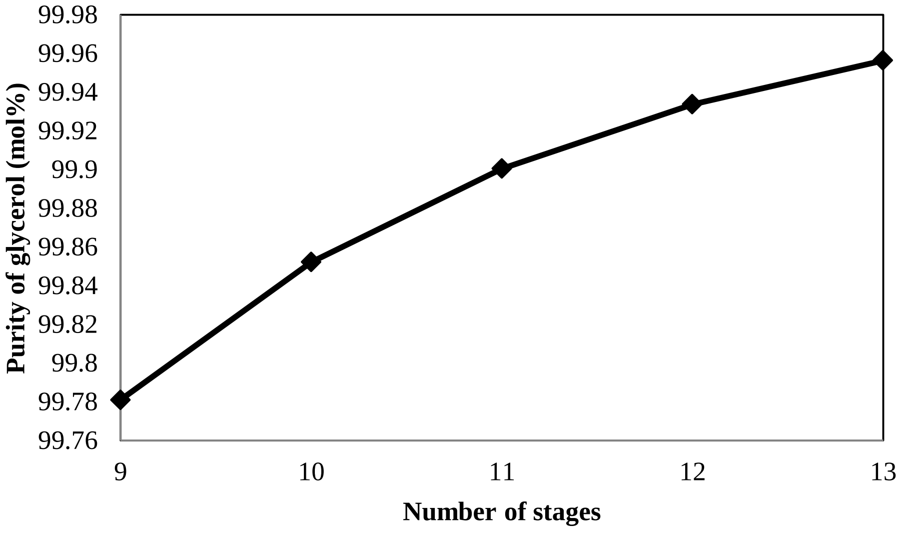

Figure 5.14 Effect of number of stages on glycerol fraction in pure glycerol stream

5.4.3 Effects of reflux ratio

Figure 5.15 indicates that glycerol flow in glycerol stream is increased with increasing reflux ratio because the glycerol at condenser is returned to distillation column. However, water contamination in glycerol stream is increased by increasing of reflux ratio.

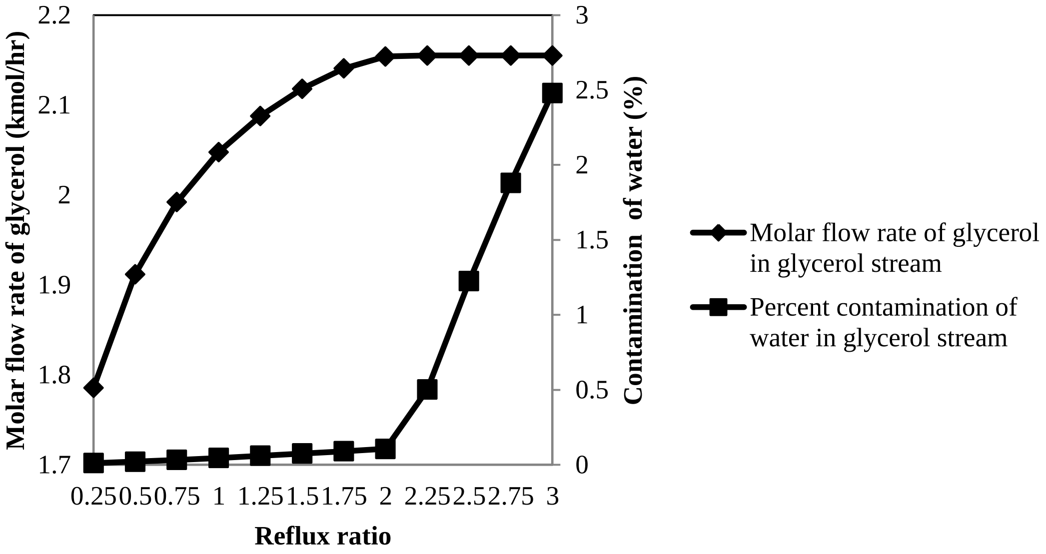

Figure 5.15 Effects of reflux ratio on molar flow rate of glycerol and mole fraction of water in pure glycerol stream

5.5 Optimal operating pressure of reactive distillation for dimethyl ether production

The operation pressure of reactive distillation for dimethyl ether production does not operate at 1 bar because temperature range of the separation must be corresponded to the reaction temperature. For this reason, an optimum pressure of reactive distillation for dimethyl ether production by using the total annual cost as the criteria was investigated. The standard condition of reactive distillation was used in this section. However, the number of reactive stages was increased to 7 reactive stages in order to increase conversion of methanol to 99%. Reflux ratio, and reboiler duty was also changed in order to meet this criteria. The total annual cost (TAC) is defined as shown below.

$$\mathrm{TAC} = \mathrm{TAC}_{\mathrm{ope}} + \frac{\mathrm{TAC}_{\mathrm{cap}}}{\text{Payback Period}}$$

The tray sizing function in aspen plus simulation was used to estimate diameter of reactive distillation. The distance between trays is kept at 2 ft. The calculation of capital cost ($\mathrm{TAC}_{\mathrm{cap}}$) and operating cost ($\mathrm{TAC}_{\mathrm{ope}}$) were calculated following the procedure in Douglas (1988). The annualized capital cost was calculated with the payback period of 3 years and using the cost data from Appendix B of Douglas (1988) book.

5.5.1 Assumption and specification for dimethyl ether stream and reactive distillation design

1. The design objective is to obtain 99 mol% conversion of methanol.
2. Purity of dimethyl ether is 99 mol%
3. The number of rectifying stages, reactive stages and stripping stages is fixed at 3, 7 and 3 respectively.
4. Feed location of crude glycerol is fixed at stages 5

The design procedure for finding optimum pressure of reactive distillation for dimethyl ether production is the following:

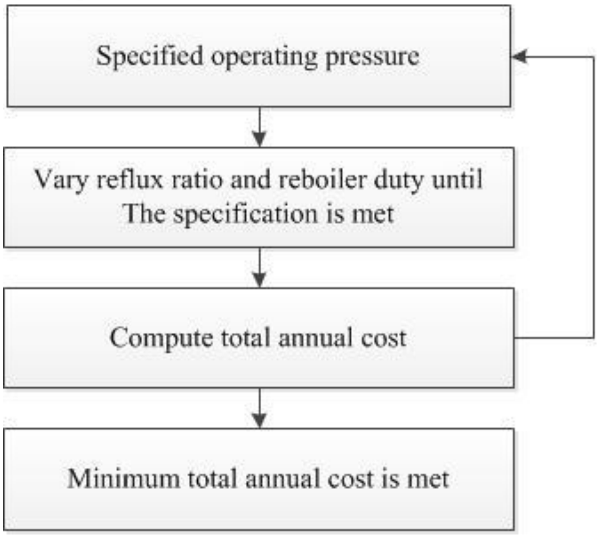

Figure 5.16 Design procedure for finding optimum pressure of reactive distillation for glycerol ether production

From the simulation result, figure 5.17 indicates that operating reactive distillation pressure at 9 bar provides the lowest total annual cost.

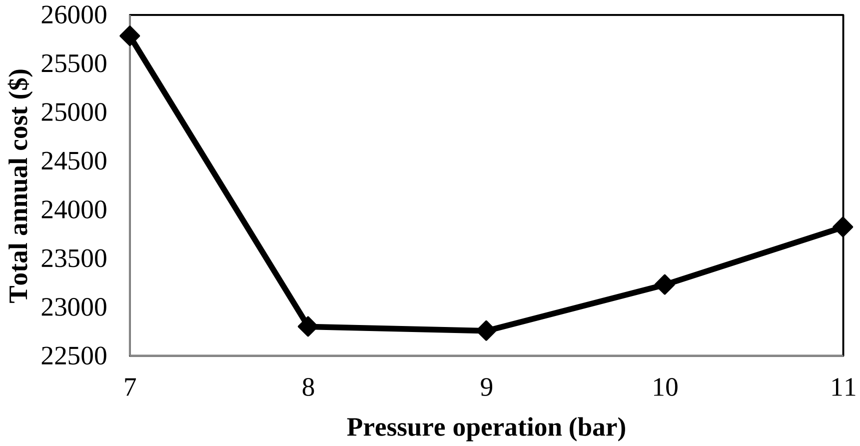

Figure 5.17 Relationship of reactive distillation pressure operation on total annual cost

5.6 Economic assessment of reactive distillation for dimethyl ether production

This section is to study the steady-state economics of reactive distillation for dimethyl ether production. An optimum reactive distillation for dimethyl ether production by using the total annual cost as the criteria was investigated. The total annual cost includes operating cost and annualized capital cost. The optimal operation parameters including the number of reactive stages, reflux ratio, reboiler duty and etc. were obtained by calculating a minimum total annual cost. The total annual cost (TAC) is defined as shown below.

$$\text{TAC} = \text{TAC}_{\text{ope}} + \frac{\text{TAC}_{\text{cap}}}{\text{Payback Period}}$$

The tray sizing function in aspen plus simulation was used to estimate diameter of reactive distillation and distillation column. The distance between trays is keep at 2 ft. The calculation of capital cost (TAC cap) and operating cost (TAC ope) were calculated following the procedure in Douglas (1988). The calculation of capital cost included the cost of reactive distillation. The calculation of operating cost included cooling water and streaming cost.

5.6.1 Assumptions and specifications for dimethyl ether stream and reactive distillation design

The annualized capital cost was calculated with the payback period of 3 years and using the cost data from Appendix B of Douglas (1988) book. The reactive distillation is operated at 9 bar.

Assumption and specification of reactive distillation for dimethyl ether production design

1. The design objective is to obtain 99 mol% conversion of methanol.
2. Purity of dimethyl ether in dimethyl stream is 99 mol%
3. Mole flow of dimethyl ether in dimethyl stream is 0.457 kmol/hr
4. Crude glycerol is fed at first stage of reactive stages

Based on these assumption and specification, there are five variables to optimize, the designs are as follows:

1. Number of rectifying stages
2. Number of stripping stages
3. Number of reactive stages
4. Reflux ratio
5. Reboiler duty

The design procedure of reactive distillation for dimethyl ether production is the following:

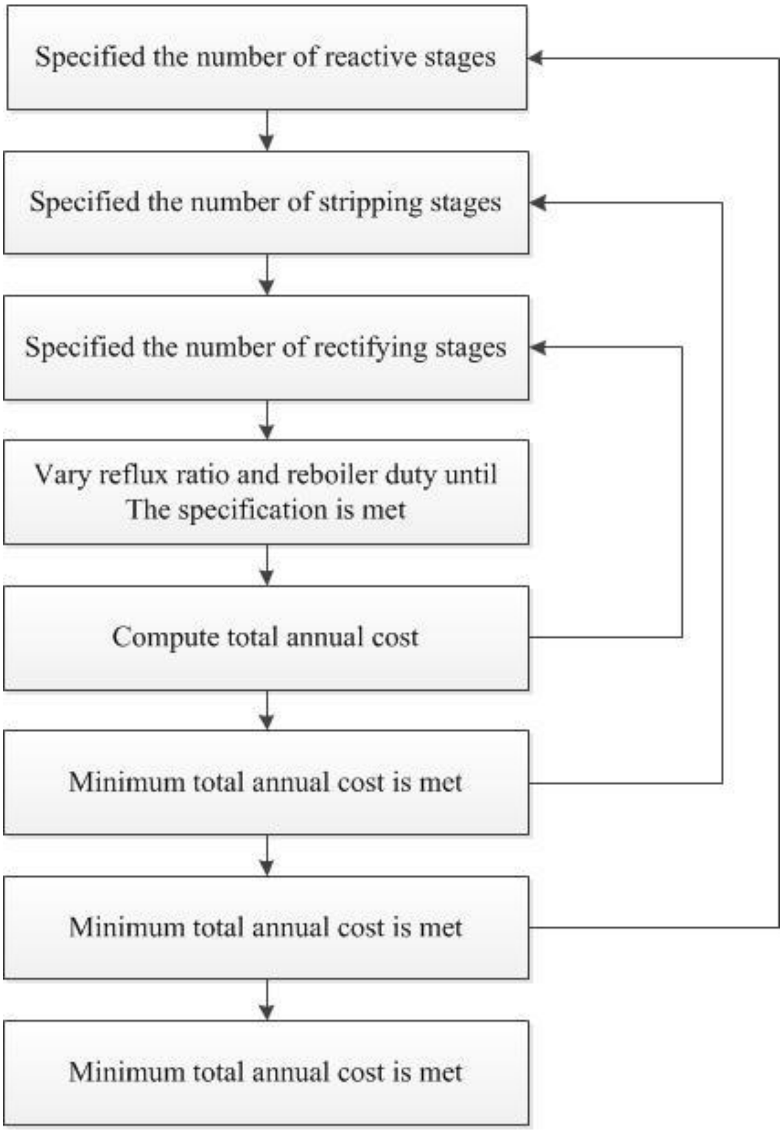

Figure 5.18 Design procedure of reactive distillation for dimethyl ether production

5.6.2 Result

Figure 5.19 shows that the number of reactive stages is important parameter. First, space time of reactant as methanol in reactive stages can be increased by increasing the number of reactive stages. For this reason, conversion of methanol is increasing. Second, increasing the number of reactive stages can help separation light product as dimethyl ether from water as by-product and glycerol. For this reason, it can reduce energy consumption in reboiler and reboiler size. For this reason, increasing the number of reactive stages can reduce operating cost and capital cost of reboiler. However, increasing the number of reactive stages more than 8 stages result in higher capital cost. We concluded that the optimum number of reactive stages is 8 stages.

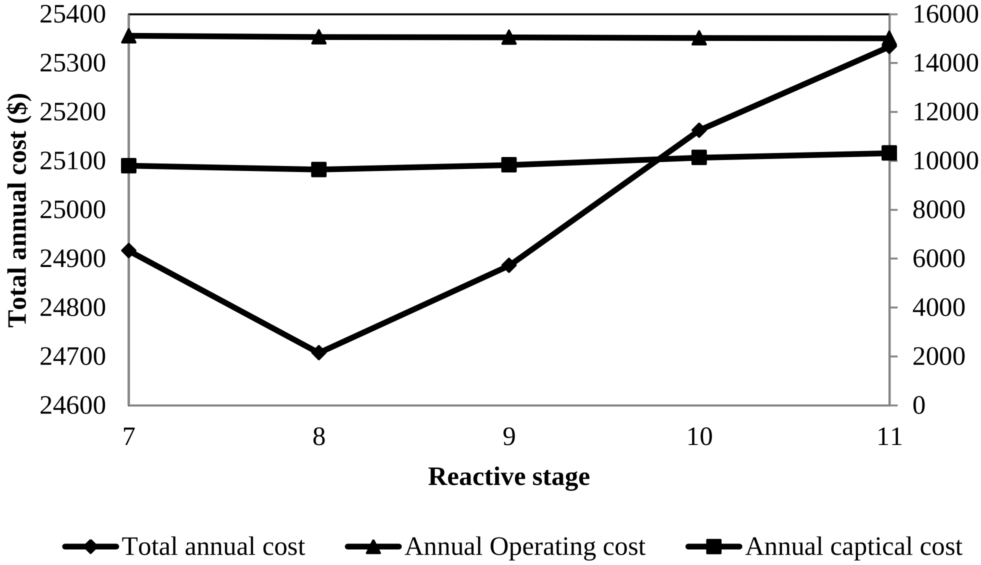

Figure 5.19 Effects of reactive stages on total annual cost

The effects of reactive stages, rectifying stages and stripping stages of reactive distillation are demonstrated in Figure 5.20, 5.21 and 5.22. Because methanol is completely used in reactive stage, all remaining components in reactive distillation are dimethyl ether, glycerol and water. Boiling point of glycerol and water are much higher than that of dimethyl ether, so separation dimethyl ether from water and glycerol requires a few rectifying and stripping stages to achieve purity specification.

Increasing the number of rectifying stages can help separation dimethyl ether out from reactive stages and separate methanol to reactive stages. This result reduces reboiler duty and condenser, so operating cost can be reduced by increasing rectifying stages.

Increasing the number of stripping stages provides many benefits. First, increasing can help separation methanol to reactive stages. For these reasons, operating cost of reboiler is reducing. Second, increase the number of stripping stages can help separation glycerol to bottom of reactive distillation. However, increasing the number of rectifying and stripping stages requires more capital cost. From Figure 5.20, 5.21 and 5.22, they show that the optimum rectifying stage is 2 stages and optimum stripping stage is 2 stages.

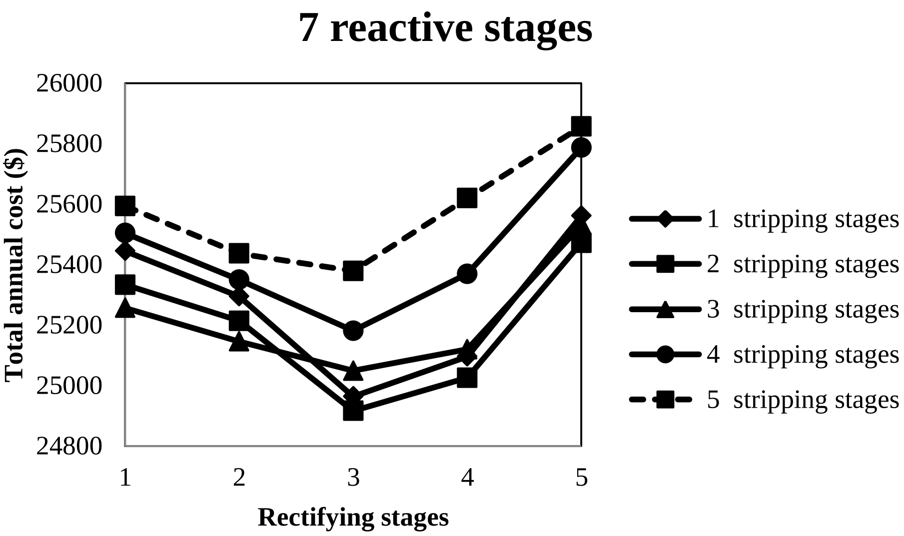

Figure 5.20 The effect of rectifying and stripping stage on total annual cost of reactive distillation for dimethyl ether production by fix reactive stages at 7 stages

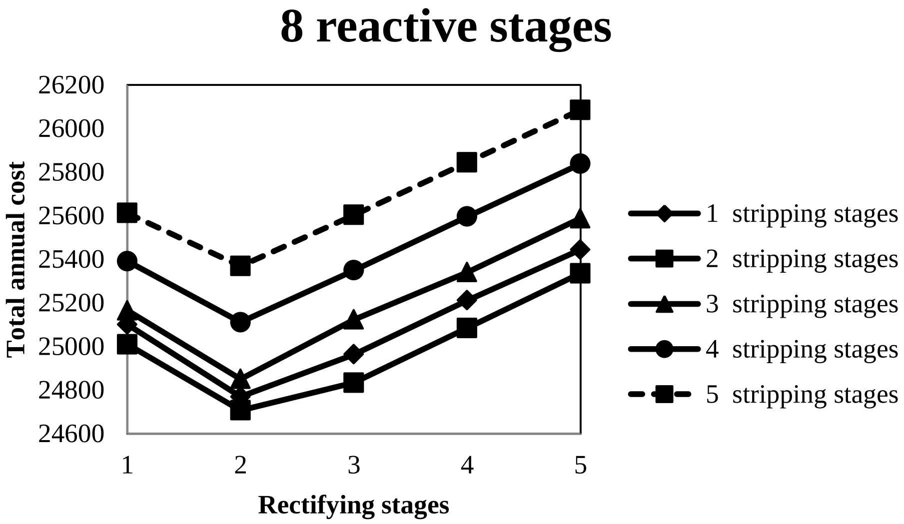

Figure 5.21 The effect of rectifying and stripping stage on total annual cost of reactive distillation for dimethyl ether production by fix reactive stages at 8 stages

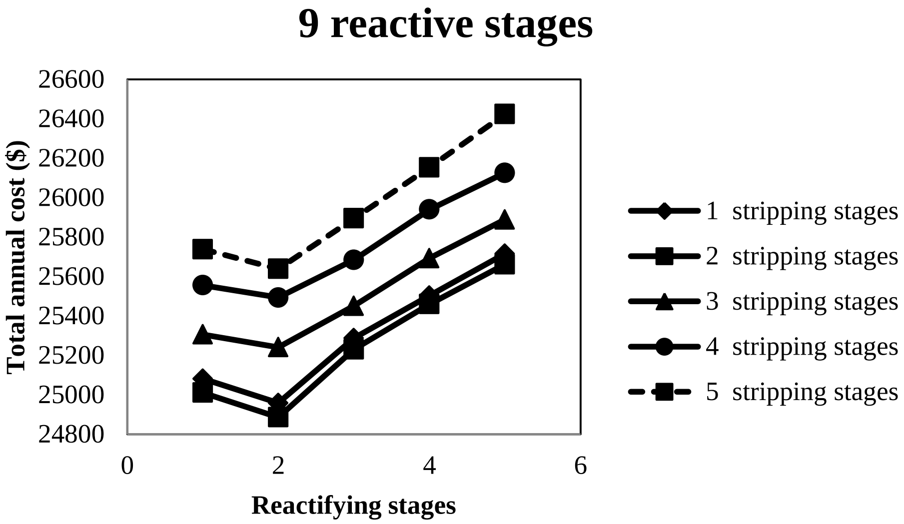

Figure 5.22 The effect of rectifying and stripping stage on total annual cost of reactive distillation for dimethyl ether production by fix reactive stages at 9 stages

For effect of reflux ratio, increasing of reflux ratio results in the methanol that not reacts is fed back to the column. For this reason, conversion of methanol can be increased by increasing reflux ratio. However, higher reflux ratio requires more operating cost.

For effects of reboiler duty, increasing reboiler duty results in increasing water in reactive stages, which is inhibited dehydration reaction of methanol, in reactive stages and decreasing amount of methanol in reactive stages. For this reason, conversion of methanol is decreased by increasing reboiler duty. However, reboiler duty must operate at decent value because reboiler duty must be high enough to separate dimethyl ether from glycerol and water. The optimal operating reboiler duty is 49.42 kW. The optimal operating parameters of reactive distillation are summarized in Table 5.4.

Table 5.4 Optimal operating parameters of reactive distillation for dimethyl ether production

Condition of feed		Column specification	
Temperature (K)	298	Rectifying stages	2
Feed flow rate (kmol/hr)		Reaction stages	8
Crude glycerol	3.078	Stripping stages	2
Feed stage		Reboiler duty (kW)	49.43
Crude glycerol	5	Reflux ratio	0.22
		Composition of crude glycerol stream (mol%)	
		Glycerol	70%
		Methanol	30%

5.7 Economic assessment of distillation column for production pure glycerol

This section is to study the steady-state economics of distillation column for separation glycerol out from water. An optimum distillation column for production pure glycerol by using the total annual cost as the criteria was investigated. The total annual cost includes operating cost and annualized capital cost. The optimal operation parameters including the number of stages, reflux ratio, reboiler duty and etc. were obtained by calculating a minimum total annual cost. The total annual cost (TAC) is defined as shown below.

$$\mathrm{TAC} = \mathrm{TAC}_{\mathrm{ope}} + \frac{\mathrm{TAC}_{\mathrm{cap}}}{\text{Payback Period}}$$

The tray sizing function in aspen plus simulation was used to estimate diameter of distillation column. The distance between trays is kept at 2 ft. The calculation of capital cost (TAC cap) and operating cost (TAC ope) was calculated following the procedure in Douglas (1988). The calculation of capital cost included the cost of distillation column. The calculation of operating cost included cooling water and streaming cost.

5.7.1 Assumptions and specifications for glycerol stream

The annualized capital cost was calculated with the payback period of 10 years and using the cost data in Appendix B of Douglas (1988) book.

Assumption and specification for glycerol stream

1. The purity of glycerol of glycerol stream is 99.9 mol%.
2. Glycerol flow rate in glycerol stream is 2.15 kmol/hr.

Based on these assumption and specification, there are four variables to optimize. The designs are as follows:

1. Number of stages
2. Feed stage location
3. Reflux ratio
4. Reboiler duty

The design procedure of distillation column for separation glycerol from water is the following:

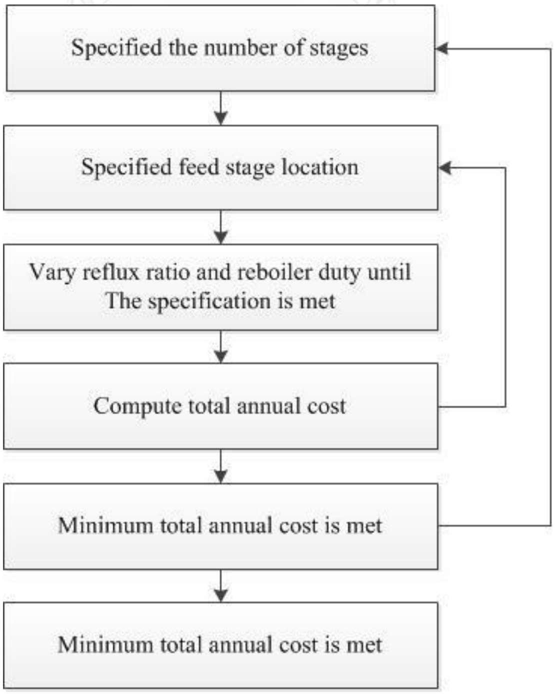

Figure 5.23 Design procedure of distillation column for separation glycerol from water

5.7.2 Result

In distillation column, which is for separation water from glycerol, reflux ratio is important parameter. Glycerol flow in glycerol stream is increased by increasing reflux ratio but water contamination in glycerol stream is increased by increasing of reflux ratio. The reflux ratio must be operated highly enough to maintain glycerol flow rate at 2.15 kmol/hr in glycerol stream. However, excessive reflux ratio results in decreasing purity of glycerol in glycerol stream. For this reason, reflux ratio must be operated at 1.92 in order to maintain both molar flow rate of glycerol and purity of glycerol constraint in glycerol stream. Moreover, higher reflux ratio results in higher total annual cost.

Increasing reboiler duty results in increasing of glycerol purity in pure glycerol stream. However, molar flow rate of glycerol stream is slightly decreased at reboiler duty more than 5 kW. Moreover, higher reboiler duty results in higher total annual cost. Figure 5-24 demonstrates effects of feed stage on total annual cost. Feed stages location must be fed at decent location in order to make appropriate amount of stages below and above feed stage location.

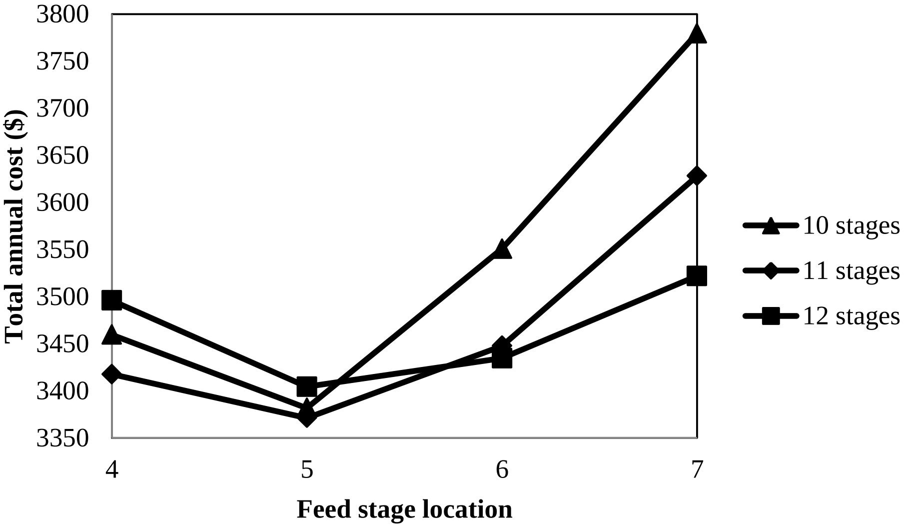

Figure 5.24 Effects of feed location on total annual cost

Figure 5.25 demonstrates that 11 stages of distillation column give lowest total annual cost at the same both purity of glycerol and glycerol flow rate in pure glycerol stream.

Because purity of glycerol stream is increasing from increasing the number of stages, reboiler for separation water from glycerol can be reduced. For this reason, operating cost is reducing. However, increasing number of stages require more capital cost. The numbers of optimal stages in distillation column are 11 stages. Effects of the number of stages on total annual cost of distillation column are showed in Figure 5.25.

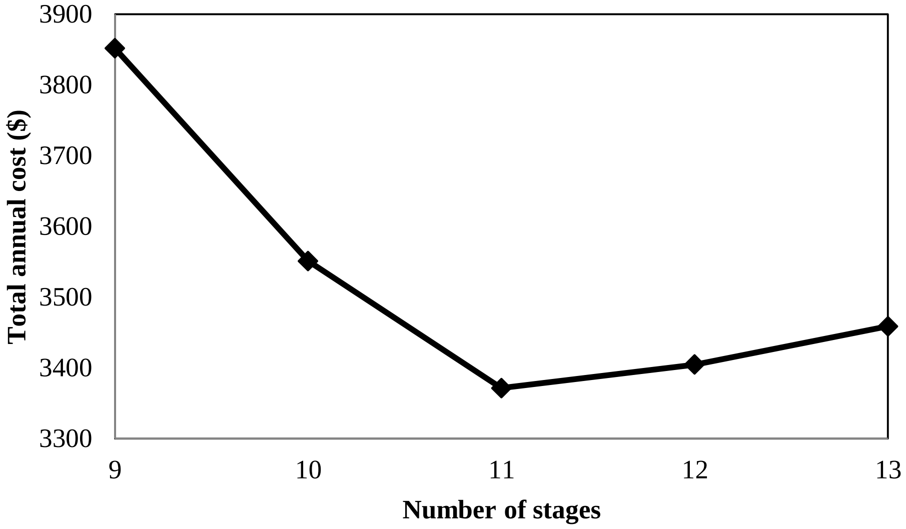

Figure 5.25 Effects of number of stages on total annual cost

The optimal operating parameters of distillation column are summarized in Table 5.5.

Table 5.5 Optimal operating parameters of distillation column

Condition of feed		Column specification	
Temperature (k)	599.64	Total stages	11
Feed flow rate (kmol/hr)	2.62	Reboiler duty (kW)	6.021
Feed stage	5	Reflux ratio	1.92
Main composition of feed (mol%)			
Glycerol	82.3 %		
Water	17.5 %		

CHAPTER VI

TERT- BUTYL ALCOHOL RECOVERY

From chapter IV, we explored the optimal operating condition of reactive distillation for glycerol ether production. The glycerol ether production process uses excess tert-butyl alcohol to get high conversion of glycerol and yield of di and tri tert-butyl ether of glycerol. For this reason, after the etherification of tert-butyl alcohol and glycerol is complete, excess of tert-butyl alcohol is available for recovery. However, this excess tert-butyl alcohol is form azeotrope with water as by-product of etherification reaction of tert-butyl alcohol and glycerol. Binary mixtures which form azeotrope are characterized like a pure component when they are sent to a distillation column. For this reason, the separation of binary mixtures which form azeotropes is not possible separation by conventional distillation (de Figueirêdo et al., 2011). Solvent for separation tert-butyl alcohol from water which was listed by Berg and Yang (1992) was used in this work. The list of solvents which is used in this work is 3-octanone, hexyl acetate and 2-heptanone. In this chapter, we demonstrate the tert-butyl alcohol recovery process. In this chapter considers extractive distillation for separation tert-butyl alcohol from water and distillation for separation tert-butyl alcohol from solvent. The optimal operating parameters of the extractive distillation and distillation column based on a total annual cost analysis are studied in section 6.3. Different solvent is compared in term of total annual cost in section 6.3.6 while comparison of solvent in term of total annual cost and potential environmental impact is shows in section 6.4.

6.1 Process flow sheet description

The design plant flow sheet of this chapter is presented in Figure 6.1. This plant flow sheet contains two units as follows: extractive distillation and distillation column. The extractive distillation is used to separate tert-butyl alcohol out from water. Solvent stream and tert-butyl alcohol – water stream are fed into extractive distillation in order to separate tert-butyl alcohol from water. The mole flow of tert-butyl alcohol – water stream is 12.9 kmol/hr. The composition in this stream is tert-butyl alcohol 66.16 % and water 33.8 %. The temperature in this stream is 79.7 ^{o}C. Waste water outs from top of extractive distillation whereas tert-butyl alcohol – solvent stream outs from bottom of extractive distillation and sent to distillation column. The distillation column is used to separate tert-butyl alcohol out from solvent. The solvent from bottom of distillation column is recovered in order to reuse in extractive distillation. However, some of solvent lost in waste water stream. For this reason, recovery solvent must be mixed with makeup solvent before being sent to extractive distillation. The temperature of solvent in solvent stream is reduced to 25 ^{o}C.

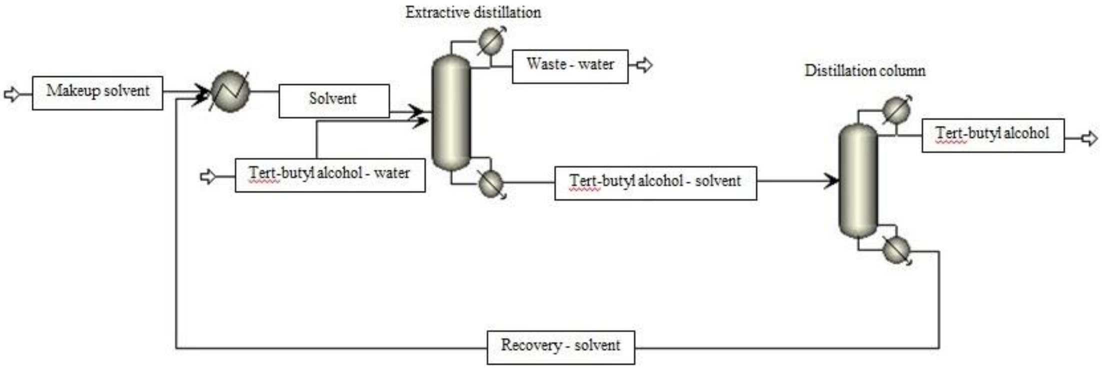

Figure 6.1 The plant flow sheet for recovery tert-butyl alcohol

6.2 Simulation method for extractive distillation and distillation column

The simulation studies of the extractive distillation and distillation column were performed by using Aspen Plus simulator. Both extractive distillation and distillation column were operated at 1 bar. The pressure drop in extractive distillation and distillation column was neglected. The numbering of the stages is top downward, with stage 1 as total condenser and stage n as reboiler. The simulation of extractive distillation and distillation column were performed based on RADFRAC module, which is a rigorous equilibrium-stage distillation model to describe a multistage vapor-liquid separation of distillation column, in Aspen Plus commercial software. The NRTL-RK model was employed to predict thermodynamic properties and phase equilibrium of substances in the system. The interaction parameters were taken from Aspen Plus database or were estimated using UNIFAC-Dortmund modified method.

6.3 Economic assessment

6.3.1 Economic assessment of extractive distillation

This section is to study the effects of different solvent on steady-state economics of single extractive distillation. An optimum condition of single extractive distillation by using the total annual cost as the criteria was investigated. The total annual cost includes operating cost and annualized capital cost. The optimal operation parameters including the number of stages, reflux ratio, reboiler duty and etc. were obtained by calculating a minimum total annual cost. The total annual cost (TAC) is defined as shown below.

$$\mathrm{TAC} = \mathrm{TAC}_{\mathrm{ope}} + \frac{\mathrm{TAC}_{\mathrm{cap}}}{\text{Payback Period}}$$

The tray sizing function in aspen plus simulation was used to estimate diameter of extractive distillation. The distance between trays is kept at 2 ft. The calculation of capital cost ($\mathrm{TAC}_{\mathrm{cap}}$) and operating cost ($\mathrm{TAC}_{\mathrm{ope}}$) was calculated following the procedure in Douglas (1988). The annualized capital cost was calculated with the payback period of 10 years and using the cost data from Appendix B of Douglas (1988) book.

The assumption and specification of extractive distillation and tert-butyl alcohol – solvent stream include:

1. Amount of water in tert-butyl alcohol – solvent stream is 0.05 mol%.
2. Mole flow of tert-butyl alcohol in tert-butyl alcohol – solvent is 8.38 kmol/hr
3. Feed stage of solvent is fixed at stage 2

Based on these assumption and specification, there are four variables to optimize, the designs are as follows:

1. The number of stages
2. Feed stage location of tert-butyl alcohol – water stream
3. Reflux ratio
4. Reboiler duty

The design procedure of extractive distillation for separation water from tert-butyl alcohol is the following:

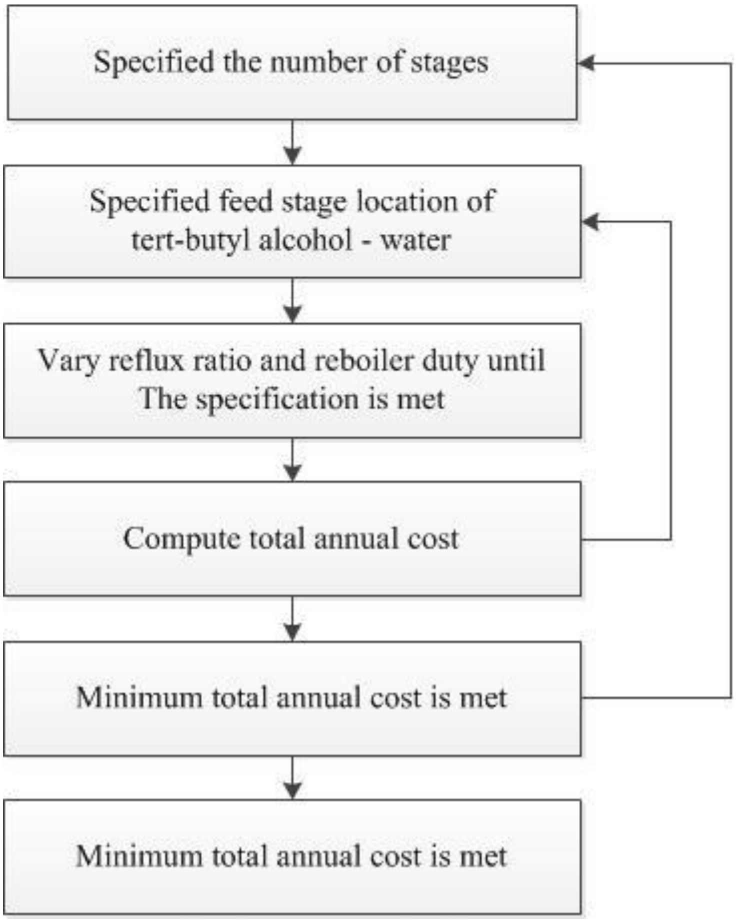

Figure 6.2 The design procedure of extractive distillation

6.3.2 Economic assessment of distillation column

This section is to study the effects of different solvent on steady-state economics of single distillation column. An optimum condition of single distillation column by using the total annual cost as the criteria was investigated. The total annual cost includes operating cost and annualized capital cost. The optimal operation parameters including the number of stages, reflux ratio, reboiler duty and etc. were obtained by calculating a minimum total annual cost. The total annual cost (TAC) is defined as shown below.

$$\mathrm{TAC} = \mathrm{TAC}_{\mathrm{ope}} + \frac{\mathrm{TAC}_{\mathrm{cap}}}{\text{Payback Period}}$$

The tray sizing function in aspen plus simulation was used to estimate diameter of distillation column. The distance between trays is kept at 2 ft. The calculation of capital cost (TAC_{cap}) and operating cost (TAC_{ope}) was calculated following the procedure in Douglas (1988). The annualized capital cost was calculated with the payback period of 10 years and using the cost data from Appendix B of Douglas (1988) book.

The Assumption and specification of tert-butyl alcohol stream and solvent stream include:

1. Purity of solvent in solvent stream is more than 99.9 mol%
2. Purity of tert-butyl alcohol in tert-butyl alcohol stream is more than 99.8 mol%

Based on these assumption and specification, there are four variables to optimize, the designs are as follows:

1. The number of stages
2. Feed stage location
3. Reflux ratio
4. Reboiler duty

The design procedure of distillation column for separation tert-butyl alcohol from solvent is the following:

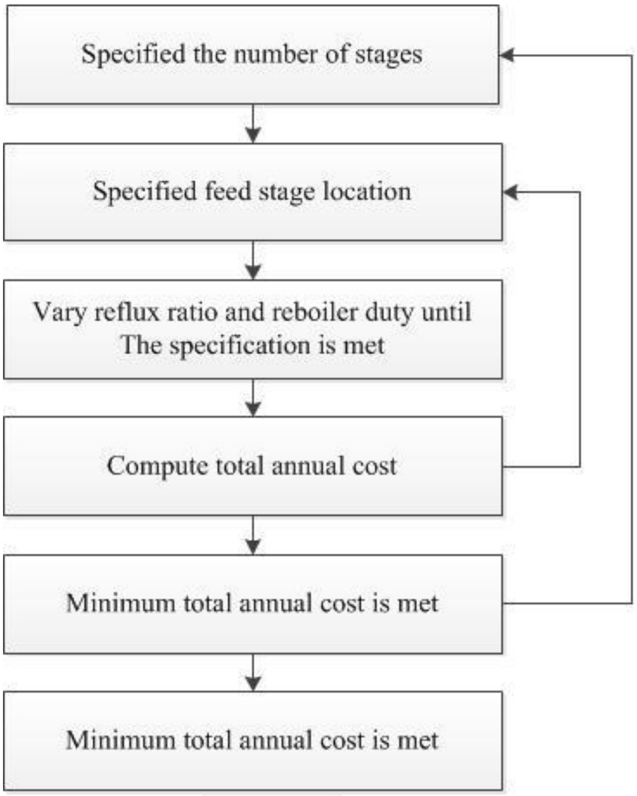

Figure 6.3 The design procedure of distillation column

6.3.3 Result of using 3-octanone as solvent

Extractive distillation

The standard conditions of extractive distillation by using 3-octanone as solvent are summarized in Table 6.1.

Table 6.1 Standard conditions of extractive distillation by using 3-octanone as solvent

Column specification	
Total stages	30
Reboiler duty (kW)	190
Reflux ratio	1.2
Feed stage location	
3-octanone	2
Tert-butyl alcohol - water	12
Mole flow of 3-octanone (kmol/hr)	11

The mole flow of 3-octanone as a solvent is investigated. The operating parameters are the same as the standard conditions. However, reboiler duty and reflux ratio are adjusted in order to reduce amount of water in tert-butyl alcohol – solvent stream to 0.05 mol% and increase mole flow of tert-butyl alcohol in tert-butyl alcohol – solvent stream to 8.38 kmol/hr. Figure 6.4 demonstrates that mole flow of 3-octanone in solvent stream at lower than 11 kmol/hr cannot achieve these objectives. Mole flow of 3-octanone at 11 kmol/hr and more are enough for these objectives. For this reason, mole flow of 3-octanone is used at 11 kmol/hr.

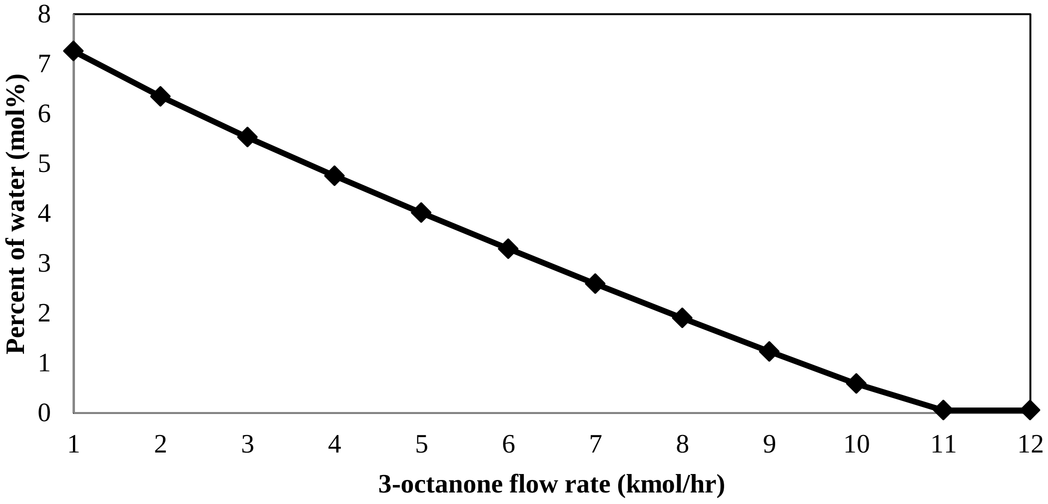

Figure 6.4 The effects of mole flow of 3-octanone at standard conditions of extractive distillation

The reflux ratio is important parameter. The operating parameters are the same as the standard conditions. However, reboiler duty is adjusted in order to reduce amount of water in tert-butyl alcohol – solvent stream to 0.05 mol%. Figure 6.5 shows that mole flow of tert-butyl alcohol in tert-butyl alcohol – solvent stream is increasing by increasing reflux ratio. However, mole flow of tert-butyl alcohol in tert-butyl alcohol – solvent stream is slightly increasing when reflux ratio is higher than 0.7. Moreover, 3-octanone lost in waste water stream is increasing when reflux ratio is higher than 0.7.

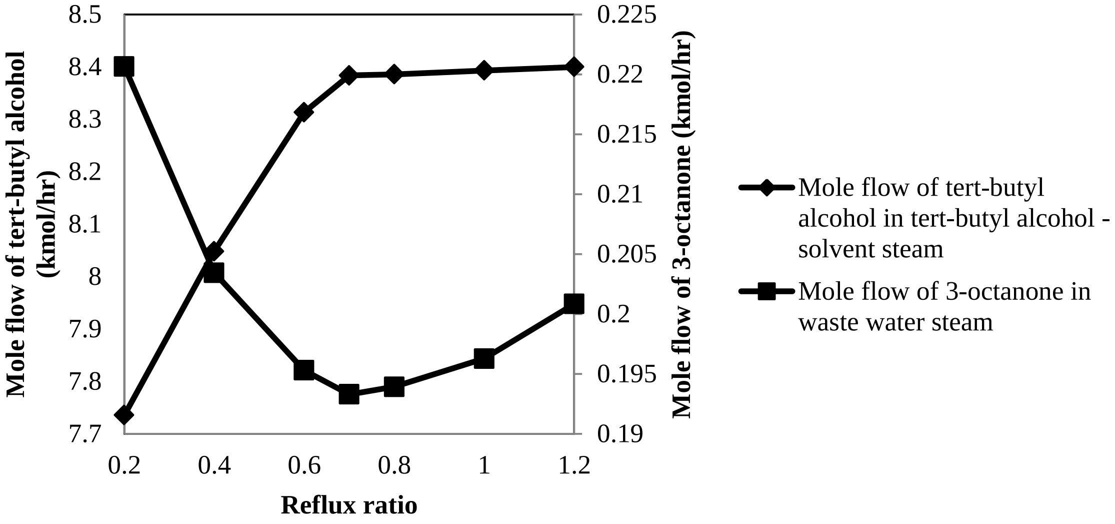

Figure 6.5 The effects of reflux ratio on mole flow of tert-butyl alcohol and mole flow of solvent loss of extractive distillation by using 3-octanone as solvent

The Figure 6.6 shows the effects of tert-butyl alcohol – water feed stage location on total annual cost at different number of stages of extractive distillation. Feed stages location must be fed at decent location in order to make appropriate amount of stages below and above feed stage location.

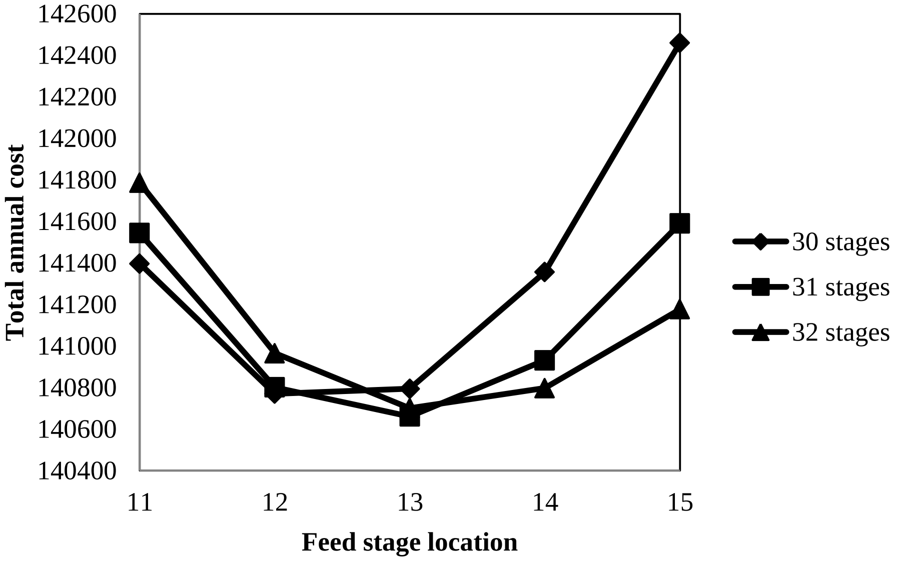

Figure 6.6 The effects of tert-butyl alcohol – water feed stage location on total annual cost at different number of stages of extractive distillation by using 3-octanone as solvent

Increasing the number of stages of extractive distillation can reduce operating cost at the same specification by decreasing reflux ratio but this increases the capital cost. Figure 6.7 demonstrates the effects of the number of stages of extractive distillation on total annual cost.

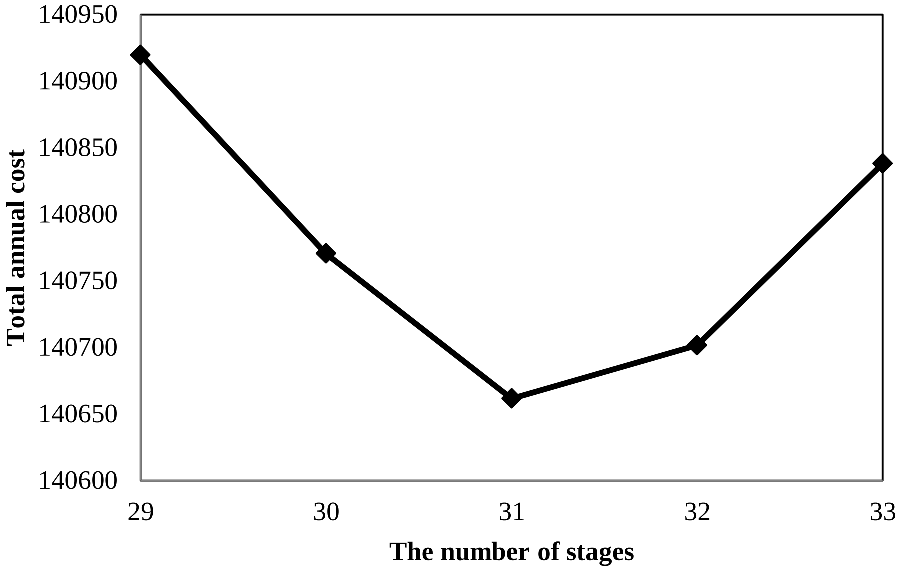

Figure 6.7 The effects of the number of stages on total annual cost of extractive distillation by using 3-octanone as solvent

The optimal operating parameters of extractive distillation column for using 3-octanone as solvent are summarized in Table 6.2.

Table 6.2 The optimal operating parameters of extractive distillation column for using 3-octanone as solvent

Column specification	
Total stages	31
Reboiler duty (kW)	164.1
Reflux ratio	0.66
Feed stage location	
3-octanone	2
Tert-butyl alcohol - water	13
Mole flow of 3-octanone (kmol/hr)	11

Distillation column

Figure 6.8 shows the effects of tert-butyl alcohol – solvent feed stage location on total annual cost at different number of stages of distillation column.

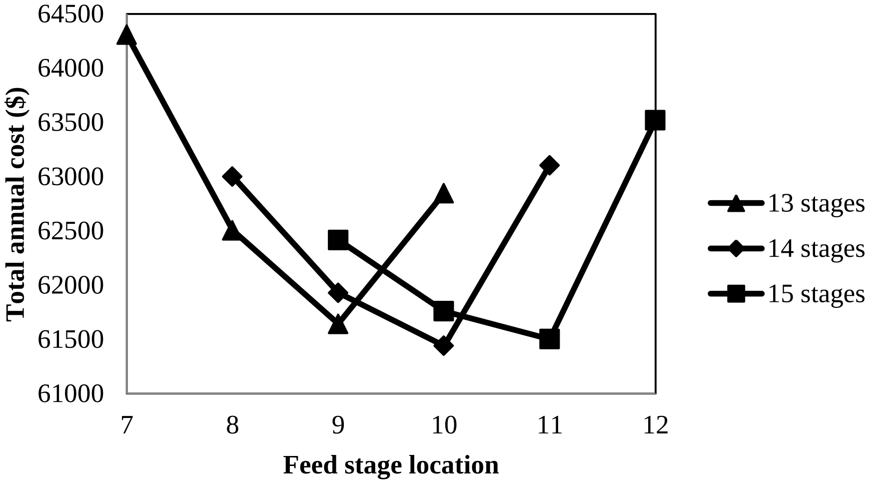

Figure 6.8 The effects of tert-butyl alcohol – solvent feed stage location on total annual cost at different the number of stages of distillation column by using 3-octanone as solvent

Increasing number of stages of distillation column can reduce operating cost at same specification by reducing reflux ratio but this requires more capital cost. The numbers of optimal stages in distillation column were 14 stages. The effects of the number of stages on total annual cost are showed in Figure 6.9.

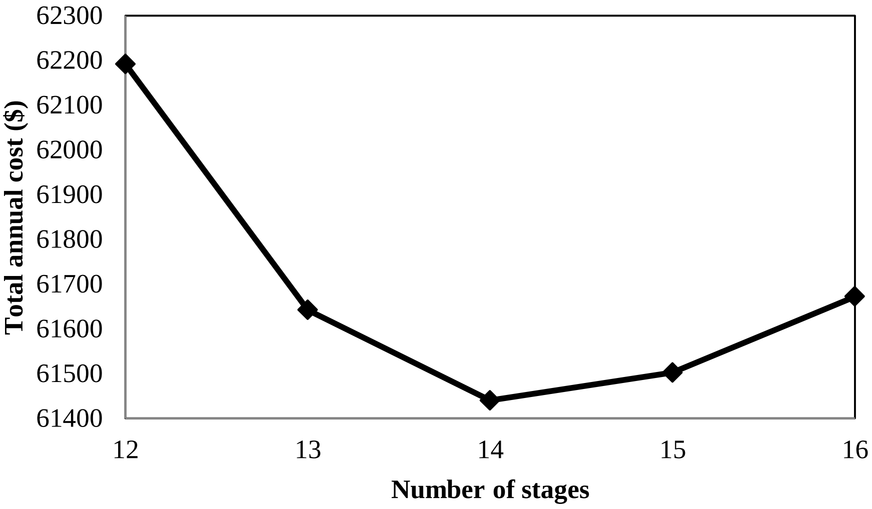

Figure 6.9 The effects of the number of stages on total annual cost of distillation column by using 3-octanone as solvent

The optimal operating parameters of distillation column for using 3-octanone as solvent are summarized in Table 6.3.

Table 6.3 The optimal operating parameters of distillation column for using 3-octanone as solvent

Column specification	
Total stages	14
Reboiler duty (kW)	164.3
Reflux ratio	0.25
Feed stage location	
Tert-butyl alcohol - 3-octanone	10

6.3.4 Result of using hexyl acetate as solvent

Extractive distillation

The standard conditions of extractive distillation by using hexyl acetate as solvent are summarized in Table 6.4.

Table 6.4 The standard conditions of extractive distillation by using hexyl acetate as solvent

Column specification	
Total stages	30
Reboiler duty (kW)	190
Reflux ratio	1.2
Feed stage location	
Hexyl acetate	2
Tert-butyl alcohol - water	12
Mole flow of hexyl acetate (kmol/hr)	9

The mole flow of hexyl acetate as a solvent is investigated. The operating parameters are the same as the standard conditions. However, reboiler duty and reflux ratio are adjusted in order to reduce amount of water in tert-butyl alcohol – solvent stream to 0.05 mol% and increase mole flow of tert-butyl alcohol in tert-butyl alcohol – solvent stream to 8.38 kmol/hr. Figure 6.10 demonstrates that mole flow of hexyl acetate in solvent stream at lower than 9 kmol/hr cannot achieve these objectives.

Mole flow of hexyl acetate at 9 kmol/hr and more are enough for these objectives. For this reason, mole flow of hexyl acetate is used at 9 kmol/hr.

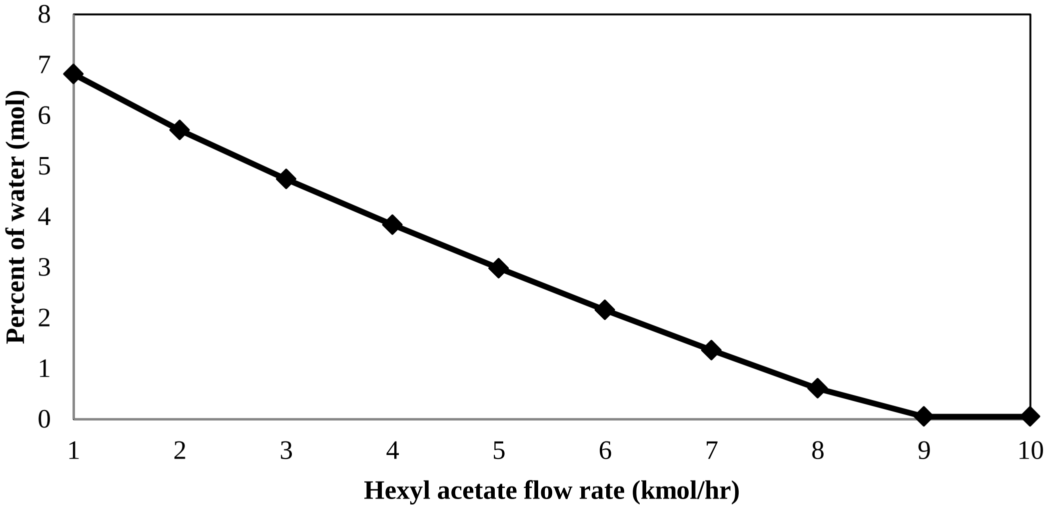

Figure 6.10 The effects of mole flow rate of hexyl acetate at standard conditions of extractive distillation

The reflux ratio is important parameter. The operating parameters are the same as the standard conditions. However, reboiler duty is adjusted in order to reduce amount of water in tert-butyl alcohol – solvent stream to 0.05 mol%. Figure 6-11 shows that mole flow of tert-butyl alcohol in tert-butyl alcohol – solvent stream is increasing by increasing reflux ratio. However, mole flow of tert-butyl alcohol in tert-butyl alcohol – solvent stream is slightly increasing when reflux ratio is higher than 1.2. Moreover, hexyl acetate lost in waste water stream is increasing when reflux ratio is higher than 1.2.

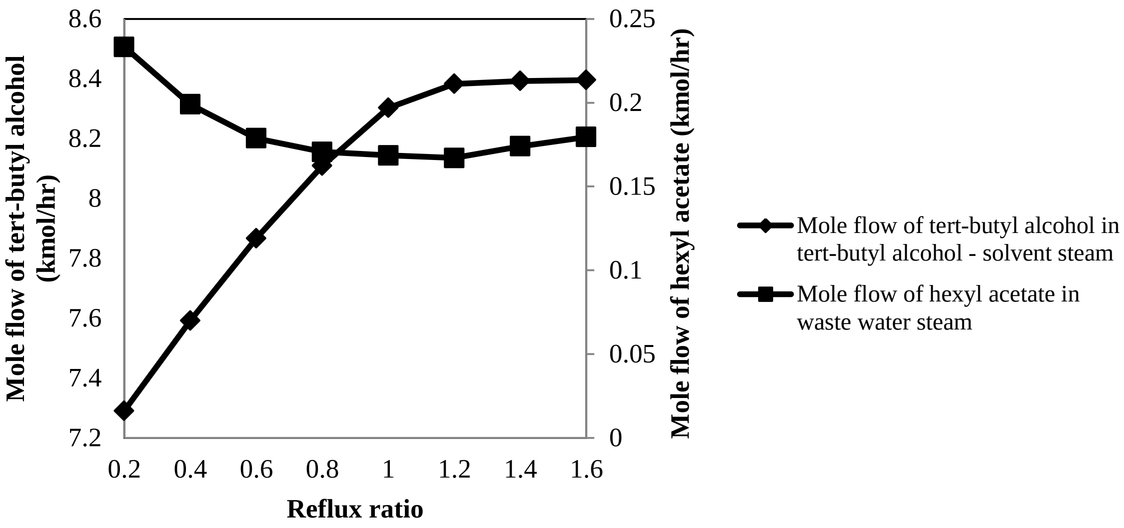

Figure 6.11 The effects of reflux ratio on mole flow of tert-butyl alcohol and mole flow of solvent loss of extractive distillation by using hexyl acetate as solvent

Figure 6.12 shows the effects of tert-butyl alcohol – water feed stage location on total annual cost at different number of stages of extractive distillation**.**

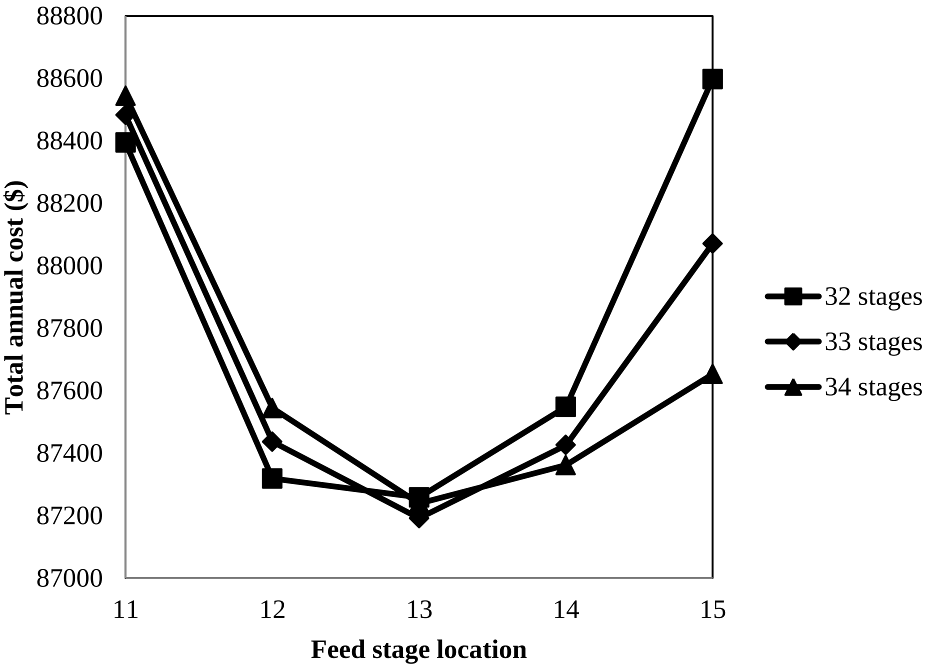

Figure 6.12 The effects of tert-butyl alcohol – water feed stage location on total annual cost at different number of stages of extractive distillation by using hexyl acetate as solvent

Increasing number of stages of extractive distillation can reduce operating cost at the same specification by decreasing reflux ratio but this increases the capital cost. Figure 6.13 demonstrates the effects of the number of stages on total annual cost of extractive distillation column.

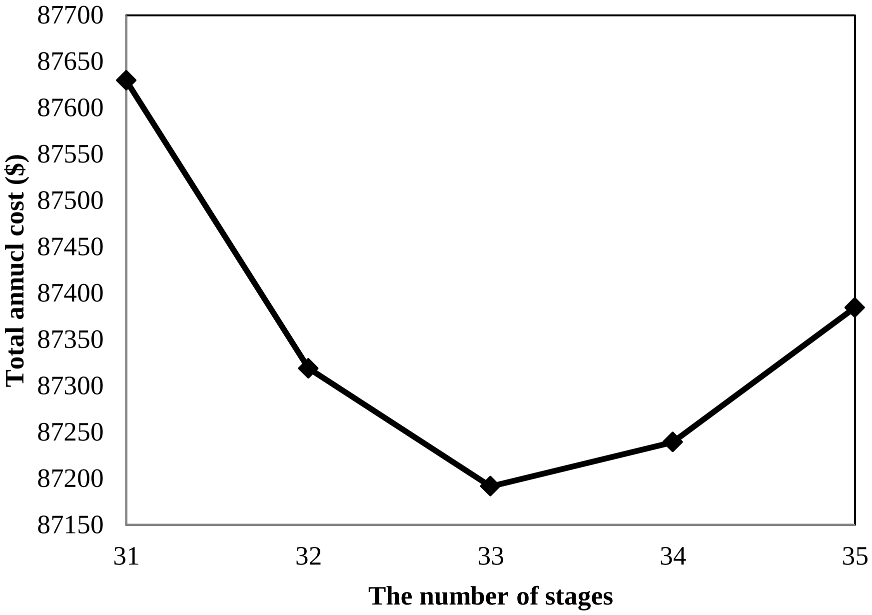

Figure 6.13 The effects of the number of stages on total annual cost of extractive distillation column by using hexyl acetate as solvent

The optimal operating parameters of extractive distillation column of using hexyl acetate as solvent are summarized in Table 6.5.

Table 6.5 The optimal operating parameters of extractive distillation column of using hexyl acetate as solvent

Column specification	
Total stages	33
Reboiler duty (kW)	174.31
Reflux ratio	1.05
Feed stage location	
Hexyl acetate	2
Tert-butyl alcohol - water	13
Mole flow of hexyl acetate (kmol/hr)	9

Distillation column

Figure 6.14 shows the effects of tert-butyl alcohol – solvent feed stage location on total annual cost at different number of stages of distillation column.

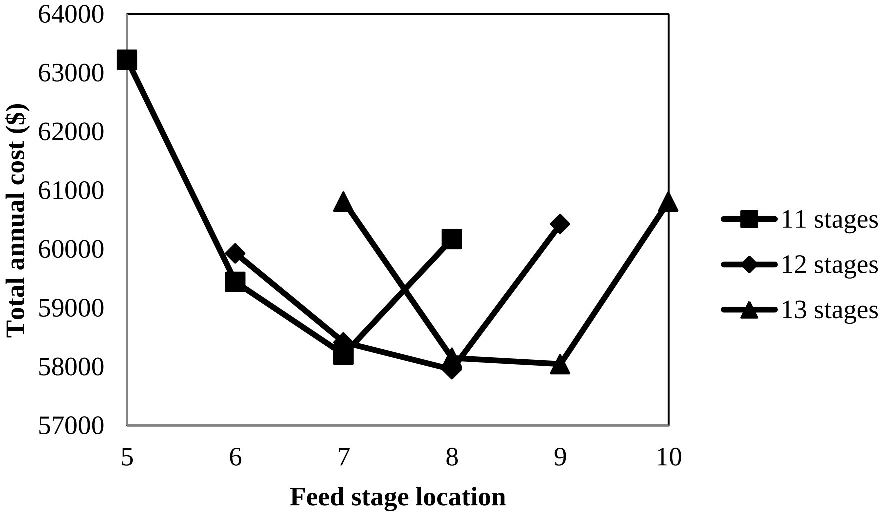

Figure 6.14 The effects of tert-butyl alcohol – solvent feed stage location on total annual cost at different the number of stages distillation column by using hexyl acetate as solvent

Increasing number of stages of distillation column can reduce operating cost at same specification but this requires more capital cost. The numbers of optimal stages in distillation column were 12 stages. The effects of the number of stages on total annual cost are showed in Figure 6.15.

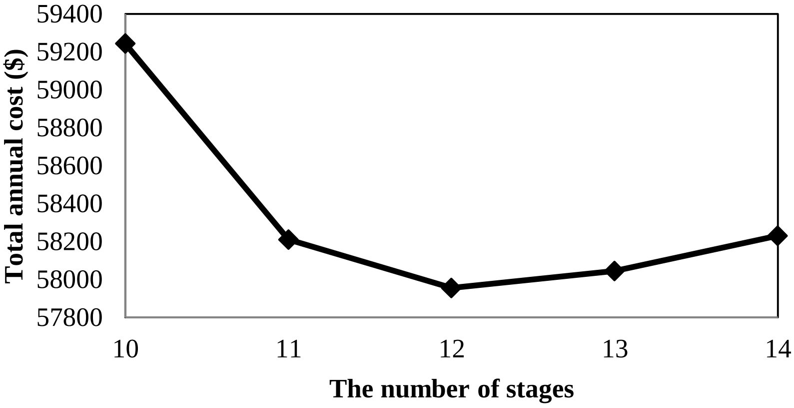

Figure 6.15 The effects of the number of stages on total annual cost of distillation column by using hexyl acetate as solvent

The optimal operating parameters of distillation column for using hexyl acetate as solvent are summarized in Table 6.6.

Table 6.6 The optimal operating parameters of distillation column for using hexyl acetate as solvent

Column specification	
Total stages	12
Reboiler duty (kW)	158.7
Reflux ratio	0.21
Feed stage location	
Tert-butyl alcohol – hexyl acetate	8

6.3.5 Result of using 2-heptanone as solvent

Extractive distillation

The standard conditions of extractive distillation by using 2-heptanone as solvent are summarized in Table 6.7.

Table 6.7 The standard conditions of extractive distillation by using 2-heptanone as solvent

Column specification	
Total stages	30
Reboiler duty (kW)	190
Reflux ratio	1.2
Feed stage location	
2-heptanone	2
Tert-butyl alcohol - water	15
Mole flow of 2-heptanone (kmol/hr)	15

The mole flow of 2-heptanone as a solvent is investigated. The operating parameters are the same as the standard conditions. However, reboiler duty and reflux ratio are adjusted in order to reduce amount of water in tert-butyl alcohol – solvent stream to 0.05 mol% and increase mole flow of tert-butyl alcohol in tert-butyl alcohol – solvent stream to 8.38 kmol/hr. Figure 6.16 demonstrates that mole flow of 2-heptanone in solvent stream at lower than 15 kmol/hr cannot achieve these objectives. Mole flow of 2-heptanone at 15 kmol/hr and more are enough for these objectives. For this reason, mole flow of 2-heptanone is used at 15 kmol/hr.

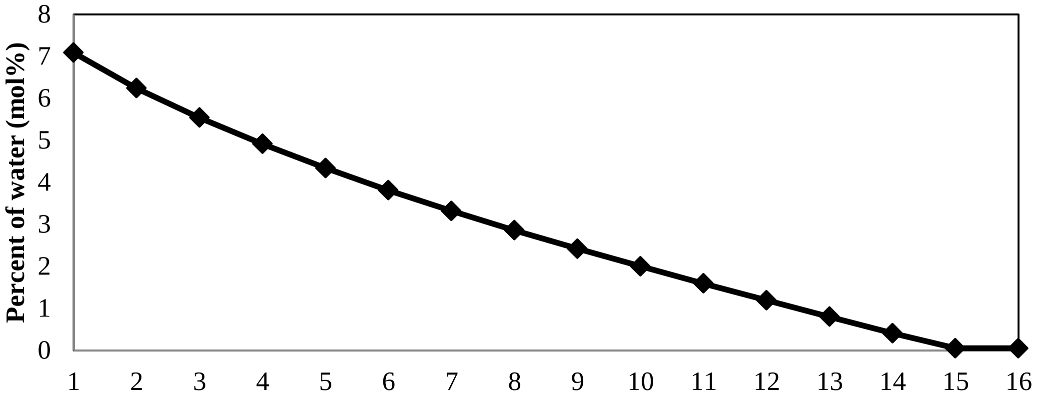

Figure 6.16 The effects of mole flow rate of 2-heptanone at standard conditions of extractive distillation

The reflux ratio is important parameter. The operating parameters are the same as the standard conditions. However, reboiler duty is adjusted in order to reduce amount of water in tert-butyl alcohol – solvent stream to 0.05 mol%. Figure 6.17 shows that mole flow of tert-butyl alcohol in tert-butyl alcohol – solvent stream is increasing by increasing reflux ratio. However, mole flow of tert-butyl alcohol in tert-butyl alcohol – solvent stream is slightly increasing when reflux ratio is higher than 1.6. Moreover, 2-heptanone lost in waste water stream is increasing when reflux ratio is higher than 1.6.

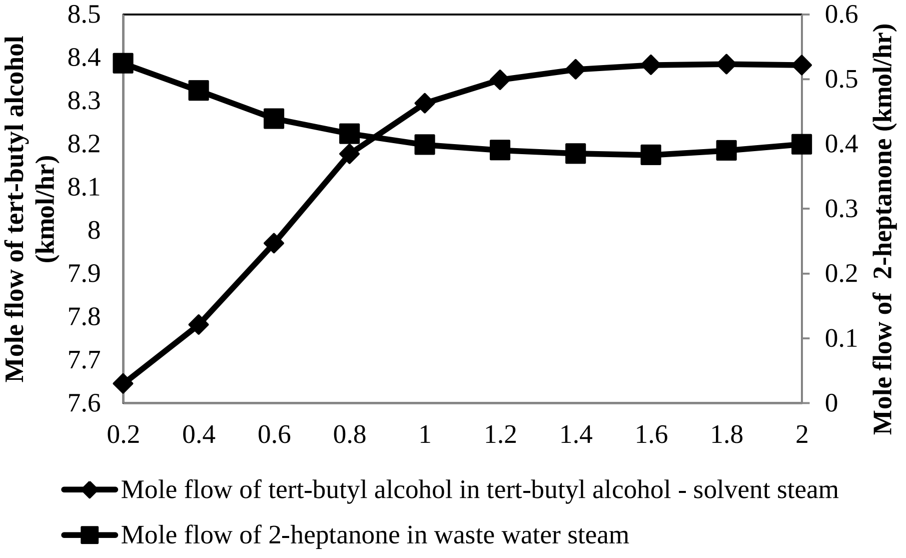

Figure 6.17 The effects of reflux ratio on mole flow of tert-butyl alcohol and mole flow of solvent loss of extractive distillation by using hexyl acetate as solvent

Figure 6.18 shows the effect of tert-butyl alcohol – water feed stage location on total annual cost at different number of stages of extractive distillation.

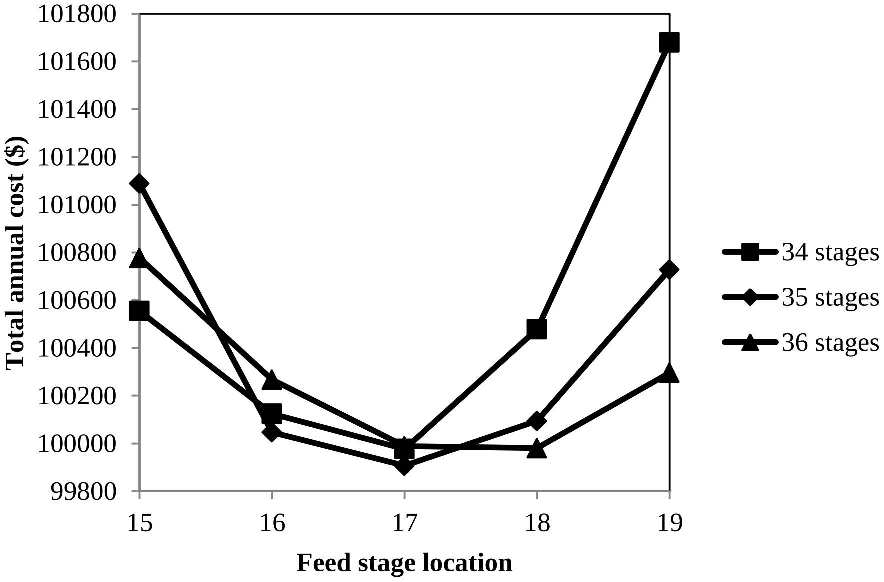

Figure 6.18 The effects of tert-butyl alcohol – water feed stage location on total annual cost at different number of stages of extractive distillation by using 2-heptanone as solvent

Increasing number of stages can reduce operating cost at the same specification by decreasing reflux ratio but this increases the capital cost. Figure 6.19 demonstrates the effects of the number of stages on total annual cost.

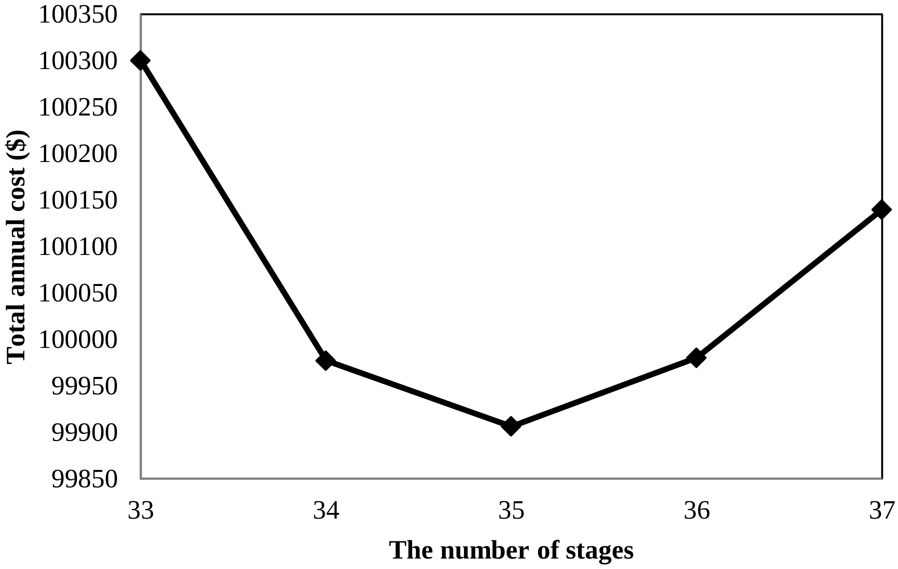

Figure 6.19 The effects of the number of stages on total annual cost of extractive distillation by using 2-heptanone as solvent

The optimal operating parameters of extractive distillation column for using 2-heptanone as solvent are summarized in Table 6.8.

Table 6.8 The optimal operating parameters of extractive distillation column of using 2-heptanone as solvent

Column specification	
Total stages	35
Reboiler duty (kW)	203.09
Reflux ratio	1.01
Feed stage location	
2-heptanone	2
Tert-butyl alcohol - water	17
Mole flow of 2-heptanone (kmol/hr)	15

Distillation column

Figure 6.20 shows the effects of tert-butyl alcohol – solvent feed stage location on total annual cost at different number of stages of distillation column.

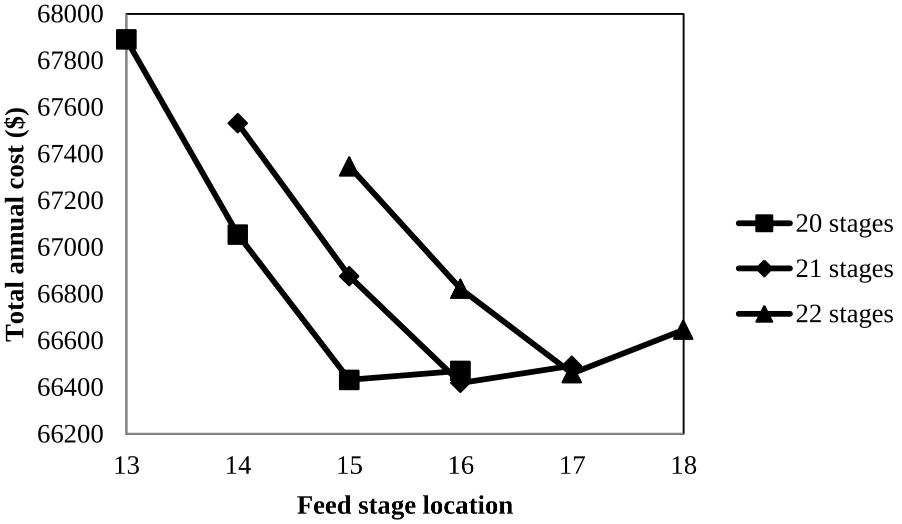

Figure 6.20 The effects of tert-butyl alcohol – solvent feed stage location on total annual cost at different the number of stages of distillation column by using 2-heptanone as solvent

The numbers of optimal stages in distillation column were 21 stages. The effects of the number of stages on total annual cost are showed in figure 6.21.

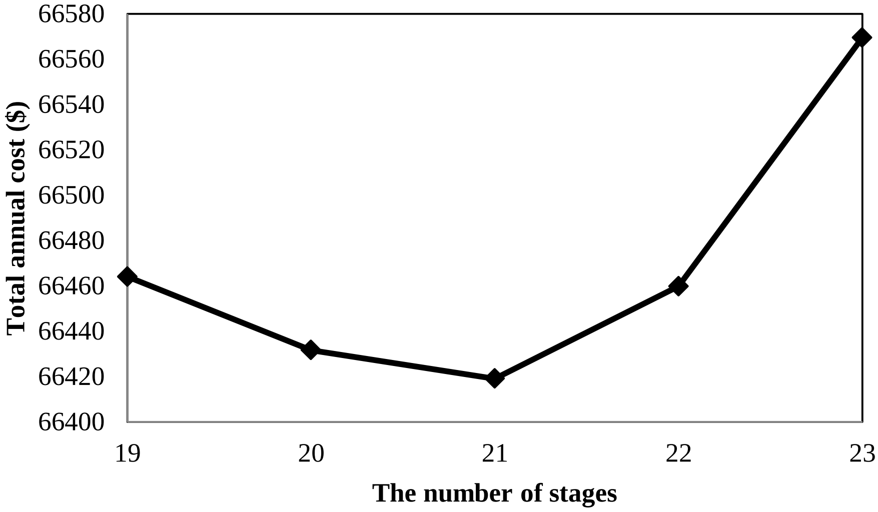

Figure 6.21 The effects of the number of stages on total annual cost of distillation column by using 2-heptanone as solvent

The optimal operating parameters of distillation column for using 2-heptanone as solvent are summarized in Table 6.9.

Table 6.9 The optimal operating parameters of distillation column for using 2-heptanone as solvent

Column specification	
Total stages	21
Reboiler duty (kW)	171.93
Reflux ratio	0.43
Feed stage location	
Tert-butyl alcohol – hexyl acetate	16

6.3.6 Comparison solvent in term of total annual cost

When comparing the total annual cost of extractive distillation, Figure 6.22 shows that using 3-octanone gives the lowest annual capital and utility cost while 2-heptanone gives the highest annual capital and utility cost. However, 3-octanone gives the highest solvent cost while hexyl acetate gives the lowest solvent cost. This is due to the fact that solvent cost of 3-octanone is higher than hexyl acetate 5.23times and 2-heptanone 8.54 times. For this reason, using hexyl acetate as solvent gives the lowest total annual cost of extractive distillation.

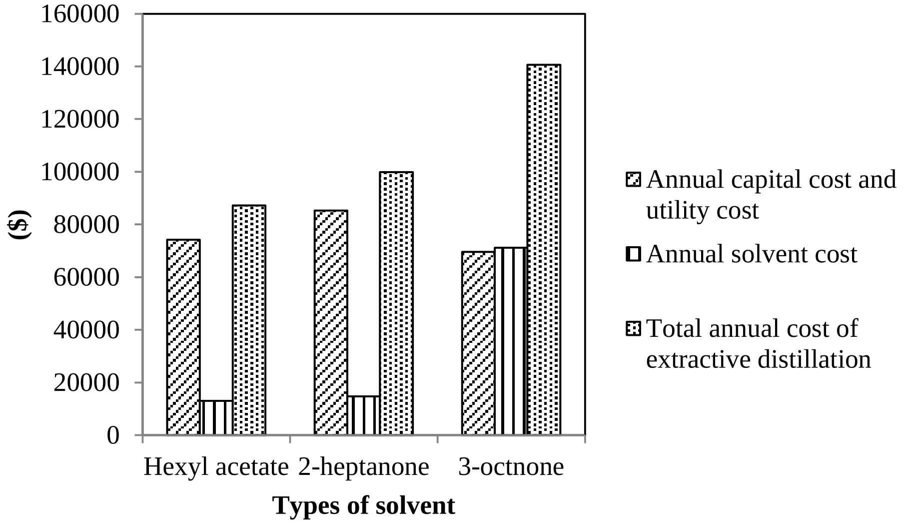

Figure 6.22 The effect of types of solvent on total annual cost of extractive distillation

When comparing the total annual cost of distillation column, Figure 6.23 shows that using hexyl acetate as solvent gives the lowest total annual cost of distillation column while 2-heptanone gives the highest total annual cost of distillation column. This is due to the fact that amount of 2-heptanone for recovery is the highest and boiling point of 2-heptanone is near boiling point of tert-butyl alcohol than other solvent. When comparing the total cost, using hexyl acetate as solvent gives the lowest total cost.

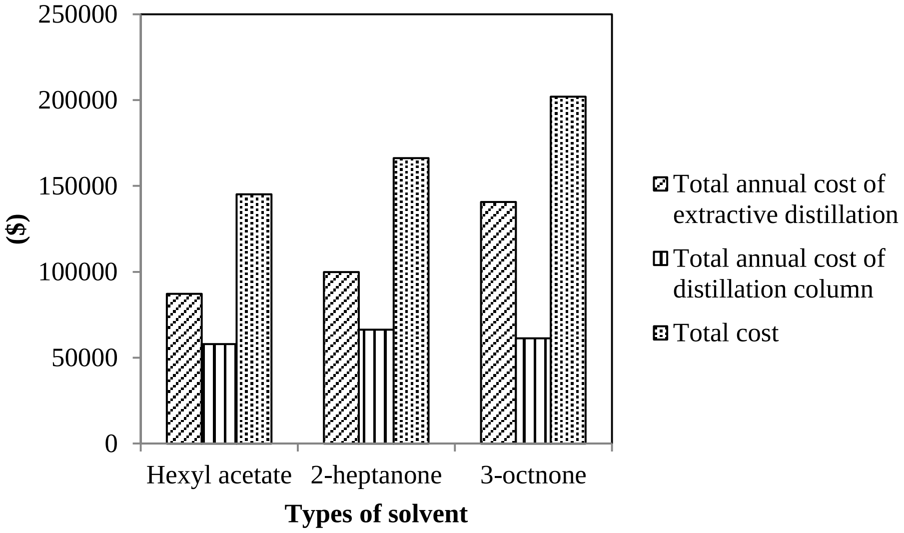

Figure 6.23 The effect of types of solvent on total cost

For the effect of reboiler duty in extractive distillation, higher reboiler duty can reduce water contamination in tert-butyl alcohol – solvent stream. However, increasing reboiler duty results in decreasing mole flow of tert-butyl alcohol in tert-butyl alcohol – solvent stream. For this reason, the reboiler duty must be operated at appropriate value because reboiler duty must be high enough to separate water from tert-butyl alcohol but not high until tert-butyl alcohol reaches to top of column. However, high reboiler duty requires higher total annual cost.

For effect of the number of stages of extraction distillation, increasing number of stages can help separation water from tert-butyl alcohol. For this reason, reflux ratio and operating cost can be reduced by increasing number of stages. However, increasing number of stages requires higher capital cost.

For the effects of reflux ratio and reboiler duty of distillation column, increasing reflux ratio results in increasing the purity of tert-butyl alcohol stream. However, mole flow rate of tert-butyl alcohol in tert-butyl alcohol stream is decreasing. The mole flow rate of tert-butyl alcohol in tert-butyl alcohol stream can be increased by increasing reboiler duty. However, contamination in tert-butyl alcohol is also increasing. The effects of reflux ratio and reboiler duty of distillation column on mole flow rate of tert-butyl alcohol and purity of tert-butyl alcohol in tert-butyl alcohol stream and are similar in every solvent. Example of the effects of reflux ratio and reboiler of distillation column for separation tert-butyl alcohol from hexyl acetate is showed in Figure 6.24 and Figure 6.25.

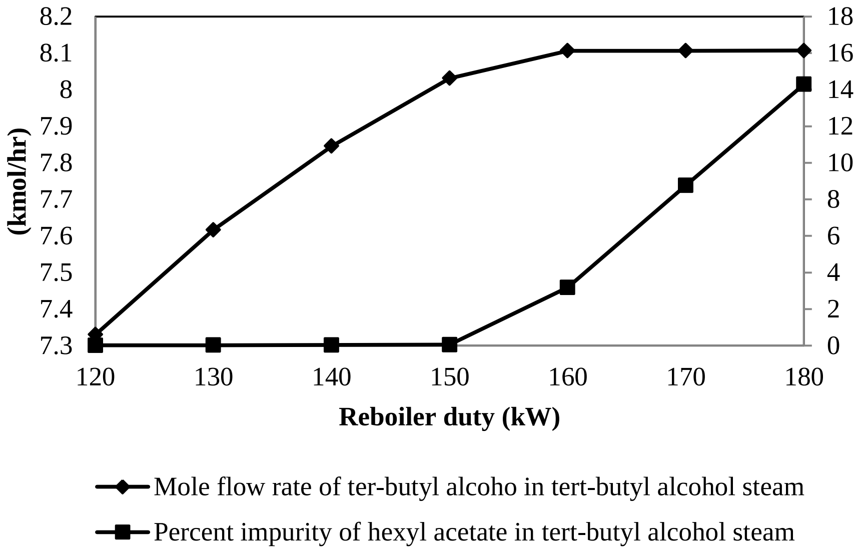

Figure 6.24 Effects of reboiler duty of distillation column for separation tert-butyl alcohol from hexyl acetate

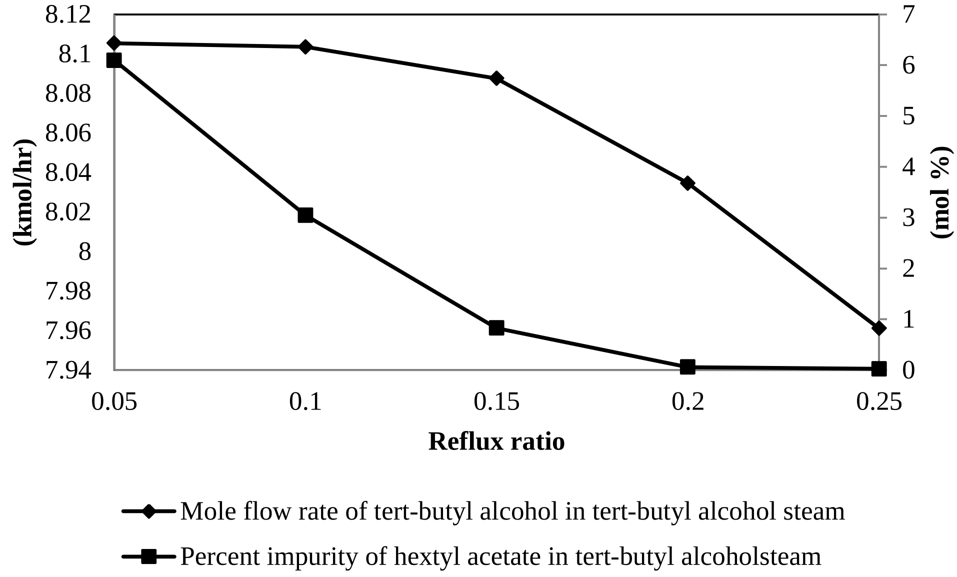

Figure 6.25 Effects of reflux ratio of distillation column for separation tert-butyl alcohol from hexyl acetate

6.4 Economic and environmental assessment

In this section, an optimum solvent by using the total cost and potential environmental impact of waste water stream as the criteria was investigated. The potential environmental impact of waste water stream is defined as shown below.

Potential environmental impact of waste water stream = $M_j X_{solvent} \varphi_{solvent}$

Where

M_j is the mass flow rate of waste water stream, $X_{solvent}$ is mass fraction of solvent in waste water stream, $\varphi_{solvent}$ is specific potential environmental impact of solvent.

The specific potential environmental impact of solvent is calculated from human toxicity potential by either inhalation or dermal exposure (HEPE) index. The HEPE index is defined as shown below.

$$\text{Index}_{solvent,HEPE} = \frac{1}{(TWA)_{solvent}}$$

$$\varphi_{solvent} = \text{Index}_{solvent,HEPE}$$

The mass flow rate of waste water stream, mass fraction of solvent in waste water stream and total cost are collected in section 6.3. The specific potential environmental impact of solvent is 0.04 for 3-octanone, 0.02 for hexyl acetate and 0.01 for 2-heptanone. It can be seen that 3-octanone is the solvent that will have the highest specific potential environmental impact of solvent while 2-heptanone is the solvent that will have the lowest specific potential environmental impact of solvent. Two parameters which are mass flow rate of solvent and specific potential environmental impact of solvent affect the potential environmental impact of waste water stream.

The total cost and potential environmental impact of waste water stream were normalized and converted to quantitative scores. The qualitative weightings of total annual cost and potential environmental impact of waste water were taken as equal. The total cost and potential environmental impact of waste water stream were normalization to scale between 0 and 1. One (1) refers to the highest total cost or potential environmental impact of waste water stream while zero (0) refers to the lowest total annual cost or the potential environmental impact of waste water stream. The normalization value of x_i is defined as shown below.

$$\text{Normalization } (x_i) = \frac{x_i - X_{min}}{X_{max} - X_{min}}$$

Where

x_i = the value of total cost or potential environmental impact of waste water stream

X_{min} = the minimum value of total cost or potential environmental impact of waste water stream

X_{max} = the maximum value of total cost or potential environmental impact of waste water stream

In this work, the normalization value of total cost and potential environmental impact of waste water stream are called economic impact index and environmental impact index respectively. Summing of economic impact index and environmental impact index is called total impact index. Lower the value of total impact indexes is preferable in this work.

6.4.1 Comparison solvent in term of total annual cost and potential environmental impact

Figure 6.26 shows that using hexyl acetate as solvent results in the lowest economic impact index while using 3-octanone as solvent results in the highest economic impact index. For effect of environmental index, 2-heptanone gives the lowest environmental impact index. This is due to the fact that specific potential environmental impact of 2-heptanone is less than potential environmental impact of 3-octanone and hexyl acetate 4 and 2 times respectively. It can be seen that specific potential environmental impact of solvent is the major impact on potential environmental impact of waste water stream. When considering the trade-offs between environmental impacts and economic impacts, using hexyl acetate as solvent provides the lowest total impact index. Consequently, the optimal solvent for separation tert-butyl alcohol from water in extractive distillation by using total cost and potential environmental impact of waste water stream as criteria is hexyl acetate.

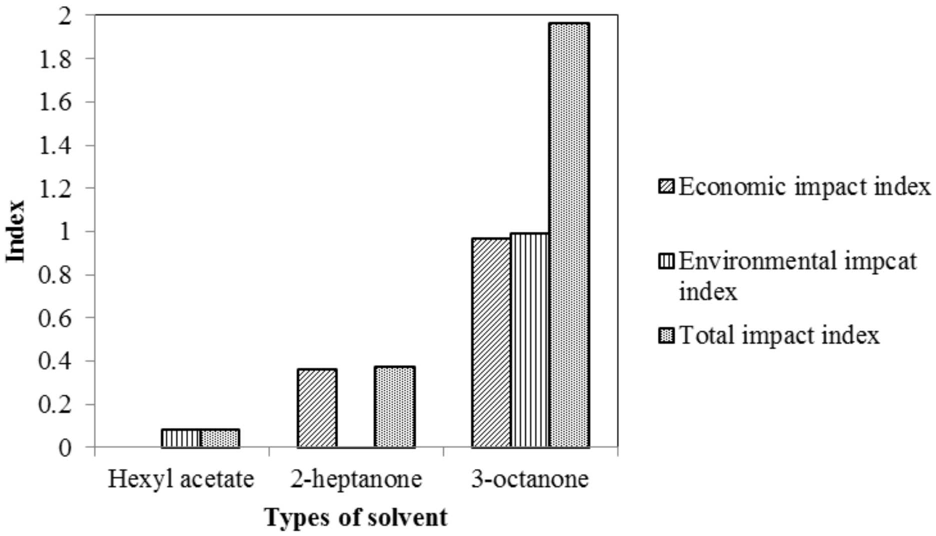

Figure 6.26 The effects of solvent on impact index at optimal operating parameters of extractive distillation by using total annual cost and potential environmental impact as criteria

The optimal operating parameters of extractive distillation by using total annual cost and potential environmental impact as criteria are summarized in Table 6.10.

Table 6.10 The optimal operating parameters of extractive distillation by using total annual cost and potential environmental impact as criteria

Column specification	
Total stages	33
Reboiler duty (kW)	174.31
Reflux ratio	1.05
Feed stage location	
Hexyl acetate	2
Tert-butyl alcohol - water	13
Mole flow of hexyl acetate (kmol/hr)	9

6.5 Integration tert-butyl alcohol recovery section to reactive distillation for glycerol ether production

The plant flow sheet of integration tert-butyl alcohol recovery section to reactive distillation is presented in Figure 6.27.

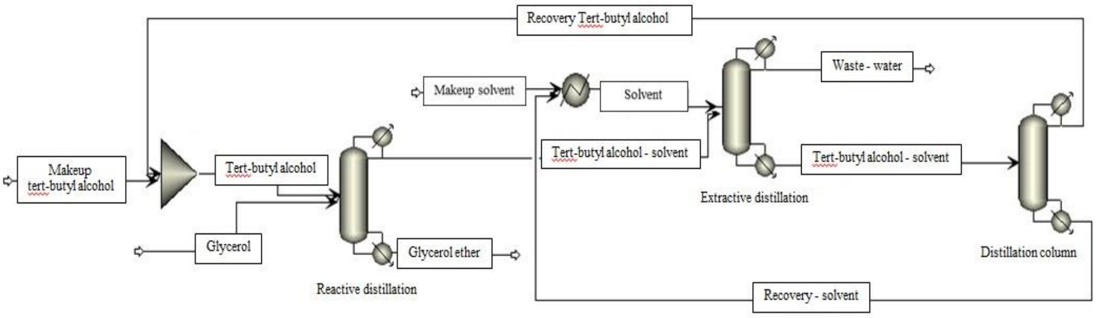

Figure 6.27 Plant flow sheet of integration tert-butyl alcohol recovery section to reactive distillation

Combination recovery tert-butyl alcohol stream with makeup tert-butyl alcohol stream results in increasing feed temperature of tert-butyl alcohol into reactive distillation. The increasing feed temperature of tert-butyl alcohol results in increasing temperature in reboiler. As the temperature in reboiler increasing, more unreacted glycerol goes up to the reactive stages and therefore reacts in reactive stages. For this reason, the reboiler duty for separation unreacted glycerol back to reactive stages is decreasing. For this reason, the reboiler duty of optimal operating condition of reactive distillation in section 4.3.2 is reduce to 237.3 kW. The optimal operating conditions of reactive distillation for glycerol ether production when integrates with tert-butyl alcohol recovery section are shown in Table 6.11.

Table 6.11 Optimal operating condition of reactive distillation when uses recovery tert-butyl alcohol

Column specification	
Rectifying stages	2
Reaction stages	8
Stripping stages	1
Reboiler duty (kW)	237.3
Reflux ratio	0.15

CHAPTER VII

CONCLUSIONS AND RECOMMENDATION

7.1 Conclusions

In this work, the reactive distillation for glycerol ether production and dimethyl ether production and extractive distillation and distillation column for recovery of tert-butyl alcohol are investigated by using Aspen Plus program. This work studies the effects of parameters of reactive distillation for glycerol ether production and dimethyl ether production, extractive distillation and distillation column and determines the optimal operating parameters by using total annual cost as criteria. The reactive distillation can increase conversion of glycerol and methanol to 99 mol% in order to reduce recycles cost. This work is divided into 3 sections.

7.1.1 Reactive distillation for glycerol ether production

The reactive distillation for glycerol ether production from etherification reaction of tert-butyl alcohol and glycerol is investigated. RADFRAC module in Aspen Plus is used to study the parameters of reactive distillation such as reflux ratio, reboiler duty, the number of stages on performance in term of conversion of glycerol and yield of di and tri tert-butyl ether of glycerol and find optimal reactive distillation configurations by using total annual cost. A 3 year of payback is used. The results show that increasing feed ratio of tert-butyl alcohol to glycerol, the number of reactive stages, the number of rectifying stages and reboiler duty result in increasing both conversion of glycerol and yield of di and tri tert-butyl ether of glycerol. However, increasing the number of stripping stages and reflux ratio gives an opposite trend but the stripping stages give benefits in separation performance. The suitable feed stages location of tert-butyl alcohol and glycerol are fed on bottom and top of reactive stages. The optimal reactive distillation configurations for glycerol ether production by using total annual cost consist of 2 rectifying stages, 8 reactive stages and 1 stripping stages.

7.1.2 Reactive distillation for dimethyl ether production

The reactive distillation for dimethyl ether production from dehydration reaction of methanol in crude glycerol and distillation column for separation glycerol out from water are investigated. RADFRAC module in Aspen Plus is used to study the effects of parameters such as reflux ratio, reboiler duty, the number of stages and find optimal configuration of reactive distillation and distillation column by using total annual cost. A 3 year of payback is used for reactive distillation whereas a 10 year of payback is used for distillation column. The reactive distillation is studied in term of conversion of methanol. The distillation is studied in term of purity of glycerol. For the effects of parameters of reactive distillation, increasing the number of reactive stages, the number of rectifying stages, the number of stripping stages and reflux ratio result in increasing conversion of methanol. However, increasing reboiler duty gives an opposite trend but this parameter is important for separation. The suitable feed stages location of crude glycerol in reactive stages is the first stage of reactive stages. For the effects of parameters of distillation column, increasing the number of stages and reboiler duty gives benefits in more purity of glycerol. Reflux ratio is also important parameter in term of molar flow rate of glycerol in glycerol stream. However, water contamination in glycerol is increasing by increasing reflux ratio. The optimal reactive distillation configurations for dimethyl ether production by using total annual cost consist of 2 rectifying stages, 8 reactive stages and 2 stripping stages. The optimal stages of distillation column for production pure glycerol are 11 stages.

7.1.3 Tert-butyl alcohol recovery

Extractive distillation and distillation column for recovery of tert-butyl alcohol which forms azeotrope with water is investigated. Solvents for separation tert-butyl alcohol from water which are listed by Berg and Yang (1992) are used in this work. These solvents are compared in term of total annual cost and potential environmental impact. RADFRAC module in Aspen Plus is used to find optimal parameters such as reflux ratio, reboiler duty, the number of stages of extractive distillation and distillation column by using total annual cost and potential environmental impact as criteria. A 10 year of payback is used. For effect of solvent, using hexyl acetate as solvent gives the lowest in total cost while using 3-octanone gives the highest in total cost. Moreover, 3-octanone gives the highest in term of potential environmental impact while using 2-heptanone gives the lowest potential environmental impact. When considering the trade-offs between environmental impacts and economic impact, the optimal solvent is hexyl acetate. Consequently, hexyl acetate is appropriate solvent for separation tert-butyl alcohol from water by using total annual cost and potential environmental impact as criteria.

7.2 Recommendation

First, heat integration among reactive distillation, extractive distillation and distillation column should be considered in order to increase energy efficiency of process. Second, solvent recovery should be considered in order to reduce solvent cost.

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APPENDIX

APPENDIX A
SIZING OF EQUIPMENT AND COST ESTIMATION

Correlations used for sizing of equipment and its parameters are shown in Table A.1 and A.2.

Table A.1 Sizing of equipment

Parameter	Remarks	Equation
A_{reb} [ft^2]	Reboiler heat-transfer area	$A_{reb}(ft^2) = \frac{Q_{Reb}}{U_{reb} \cdot \Delta T_{Reb}}$
A_{cond} [ft^2]	Condenser heat-transfer area	$A_{Cond}(ft^2) = \frac{Q_{Cond}}{U_{Cond} \cdot \Delta T_{Cond}}$
H [ft]	Column height	H=(tray spacing)(N_{tray})

Table A.2 Notion and parameter values for sizing of equipment and cost calculation

Parameter	Value	Remarks
C_{MS}[\$]	1473.3	Marshall and Swift index
U_{reb} [Btu/hft^{2}F^o]	100	For reactive distillation in chapter IV
	325	For reactive distillation in chapter V
	200	For distillation column in chapter V
	100	For extractive distillation and distillation column in chapter VI
T_{reb} [F^o]	Calculate	Temperature driving force of reboiler
U_{cond} [Btu/hft^{2}F^o]	250	For reactive distillation in chapter IV
	112.5	For reactive distillation in chapter V
	250	For distillation column in chapter V
	250	For extractive distillation and distillation column in chapter VI
T_{cond} [F^o]	Calculated	Log-mean driving force of condenser
h_{weir} [m]	0.1	Weir height for tray

Table A.3 Cost of solvent

List	Cost
Hexyl acetate	0.067 \$/kg
2-heptanone	0.041 \$/kg
3-octanone	0.35 \$/hg

(http://www.vigon.com)

The assessment of equipment cost follows the procedures of Douglas (1988) Details are as follows:

Capital cost

Column cost

$$\text{Cost \$} = \left(\frac{C_{MS}}{280}\right)101.9D^{1.066}H^{0.802}(2.18+F_mF_p)$$

F_m=3.67 ,F_p=1 for all case except reactive distillation unit in chapter V F_p=1.15

Tray cost

$$\text{Cost \$} = \left(\frac{C_{MS}}{280}\right)4.7D^{1.55}H(F_s+F_t+F_m); \qquad F_s = 1.00,\ T_t = 1.8,\ F_m = 1.7$$

Where D =diameter of the column (ft)

H = high of the column (ft)

Heat-exchanger cost

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

F_d = 1.35 for reboiler, F_d = 1.00 for condenser, F_p= 0, F_m=3.75

Operating cost

Steam cost

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

Where C_s = cost of steam (\$/1000 lb steam)

Cooling cost

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

Where C_W = cost of cooling water (\$/1000 gal cooling water)

APPENDIX B
MESH EQUATIONS

The equations for equilibrium stages model are known as the MESH equations. MESH is a group of equation that is used in the model

Material balance equation (M equation) is general model equation that predicts the flow component i in and out stage n. The material balance is shown below.

Material balance: (C equations for stage)

$$L_{n-1}x_{i,n-1} + V_{n+1}y_{i,n+1} + F_n z_{i,n} - (L_n + U_n)x_{i,n} - (V_n + W_n)y_{i,n} = 0$$

Equilibrium relationship (E equation) is based on assumption that vapor liquid equilibrium exists on every stages. The equilibrium relationship is shown below.

Equilibrium balance: (C equations for stage)

$$Y_{i,n} - K_{in} \cdot X_{in} = 0$$

Summations of mole fraction (S equation) are shown below.

Summations of mole fraction balance: (One for stage)

$$\sum_{i=1}^{C} Y_{i,n} - 1 = 0$$

$$\sum_{i=1}^{C} X_{i,n} - 1 = 0$$

Heat or enthalpy balance (H equation) is based on ideal heat transfer that temperature of vapor and liquid has same temperature. The heat balance is shown below.

Heat balance: (One for stage)

$$L_{n-1}h_{L_{n-1}} + V_{n+1}h_{V_{n+1}} + F_n h_{F_n} - (L_n + U_n)h_{Ln} - (V_n + W_n)h_{V_n} - Q_n = 0$$

Q_j= (+) for condenser or heat from stage

(-) for reboiler or heat to stage

Where

C = Number of composition in distillation column, F_n = Feed flow rate on stage n, $z_{i,n}$ = Over all composition in feed on stage n in mole fraction, T_{F_n} = Feed temperature, P_{F_n} = Feed pressure, h_{F_n} = Corresponding overall molar enthalpy of feed,

L_{n-1} = Liquid molar flow rate from stage n-1, $x_{i,n-1}$ = Composition of liquid in mole fraction from stage n-1, $h_{L_{n-1}}$ = Enthalpy of liquid from stage n-1, L_n = liquid from stage n, $x_{i,n-1}$ = Composition of liquid in mole fraction from stage n, $h_{L_{n-1}}$ = Enthalpy of liquid from stage n-1, U_j = Liquid side stream, V_n = Vapor from stage n, $y_{i,n}$ = Composition of vapor in mole fraction from stage n, h_{L_n} = Enthalpy of vapor from stage n, W_j = Vapor side stream, V_{n+1} = Vapor from stage n+1, $y_{i,n+1}$ = Composition of vapor in mole fraction from stage n+1, $h_{V_{n+1}}$ = Enthalpy of vapor from stage n+1, W_j = Vapor side stream,

The general scheme example of stage n is shown below.

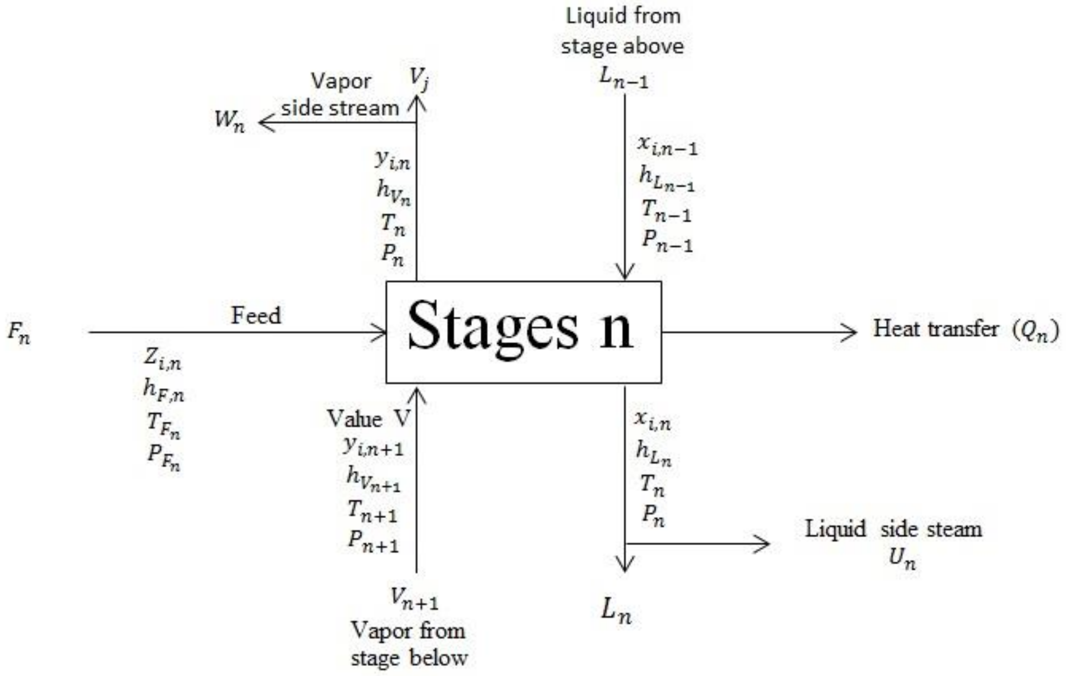

Figure A.2 general scheme example of stage n

All of equation and information in appendix B are referred from Seader, Henley, and Roper, 2011.

APPENDIX C

NORMAL BOILING POINT OF COMPONENT IN THIS WORK

Table C.1 Normal boiling point of component

List of component	Normal boiling point (^oC)
Dimethyl ether	-24.84
Di tert-butyl ether of glycero;	240.44
Glycerol	287.85
Hexyl acetate	171.5
Methanol	64.7
Mono tert-butyl ether of glycerol	256.61
Tert-butyl alcohol	82.42
tri tert-butyl ether of glycerol	253
Water	100
2-heptanone	151.03
3-octanone	167.5

VITA

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