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สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
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SYSTEMATIC DESIGN OF BIODIESEL AND FATTY ALCOHOL PRODUCTION PROCESS

Miss Lida Simasatitkul

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Thesis Title	SYSTEMATIC DESIGN OF BIODIESEL AND FATTY ALCOHOL PRODUCTION PROCESS
By	Miss Lida Simasatitkul
Field of Study	Chemical Engineering
Thesis Advisor	Assistant Professor Amornchai Arpornwichanop, D.Eng.
Thesis Co-advisor	Assistant Professor Woranee Paengjuntuek, D.Eng.

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Doctoral Degree

....Dean of the Faculty of Engineering
(Associate Professor Boonsom Lerdhirunwong, Dr.Ing.)

THESIS COMMITTEE

....Chairman

(Associate Professor Sarawut Rimdusit, Ph.D.)

....Thesis Advisor

(Assistant Professor Amornchai Arpornwichanop, D.Eng.)

....Thesis Co-advisor

(Assistant Professor Woranee Paengjuntuek, D.Eng.)

....Examiner

(Assistant Professor Soorathep Kheawhom, Ph.D.)

....Examiner

(Assistant Professor Apinan Soottitantawat, Ph.D.)

....External Examiner

(Dr. Wisitsree Wiyaratn, Ph.D.)

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ไบโอดีเซลเป็นพลังงานทางเลือกที่สามารถใช้ทดแทนน้ำมันปิโตรเลียมดีเซลได้ เพื่อลดความเสี่ยงที่มีต่อผู้ผลิตไบโอดีเซลซึ่งพึ่งพาผลิตภัณฑ์ไบโอดีเซลเพียงอย่างเดียว การนำผลิตภัณฑ์ที่ได้จากการผลิตไบโอดีเซลไปใช้ในการผลิตผลิตภัณฑ์ที่มีมูลค่าสูงขึ้น ได้แก่ แฟตตี้แอลกอฮอล์ จึงเป็นเรื่องที่สำคัญ การรวมกระบวนการผลิตแฟตตี้แอลกอฮอล์และไบโอดีเซลเข้าด้วยกันทำให้กระบวนการมีความซับซ้อน งานวิจัยนี้จึงให้ความสนใจการออกแบบและวิเคราะห์กระบวนการผลิตไบโอดีเซลร่วมกับการผลิตแฟตตี้แอลกอฮอล์ การศึกษาแบ่งเป็นสี่ส่วน งานส่วนแรกจะพัฒนาระเบียบวิธีการออกแบบอย่างเป็นระบบสำหรับการผลิตไบโอดีเซลและแฟตตี้แอลกอฮอล์ แผนภาพรวมกระบวนการผลิตจะถูกสร้างขึ้นจากข้อมูลที่มีโดยพิจารณากระบวนการเกิดปฏิกิริยาและการแยกสารที่เป็นไปได้ทั้งหมด ข้อจำกัดต่างๆ จะถูกนำมาพิจารณาสำหรับลดทางเลือกกระบวนการผลิตและการวิเคราะห์ทางเศรษฐศาสตร์จะถูกใช้ในการเลือกกระบวนการที่เหมาะสมที่สุด จากการศึกษาพบว่ากระบวนการผลิตไบโอดีเซลที่ใช้ตัวเร่งปฏิกิริยาชนิดกรดของแข็งร่วมกับการผลิตแฟตตี้แอลกอฮอล์เป็นกระบวนการผลิตที่ดีที่สุด งานในส่วนที่สองเกี่ยวข้องกับการปรับปรุงกระบวนการผลิตไบโอดีเซลโดยใช้หอกลั่นแบบมีปฏิกิริยา งานวิจัยนี้ได้ประยุกต์ใช้วิธีเชิงอีลีเมนท์ (element-based method) ในการออกแบบหอกลั่นแบบมีปฏิกิริยา งานในส่วนที่สามเกี่ยวข้องกับการประยุกต์แนวคิดการเบ็ดเสร็จความร้อนของหอกลั่นแบบมีปฏิกิริยาเพื่อเพิ่มประสิทธิภาพการใช้พลังงานภายในหอกลั่น งานวิจัยนี้ได้พิจารณาหอกลั่นแบบมีปฏิกิริยาที่มีการเบ็ดเสร็จความร้อนหลายรูปแบบ เมื่อพิจารณาค่าใช้จ่ายรวมรายปีเป็นเกณฑ์ในการออกแบบหอกลั่นพบว่า หอกลั่นแบบมีปฏิกิริยาที่จัดเรียงแบบแยกเชิงอ้อม (multi-effect indrect split arrangement) เป็นหอกลั่นที่เหมาะสมสำหรับการผลิตไบโอดีเซล งานในส่วนสุดท้ายเกี่ยวข้องกับการศึกษากระบวนการแยกแฟตตี้แอลกอฮอล์ จากการศึกษาพบว่าพลังงานที่ใช้ในกระบวนการแยกแฟตตี้แอลกอฮอล์จะมีค่าลดลงเมื่อหอกลั่นที่ใช้มีการคู่ควบความร้อน (thermal coupling distillation) นอกจากนี้ค่าใช้จ่ายในกระบวนการแยกยังลดลงเนื่องจากจำนวนหน่วยปฏิบัติการที่ใช้ลดลง

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สาขาวิชา วิศวกรรมเคมี ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก
ปีการศึกษา 2555 ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม

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KEYWORDS : DESIGN METHODOLOGY / BIODIESEL PRODUCTION / FATTY ALCOHOL PRODUCTION / THERMODYNAMIC INSIGHTS / REACTIVE DISTILLATION

LIDA SIMASATITKUL : SYSTEMATIC DESIGN OF BIODIESEL AND FATTY ALCOHOL PRODUCTION PROCESS. ADVISOR : ASST. PROF. AMORNCHAI ARPORNWICHANOP, D.ENG., CO-ADVISOR : ASST. PROF. WORANEE PAENGJUNTUEK, D.ENG., 294 pp.

Biodiesel is regarded as a promising alternative to a conventional petroleum-based diesel fuel. To reduce any risk for biodiesel producers, who rely only on the biodiesel product, the use of chemicals obtained from the biodiesel production to synthesize other high value-added products, such as fatty alcohol, has gained growing significance. The integration of fatty alcohol and biodiesel production results in a complicated process involving multi-components and various unit operations. The aim of this study is focused on the design and analysis of the production process of biodiesel integrated with fatty alcohol. The study is divided into four parts. In the first part, a systematic step by step methodology is developed for producing biodiesel and fatty alcohol products. A superstructure that includes all possible reaction and separation operations is generated through thermodynamic insights and available data. The number of alternative processes is systematically reduced through a screening procedure and economic analysis is performed to find the best economically and operationally feasible process. According to the methodology, a heterogeneous acid catalyzed process for biodiesel production integrated with fatty alcohol production is better than other process alternatives. In the second part, process intensification is applied to improve process performance in terms of productivity and energy consumption. A reactive distillation, which combines the reaction and separation tasks in the biodiesel production, is designed based on based on the element-based method. To further improve the performance of the reactive distillation in term of the energy consumption, a heat integration concept of the reactive distillation column is studied in the third part of the research. Various types of the heat-integrated reactive distillation are considered. Based on the minimization of a total annual cost, the multi-effect indirect split arrangement reactive distillation is the most attractive choice. In the final part of this study, the separation process of the fatty alcohol products is designed taking into account the total annual cost. The results indicate that the energy consumption of the fatty alcohol separation process can be minimized when the thermal coupling distillations are applied. In addition, the capital cost of the separation process is decreased because the number of unit operations, such as a condenser and a distillation column can be reduced.

Department : Chemical Engineering Student's Signature
Field of Study : Chemical Engineering Advisor's Signature
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LIST OF ABBREVATIONS

A_n	Net cash flow at end of period n [$/year]
AHP	Analytic hierachy process
b^B	Element flow at bottom stream
b^D	Element flow at distillate stream
b^F	Element flow at feed stream
b_n^l	Element flow of liquid phase at stage n
b_n^v	Element flow of vapor phase at stage n
BC	Bare module cost [$/year]
C_0	Base cost [$/year]
D	Diameter [ft]
D_0	Diameter in base cost[ft]
D_x	The point Dx in driving force diagram
F_{ij}	Driving force of component i
F_d	Design type factor in Guthrie method
F_m	Material factor in Guthrie method
F_p	Pressure factor in Guthrie method
F_s	Tray spacing in Guthrie method
F_t	Tray type in Gurthrie method
GE	General expense [$/year]
i	Interest rate
L	Length [ft]
L_0	Length in base cost [ft]
L_∞	Liquid flow rate at stage ∞ [kmol h^{-1}]
M	Number of element
MC	Manufacturing cost [$/year]
MF	Module factor
MPF	Materials and pressure correction factor
N_F	Feed stage location

N	Total stage
NC	Number of component
NR	Number of reaction
NPV	Net present value [$/year]
$p_{A,j}$	Properties value of component A
P_{econ}	Normalization of NPV
P_{env}	Normalization of environment
q	Feed condition that sent to distillation column
R_{min}	Minimum reflux ratio
ROI	Return in investment
r_{ij}	Ratio of properties of adjacent components
S	Area [ft^2]
S_0	Area in base cost [ft^2]
W_j^B	Element fraction of component j at bottom stream
W_j^D	Element fraction of component j at distillate stream
W_j^F	Element fraction of component j at feed stream
$W_{j,n}^l$	Element fraction of component j of liquid phase at stage n
$W_{j,n}^v$	Element fraction of component j of vapor phase at stage n
x_i	Composition of component i in liquid phase
$x_{HK,B}$	Mole fraction of heavy key component at bottom stream
$x_{HK,F}$	Mole fraction of heavy key component at feed stage
$x_{LK,D}$	Mole fraction of light key component at distillate stream
$x_{LK,F}$	Mole fraction of light key component at feed stage
y_i	Composition of component i in vapor phase
$Z_{i,F}$	Mole fraction of component i in feed stream

Greek symbols

α	Factor in Guthrie method
β	Factor in Guthrie method

β_{ij}	Relative separablility factor for component i

CHAPTER I

INTRODUCTION

1.1 Introduction

1.1.1 Biodiesel production

Due to the limited availability of petroleum-based fuels and worldwide environmental concern, it is a challenging problem to explore alternative energy and reduce the use of conventional fuel. Biodiesel is considered as an alternative potential fuel to be replaced a petroleum diesel because their properties such as flash point, cloud point, viscosity, specific gravity and cetane number are similar. In addition, biodiesel can be produced from local available renewable resources so that the promotion of its use can decrease the dependence on petroleum diesel. As a result, there are a number of studies concerning a biodiesel production in various aspects and a number of biodiesel processes have been developed in an industrial level.

Presently, development of alternative energy sources has become important for sustainable and environmental reasons. Biodiesel is considered an alternative potential fuel to replace a petroleum diesel. It can be produced from local available renewable resources (e.g., vegetable oils and animal fats), so that the promotion of its use can decrease the dependence on a petroleum diesel (Ma & Hanna, 1999).

Biodiesel consists of a fatty acid alkyl ester derived from the transesterification reaction of triglyceride, the major component in vegetable oils, and alcohol under the presence of an alkali catalyst for a conventional biodiesel production. Glycerol is found to be the byproduct of this process. Methanol is commonly used as a reactant because of its low cost and fast reaction rate (Lam et al., 2010) while various vegetable oils, such as soybean oil, palm oil, palm kernel oil and sunflower oil, can be used as feedstock. Since the price of crude vegetable oils changes over time, a biodiesel price is usually unstable. Moreover, the biodiesel price is closely related to the petroleum diesel price, which varies according to the worldwide market demand. To reduce any risk for biodiesel producers, who rely only on the biodiesel product, the use of chemicals obtained from the biodiesel production to synthesis other high value-added products has gained growing significance.

1.1.2 Fatty alcohol production

Fatty alcohol is among the important chemicals that are used for cosmetic and pharmaceutical industries. Fatty alcohol is also used as intemediate reactant to synthesize other products such as epoxide fatty alcohol, fatty alcohol ethoxylate, and fatty alcohol sulfate. In general, it is produced from hydrocarbons via the Ziegler process; however, this process involves unstable intermediate (e.g., aluminium alkyls), which is difficult to handle. Instead of using petroleum-based feedstock, it can be synthesized from fatty acid alkyl ester obtained from the biodiesel production through a hydrogenation process (Dupont & Simonet, 1991). The integration of fatty alcohol and biodiesel production results in a complicated process involving multi-components and products (e.g., triglycerides, free fatty acids, methanol, fatty acid methyl esters, fatty alcohols and glycerol) and various unit operations (e.g., reaction and separation units). This requires a systematic design methodology for synthesis of an optimal, efficient, flexible process in terms of operation and economics. In addition, the separation of fatty alcohol is necessary because type of fatty alcohol is divided into 2 types such as C12-C14 fatty alcohol and C16-C18 fatty alcohol.

1.1.3 Process design synthesis

Presently, various methods for synthesis and design of chemical processes are available. The most commonly used method is heuristic by nature, which involves a set of rules for decision making in process design; choosing batch or continuous processes, designing vapor and liquid recovery systems, evaluating benefit of heat integration and determining separation system and sequence (Douglas, 1988). Kirkwood et al., (1988) suggested that economic analysis should be taken in account in all design steps to reduce a number of process alternatives. Smith (2005) also proposed the onion diagram for decomposing the chemical process design into sub-layers so the number of reactors and separators can be reduced and the time demand for a preliminary process design is minimized. Seider et al. (2004) proposed a step by step method for design of chemical processes. A set of criteria to be used to evaluate the process alternatives was proposed by Turton et al. (2009). Alqahtni et al. (2007) developed the design method for synthesis of reaction-separation-recycle systems. Since the physical and chemical properties of the involved chemical system play a very important role for the design/synthesis of a process, a thermodynamic insights based hybrid method to select the separation process was proposed by Jaksland et al. (1994). Hostrup et al. (2001) further developed this method by including a reverse design approach where process design variables are "back-calculated" for known design targets. The proposed method was applied to methyl acetate and cyclohexane productions. A reverse approach based on the knowledge of molecular structure was proposed by d'Anterroches and Gani (2005).

To date, a few studies on the a systematic step by step methodology to developed for design, synthesis and analysis of a flexible process that can economically produce multiple products (biodiesel and fatty alcohol) have been reported . Design of a multi-product production process is generally based on an optimization approach, resulting in a large-scale, nonlinear optimization problem. Solving this problem is a difficult task due to the presence of a large number of alternative processes.

1.1.4 Reactive distillation

It has been known that the transesterification of biodiesel production is an equilibrium reaction. A large excess ratio of methanol to oil is required to achieve high degree of conversion. Process intensification such as reactive distillation has a offers an opportunity to improve the performance of process in terms of product purity, reaction conversion, product yield, because reaction task and separation task are combined and they occurred simultaneously within a column.

Although a number of researches have been reported on the implementation of a reactive distillation to biodiesel production, most of them focus on the utilization of free fatty acid extracted from vegetable oils as a reactant for an esterification processes (Kumar and Mahajani, 2007) A transesterification process of vegetable oils is more interesting option because there is no need to convert all triglycerides to fatty acids. Recently, Silva et al. (2010) preliminary studied the synthesis of biodiesel from the transesterification of soybean oil and ethanol in the reactive distillation. It is shown that the use of reactive distillation can reduce the excess use of methanol, number of unit operation and operating cost.

1.1.5 Heat integrated reactive distillation

Reactive distillation can be implemented for biodiesel production from pure vegetable oils and waste cooking oils. The biodiesel production process by using heterogeneous acid catalyst generally requires high energy consumption because of its high pressure operation. The implementation of a heat integration concept to a reactive distillation can reduce an overall process energy consumption, especially for the reactant and product mixture having small difference in their boiling points and requiring high operating pressure. In the past years, a number of heat-integrated reactive distillation configurations were proposed, such as a petlyuk reactive distillation (Gomex-Castro et al., 2010), a thermal coupling reactive distillation (Wang et al., 2010) and an internal heat integrated reactive distillation (Mali et al., 2009). A multi-effect reactive distillation is another column design for improving the energy usage (Lee et al., 2010). Although the heat integration of conventional and reactive distillation columns has been studied, a limited works have focused on a systematic design of the heat-integrated reactive distillation. For example, Caballero et al. (2008) proposed the design methodology for the distillation column and thermally coupling distillation column connecting in series. Seader et al. (2004) proposed the selection method of the distillation configuration for a ternary mixture which is based on the ease-of –separation index (ESI); however, this method cannot be applied to the heat integrated distillations. It is noted that the previous design methodologies for the heat integration of distillations did not cover all types of column configurations.

1.1.6 Separation process of fatty alcohol

Fatty alcohol is produced from the hydrogenation reaction of methyl ester and hydrogen. In this process, methanol is found to be another major product and other by-products, such as heavy hydrocarbons and wax ester, are also generated (Rieke et al., 1997). Design of the separation process of fatty alcohol is required to achieve the desired product purity. There are several methods to eliminate impurities from the fatty alcohol product. Wilmott et al. (1992) studied the removal of wax ester by reacting with methanol. Transesterification of wax ester and methanol will produce methyl ester that is raw material for fatty alcohol. Alkali, such as NaOH and KOH can be reacted with wax ester to produce soap; so it can be separated from unreacted methyl ester (Namba et al., 2005). Their works claimed how to eliminate side product; however, the sequence of unit operations can purify without reaction. Lurgi (1991) proposed the configuration of the fatty alcohol separation process when mostly methyl ester is consumed. Although the separation of crude fatty alcohol was identified as the difficult task, the design of the purification process of crude fatty alcohol was not given in detail. Furthermore, study on the separation of crude fatty alcohol is quite limited.

1.2 Objectives

The objective of this research is to design the production process of biodiesel integrated with fatty alcohol. A systematic step by step methodology is developed for design, synthesis and analysis of such a process according to demand and economic state. A reactive distillation as a process intensification is proposed to improve the performance of the biodiesel production process in terms of productivity, energy consumption and economic criteria. Design of the reactive distillation with and without heat integration is performed. Finally, design of the separation process of fatty alcohol is presented.

1.3 Dissertation Overview

Chapter II reviews the literature that is related to biodiesel production process, fatty alcohol production process, process design and synthesis including heuristic method and thermodynamic insights method, economic analysis and process intensification such as reactive distillation.

Chapter III gives the principle of biodiesel production processes with different catalysts, such as alkali catalyst, acid catalyst, heterogeneous base catalyst, heterogeneous acid catalyst and enzyme catalyst. The theoretical background of fatty alcohol production processes, process design and synthesis**,** design of distillation column and process economic analysis is also introduced.

Chapter IV gives the details of the proposed design methodology for the process producing multiple products, according to demand and economic states. According to this methodology, all possible flowsheet configurations are first generated and illustrated as a generic superstructure. A systematic screening procedure, applying constraints in a hierarchical manner, is also proposed. The number of alternatives is decomposed until the feasible one is obtained. In addition, design of a reactive distillation for biodiesel production from pure palm oil and waste cooking palm oil is proposed. A element based method is modified and implemented to design the reactive distillation. Furthermore, design of a heat integrated reactive distillation for biodiesel production is proposed by considering the minimization of a total annual cost.

Chapter V presents the application of the design methodology including producing main products plus side product. The economic analysis for biodiesel production is investigated. The optimal fractions (diversion of source) to produce multiple products is determined. Sensitivity analysis of parameters such as biodiesel price and glycerol price on net present value is included. The last part of this chapter is to combine the reaction task and separation task by using reactive distillation. It will improve the process performance. The details of reactive distillation are described in next chapter.

Chapter VI presents the design of reactive distillation for biodiesel production from pure palm oil and waste cooking oil including free fatty acid. Element – based method is implemented to determine the suitable number of reactive stages and suitable parameters.

Chapter VII presents the application of design methodology for heat integrated reactive distillation for biodiesel production. The selecting type of heat integrated reactive distillation is proposed through the criteria. The suitable type of heat integrated reactive distillation is designed by considering the minimization of a total annual cost.

Chapter VIII presents the design of fatty alcohol based on thermodynamic insights algorithm (Jaksland et al., 1994). The types of heat integration for purification is concerned to reduce energy consumption in term of the total annual cost.

Chapter IX gives the conclusion of this dissertation.

CHAPTER II

LITERATURE REVIEWS

2.1 Biodiesel production process

There are several way to produce biodiesel depending on type of catalysts such as alkali catalyst, acid catalyst, solid base catalyst, solid acid catalyst and enzyme catalyst (Lam et al, 2010; Marchetti et al, 2007; Glisic and Skala, 2009). Beside of type of catalysts, other processes such as supercritical methanol and hydrolysis of triglyceride then esterification of fatty acid can produce biodiesel. Biodiesel production processes is different operating conditions and type of feedstock; for example, alkali catalyst is used as a catalyst when free fatty acid contents was lower than 1 wt% (You et al, 2007) because alkali catalyst was sensitive to free fatty acid contents in vegetable oil. Otherwise, other catalysts were be considered for biodiesel production from waste cooking oil. Two-steps catalyzed process was also preferred for biodiesel production from waste cooking oil. The first step was to reduce free fatty acids by esterification. While second step was transesterification of refined vegetable oil (Wang et al, 2006). Acid catalyst from esterification could be neutralized with alkali catalyst from transesterification. Therefore, additional catalyst and reactor were not required (Zhange et al, 2003). Solid based catalyst such as became to use as a catalyst to avoid neutralization step; however, the catalyst was sensitive to free fatty acid contents (Gerpen, 2005) Therefore, solid acid catalyst was more preferred. Supercritical methanol was another option for biodiesel production because the reaction was fast and catalyst was not required (Lee et al, 2011). In addition, waste cooking oil was also to use as raw material. However, this process was not economical because of severe conditions and specified material. Enzyme catalyzed process was operated at mild conditions such as 25 ^{o}C and 1 atm. In addition, this process was friendly to environment (Lam et al, 2010).

Operating conditions for biodiesel production are different depending on type of catalysts . The advantages and disadvantages for each type of catalysts are shown in table 2.1

Table 2.1 The advantage and disvantage for biodiesel production by using different catalysts

process	Advantage	Disadvantage
Alkali process	Reaction is fast.	Free fatty acid in oil is sensitive to catalyst. The use of this catalyst is limited only for refined vegetable oil with less than 0.5 wt.% FFA
	Reaction temperature is moderate.	Soap is occurred.
	Catalyst is widely available and economical.	Separation of glycerol from biodiesel is difficult.
		High water content in waste cooking oil also affects the methyl ester yield, because water can hydrolyze with triglycerides to form free fatty acid at high temperature.
Acid process	The performance of the acid catalyst is not strongly affected by the presence of FFAs in the feedstock.	Reaction time is slower than the homogeneous base-catalyzed reaction.
	Acid catalysts can simultaneously catalyze both esterification and transesterification.	High molar ratio of alcohol to oil is used.
		Separation of the catalyst, is serious for environment.
		Severe reaction conditions (such as longer reaction time) are required.

Table 2.1 the advantage and disvantage for biodiesel production by using different catalysts (Cont)

process	Advantage	Disadvantage
Solid base	Solid catalysts could be easily incorporated into a packed bed continuous flow reactor.	Free fatty acid in oil is sensitive to catalyst.
	Catalyst such as CaO can be synthesized from cheap sources like limestone.	Soap is occurred.
	Separation of the catalyst is easy from the reaction medium, resulting in lower product contamination level.	
Solid acid	Acid catalysts can simultaneously catalyze both esterification and transesterification.	Severe conditions are used.
	Solid catalysts could be easily incorporated into a packed bed continuous flow reactor.	Reaction rate is slow.
	The washing step of biodiesel is eliminated.	
	Easy separation of the catalyst from the reaction medium results lower product contamination level	
	The regeneration and recycling of catalyst is easy.	
enzyme	Recovery of glycerol is easy.	Cost of catalyst is expensive.
	Reaction temperature is low.	Number of support enzyme is not uniform.
	Less methanol is required.	
	Waste cooking oil can be used.	

Table 2.1 the advantage and disvantage for biodiesel production by using different catalysts (Cont)

process	Advantage	Disadvantage
Supercritical methanol	Catalyst is not needed in the reaction. Separation of product mixtures is easy.	High pressure and temperature are required.
	The waste cooking oil including high free fatty acid contents and water can be used as raw materials. Supercritical reaction takes a shorter reaction time than the traditional catalytic transesterification reaction.	Methanol-to oil ratios is high.
Hydrolysis of trilglyceride	The waste cooking oil including high free fatty acid contents and water can be used as raw materials. Mild conditions are required.	Reaction time is large.

The purification of biodiesel production is necessary to meet the product specification of biodiesel. However, the purification processes are different depending on type of catalysts. For example, homogeneous catalysts such as NaOH and H_2SO_4 require the neutralization of catalyst before catalysts are released to environment (Gerpen, 2005). While solid catalysts can be reused in the system. To separate crude glycerol from crude biodiesel, water washing, sedimentation, centrifuge and decanter are required because the solubility is different (Berrios and Skelton, 2008). However, decanter is preferred to separate crude glycerol. Other equipments can be used for purification of biodiesel (Predojević et al., 2008). Decanter can be replaced to liquid-liquid extractor for enzyme catalyzed process (Sotoft et al, 2010). Generally, methanol is the first component to remove from product mixtures (Zhange et al, 2003; West et al., 2007). Excess methanol can be recycled to transeterification reactor. West et al. 2007 proposed biodiesel production process with different catalysts. The flowsheet of supercritical methanol process was heterogeneous acid catalyzed process. However, the configuration of supercritical methanol process was different from other processes because of severe conditions (Diaz et al, 2009). Two flash separators were required to separate excess methanol and steam stripper can remove excess methanol completely. Methanol may be removed earlier or later in the process (Myint et al, 2008). The sequence of unit operations were different. For example, methanol was removed first before water washing. Biodiesel and glycerol were removed first before remove methanol and water washing. The simulation results shew that the first removal of excess methanol is preferred because removal catalyst shifted equilibrium reaction and less energy for the separation was required. After removal crude glycerol from crude biodiesel, vacuum distillation was used to purify until purity of biodiesel is 99.5 wt% (Helwani et al., 2009). Partial vacuum distillation remove excess methanol in vapor phase so purified biodiesel was obtained at the top of column while unreacted triglyceride was removed at the bottom of column (Zhange et al, 2003).

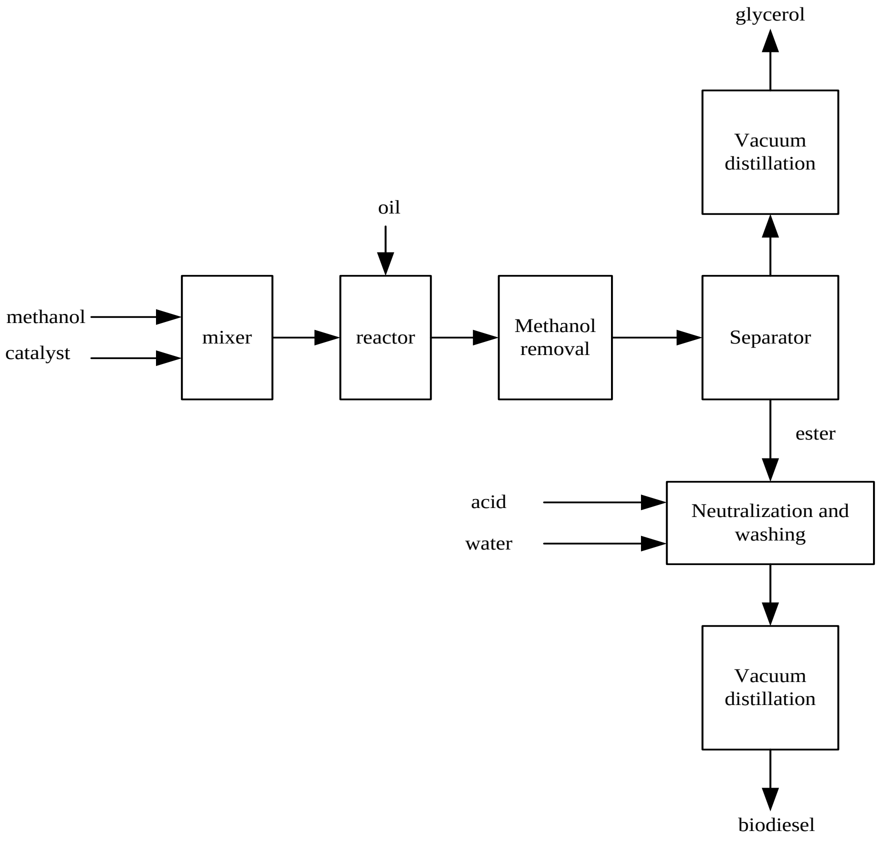

Fig.2.1 biodiesel production process

2.2 Fatty alcohol production process

Fatty alcohol is an important chemical for industries such as pharmaceutical, cosmetics and foods. It is derived from hydrogenation reaction between methyl ester and hydrogen. Methyl ester is produced from transesterification of vegetable oil with methanol or esterification of fatty acid with methanol. Both reactions are the main reactions for biodiesel production. There are many studies in operating within reactor such as temperature, type of methyl ester and fatty alcohol production process.

In general, the common routes to produce fatty alcohol can be divided into three classes such as the hydrogenation of triglyceride, fatty acid, and fatty acid methyl ester. The hydrogenation of triglyceride rarely use because this process operate at high condition so glycerol can be decomposed (Kreutzer et al., 1984). Triglyceride should be converted to free fatty acid or fatty acid methyl ester before the hydrogenation process.

Therefore, fatty alcohol production has been improved by using free fatty acid as a raw material (Mendes et al., 2001). Various catalysts such as RuSn, Al, RuAl and SnAl were studied at high condition 250 ^{o}C and 25 MPa to determine the performance of reaction in term of selectivity. Side products such as saturated fatty alcohol and stearic acid were obtained. However, there is disadvantage in this process because free fatty acid is corrosive for equipments and catalyst. In addition, there is no detail in configuration of reactor and purification of crude fatty alcohol.

Well-known fatty alcohol production is the hydrogenation of methyl ester because free fatty acid is not suitable raw material (Dupont et al., 1991). It has been known that products were fatty alcohol and methanol which can be used in two ways. Methanol can be purified and used in esterification to produce methyl ester or reformed to produce hydrogen. These two ways were different in the production and used energy consumption; therefore, studing fatty alcohol production route is interesting. The way to produce fatty alcohol is followed in Fig 2.2 and 2.3.; however, this study did not consider the purification of methyl ester before using it as raw material for hydrogenation process and the purification of crude fatty alcohol did not mention despite this process is important to follow product specification.

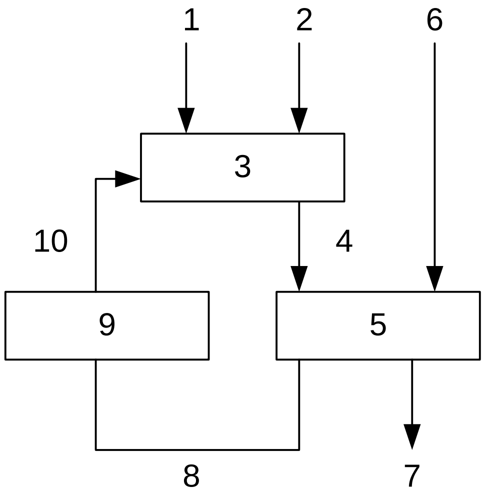

Fig 2.2 The first way to produce fatty alcohol (Carduck et al., 1994)

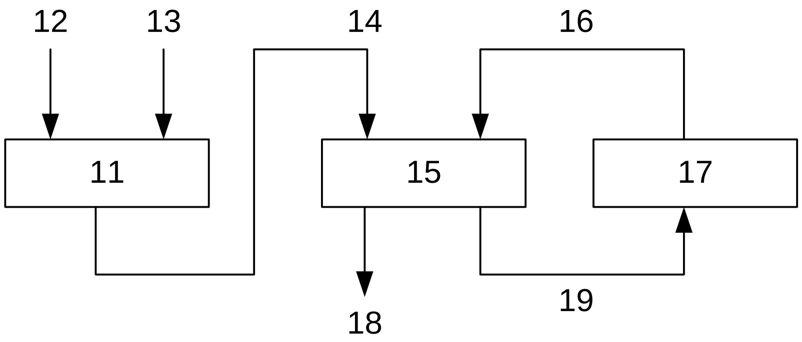

Fig 2.3 The second way to produce fatty alcohol (Carduck et al., 1994)

Where 1 is fatty acid; 2 is methanol; 3 is esterification reaction; 4 is methyl ester; 5 is hydrogenation reaction; 6 is hydrogen; 7 is fatty alcohol; 8 is impured methanol; 9 is distillation column; 10 is pured methanol; 11 is esterification reaction; 12 is methanol; 13 is fatty acid; 14 is methyl ester, 15 is hydrogenation reaction; 16 is hydrogen; 17 is steam reforming; 18 is fatty alcohol; 19 is methanol.

Although CuCr was commonly used as a catalyst, hydrogenation of methyl ester such as methyl oleate could be carried out in the presence of $CoSn/Al_2O_3$ catalyst at 270 ^{o}C and hydrogen pressure 8 MPa (Pouilloux et al., 1998). The results were shown that side products such as methyl stearate, stearyl alcohol and wax ester were found. Moreover, the amount of wax ester was similar to main product. Conversion of methyl ester increased with an increasing temperature while selectivity decreased with an increasing pressure but conversion increased at high pressure.

Similarity, the hydrogenation of methyl laurate in the presence of various catalysts was studied (Miyake et al., 2009). Side products such as dodecane, lauric acid and lauryl laurate were obtained. Therefore, it can be seen that side products cannot be avoided especially, wax ester. This was because the esterification of fatty acid with fatty alcohol occurred easily at high condition. Although side products cannot be avoided, the amount of side products can be reduced (Singleton et al., 1995). Reaction temperature should not be greater than 250 ^{o}C; therefore, the amount of alkane can be decreased and the amount of wax ester was lower than amount of fatty alcohol. However, ratio of hydrogen to methyl ester was quite high to enhance 97% of conversion.

Because blending of various methyl ester enhanced various fatty alcohol, Heck et al. (2002) synthesized only unsaturated fatty alcohol by using distillation column to separate unsaturated methyl ester from saturated methyl ester. Then unsaturated methyl ester was hydrogenated with hydrogen to obtain unsaturated fatty alcohol. However, this study did not mention in the purification of fatty alcohol.

According to literature review, most studies focused on the fatty alcohol production; therefore, the fatty alcohol production process was developed by improving the purification of crude fatty alcohol (Lurgi, 2001). The distillation columns were used for the separation fatty alcohol from unconverted methyl ester. For this process, alkane which was a side product was considered. The first distillation column was used for separation the alkane while the other column was used for purification of fatty alcohol.

Because the boiling point of fatty alcohol was close to the boiling point of methyl ester, Namba et al., (2005) improved the purification process by using KOH to mix in the fatty alcohol produced from methyl palmitate before distillate at vacuum pressure. This hot aqueous alkali solution help remove unreacted methyl ester. The amount of KOH added was approximately 1000 ppm. Fatty alcohol was withdrawn at the distillate stream while unreacted methyl ester and KOH were driven at the bottom stream then hot water washing was used to separate KOH from unreacted methyl ester. The amount of KOH in distillation residue should be less than 10 to 30 ppm so Unreacted methyl ester can be recycled in hydrogenation process. In this research, the removal of KOH with various amount of KOH in distillation residue was studied. The result showed that removal of KOH was efficient when hot water washing was used; however, the amount of KOH content in unreacted methyl ester after alkali removal was higher than the recommended value.

Some remaining methyl ester in product was converted to a fatty acid salt which was lost in the aqueous phase when alkali solution was used to separate fatty alcohol from methyl ester. In addition, it was necessary to separate the alkali solution and treat waste water (Wilmott et al. 1992). For this process, distillation column was wused for the separation of fatty alcohol from unreacted methyl ester. Wax ester, another by product, is also considered. This process included hydrogenation unit, esterification units of crude fatty alcohol with methyl ester to obtain wax ester, distillation column for separation of alkane from fatty alcohol and separation of methanol. This work focused on the esterification of crude fatty alcohol with unconverted methyl ester. Although this work claimed that the separation of crude fatty alcohol was difficult, a few details of the purification of crude fatty alcohol such as optimum condition and optimum configuration of purification which obtain production specification did not mention. In addition, wax ester can be recycled within hydrogenation unit.

Although there are literature reviews concerning about the design of fatty alcohol production process which used pured methyl ester, a few study focused on the effect of free fatty acid content for the hydrogenation of methyl ester. Residue free fatty acid content in methyl ester from triglyceride was sensitive to catalyst. Scheur et al. (1995) studied the influence of free fatty acid on the performance of catalyst of hydrogenation of methyl palmitate. Copper zinc oxide was used as a catalyst. The results were shown that higher free fatty acid content reduced methyl palmitate conversion. This was because free fatty acid inhibited the reaction rate. The acid and methyl ester competed for the same active sites so only small free fatty acid content was signification the performance of the hydrogenation of methyl ester. The acid values around 1 mg KOH/g or 99.95 % purity of methyl ester was recommended to use as feedstock for hydrogenation of methyl ester.

According to literature reviews, there are several by products formed in fatty alcohol production such as hydrocarbons, wax ester, and saturated fatty alcohol. Components of by product depend on type of catalyst and ratio of hydrogen to methyl ester. Table in appendix A shows the literature reviews for fatty alcohol production with several raw materials, catalysts, condition and products. It can be seen that most of by products is hydrocarbon; therefore, the separation of by products from fatty alcohol should be concerned.

2.3 Process synthesis

Various methods for synthesis and design of chemical processes such as reactor systems and separation systems are available such as heuristic method (Douglas, 1988) , thermodynamic insights method, optimization method and hybrid method. The main objective of design chemical process is to determine the optimal reactors and separation equipments that produce the desired product, as well as the sequence of separation unit operations and select the best alternatives that give the optimal conditions.

2.3.1 Heuristic method

The complicated problem statement was decomposed into a small problem by decision steps. The most commonly method was heuristic approach of decision steps (Siirola and Rudd, 1971). Douglas (1988) proposed process synthesis procedure based on a hierarchy of decision level such as the selection of batch or continuous process, input-output Structure of flowsheet, recycle structure of flowsheets, separation system specification and heat exchanger network. The procedure was further extended by adding energy integration, evaluation alternatives and safety. The selection of reactor were divided to two cases such as liquid phase and vapor phase. The selection of separation system was further developed such as separation the most plentyful first, removing the lightest component first, favor equimolar split. The economic evaluation in each level was estimated in term of economic potential that add the details in each step. However, this method was not considered intermediate product. Stephanopoulos and Han et al., (1995) further developed this approach from Douglas, but the limitation of this method is conventional reactor and sizing is not concerned.

Barnicki and Fair (1990) proposed separation system for liquid mixtures and vapor mixtures based on properties then equipments for the separation were selected. The chemical process wa decomposed that the number alternatives is reduced by using onion diagram (Smith, 2005). Another heuristic approach was proposed by Seader et al., 2004. Reaction pathways were searched and selected that gave the highest gross profit. Disadvantage of this method was that gross profit was computed before equipment designs. In addition, each reaction pathways was assumed as complete reaction that meant limiting reactant is comsumed. Reaction that depended on catalysts were not concerned.

The knowledge for selecting type of reactors, separators by given a score and flowsheet alternatives were proposed (Alqahtani et al., 2007). Economic potential was used to reduce the number of alternatives. This method was studied through a case study, ethylene glycol production. The use of this method could save time during preliminary design.

2.3.2 Optimization method

Biegler et al. (1997) formulated problems into mathematical expression and solve problem with optimization, thereby the optimal variables were provided. The advantage of this method was that configuration of flowsheet and operating conditions could be solved simutaneously. Furthermore, maximum profit or minimum total investment cost can be found. A full set of separation tasks was generated in superstructure (Linke and Kokossis, 2003) that was optimized by MINLP in term of annual profit until a feasible one was obtained. However, complex problem was difficult to converge. So Marquardt et al., (2008) developed the fast screening step for the azeotropic mixture before the optimization of superstructure. The criteria for the fast screening step was energy consumption of process alternatives and linear the profile of component in distillation column in diagram. Only a few optimization was necessary in a final step. However, this method proposed the fast screen for distillation column not including other unit operations. Optimization method could be applied with process synthesis for biorefinery by optimization of the reaction pathways to obtain the optimal route (Pham and El-Halwagi, 2012). The criteria of selection pathways for biorefinery was the maximum yield. Pathway of biodiesel production including heat integration (Severson et al., 2012) was determined by optimization approach. The optimal condition in the reactor after optimization differed from conventional process. The result shew that alkali catalyzed process gave the higher yield while enzyme catalyzed process gave the lower energy consumption. Superstructure included raw material selection, reaction pathway and intermediate product for biomass pretreatment to biorenewable product (Marquardt et al., 2010). The optimized problem was formulated to maximize product yield.

2.3.3 Thermodynamic insights method

Since the physical and chemical properties of the involved chemical system play a very important role for the design/synthesis of a process, a thermodynamic insights based hybrid method has been proposed by Jaksland et al. (1995). Hostrup et al. (2001) further developed this method by including a reverse design approach where process design variables were “back-calculated” for known design targets. The method consisted of pre- analysis by identifying the reaction and separation knowledge, problem formulation, generation of flowsheet and and optimization of sturcture. The thermodynamic insights method also combined with optimization method, so mathematical problem was needed for further analysis. The application of this method was the separation of methyl acetate production, and the production of cyclehexane.

d’Anterroches and Gani (2005) proposed the reverse approach by using group contribution. The process group could represent one or more unit operations. For further step, possible alternatives were generated. The model of flowsheet property was generated in mathematical problem to find the energy consumption of flowsheet. The application of this method was the separation of mixtures in five compounds.

All these methods could applied for many pathways to produce a desired product. Superstructure for biorefinery was generated (Pham and El-Halwagi, 2012). The starting point was beginned at the raw material and desired product and listed the pathways that lead to them. So some pathways could be matched the intermediate product before desired product. However, the number of pathways was reduced from the yield and production cost.

All these methods, however, focus on processes with one main product for a fixed reaction-catalyst and do not consider process alternatives in terms of diversion of resources to another product within the same overall process.

2.4 Economic analysis

Economic analysis is necessary for design process because it can know that which process is the most economical. Although there are no details about economic analysis for fatty alcohol production, there are many studies the evaluation economic for biodiesel production which can be applied with fatty alcohol production. Some studies investigated economic analysis based on break even price, profitability, total capital investment and total product cost. For example, Zhang et al. (2003) and You et al, (2007) compared biodiesel production processes such as alkali catalyzed process, acid catalyzed process and two-steps catalyzed process in term of break even price of biodiesel. Total capital investment and total product cost were estimated in each process. The results were shown that acid catalyzed process was the most economical because the vegetable oil price was sensitive. In addition, plant capacity was the factor which affected the economic for biodiesel production.

Similarity, biodiesel production processes such as alkali catalyzed process, heterogeneous catalyzed process, acid catalyzed process were designed. total capital investment including fixed capital investment and working capital cost was calculated in designed biodiesel production process to determine the most economical process (West et al., 2008). The result was shown that heterogeneous catalyzed process was the best biodiesel production process which was different from other work. While Marchetti et al., (2008) designed biodiesel production processes and determined the most suitable process by using the profitability in term of return on investment including total investment and profit. Uncertainty of variables such as feed oil price and biodiesel price was investigated. Two-steps catalyzed process (esterification and transesterification) was not a preferrable option when feed oil price was varied more than 11% from original value. Alkali catalyzed process and enzymed catalyzed process were compared by using economic criteria (Jegannathan et al., 2011). Production cost of enzyme catalyzed process were found. Enzyme catalyzed process provided the highest yield and production cost when compared with alkali catalyzed process because of the high price of catalyst. Another enzyme catalyzed process by using co-solvent was proposed because it could reduce methanol content that inhibited to enzyme catalyst(Sotoft et al, 2010). However, total production cost of enzyme catalyzed process without co-solvent had lower. The number of unit operations for enzyme catalyzed process was less than conventional process. From economic analysis, raw materials had a large affect on total production cost. Glycerol considered as byproduct was also important for the economy.

In contrast, the effect of crude raw material cost on biodiesel price for biodiesel production process was investigated (Hass et al., 2006). While Apostolakou et al. (2009) studied the effect of plant capacity on fixed capital investment, total production cost and profitability in term of return on investment for biodiesel production process.

To compare biodiesel production using supercritical methanol and conventional process from pure vegetable oil and waste cooking oil, supercritical methanol process giving the higher net present value although conventional process provided less energy consumption. In addition, conventional process for biodiesel production when pure vegetable oil used as raw material was unacceptable process because of the negative value of net present value. Therefore, it implied that supercritical methanol process was more economical process (Lee et al., 2011). In addition, supercritical methanol process produced higher purity and amount of glycerol and higher production yield. Therefore, supercritical methanol process was more profitable process (Lim et al., 2009).

Kiss et al., (2010) investigated the effect of economical, and enviromental impacts on alkali catalyzed biodiesel process and heterogeneous catalyzed process. Utilities cost, biodiesel price and glycerol price were analyzed to determine the effect of total production cost. The results shew that energy consumption would affect the total production cost if utility cost was quite large. Glycerol price affected on the process when biodiesel production plant capacity was increased because it increased glycerol production. The use of glycerol from biodiesel production plant should be developed by converting to value –added products.

2.5 Reactive distillation for biodiesel production

2.5.1 Conventional reactive distillation for biodiesel production

It has been known that the transesterification of vegetable oils converted triglyceride to methyl ester and glycerol as a by product is an equilibrium-limited reaction. A large excess of alcohol over a stoichiometric ratio is usually employed in conventional reactors to achieve a high degree of the conversion of a vegetable oil and thereby, requiring the expensive separation of unreacted reactants from the biodiesel product. As a consequence, potentially alternative processes to overcome such a difficulty should be explored. Reactive distillation is one type of process intensification has a potential for chemical process such as biodiesel production process. A combination of chemical reaction and separation can improve efficiency of production. The simultaneous separation and reaction inside the column allow the equilibrium-limited reaction to take place efficiently and reduce the separation cost of unreacted reactants. Although a number of researches have been reported on the implementation of a reactive distillation to biodiesel production, most of them focus on the utilization of free fatty acid extracted from vegetable oils as a reactant for an esterification process . Kumar and Mahajani (2007) applied reactive distillation for the esterification of lactic acid with n- butanol catalyzed by Amberlyst-15. The production of isopropyl palmitate in a reactive distillation column was experimentally and numerically studied by Bhatia et al. (2006). The optimal distillate to feed ratio was 0.59 when the molar ratio of isopropanol and palmitic acid was 2:1. To date, a few studies on the reactive distillations have been performed for the transesterification of vegetable oils. Recently, Silva et al. (2010) preliminary studied the synthesis of biodiesel from transesterification of soybean oil with ethanol by using reactive distillation. The effect of operating conditions such as catalyst concentration and ratio of ethanol to oil on the performance of biodiesel production was only studied without considering design parameters.

2.5.2 Heat integration of reactive distillation for biodiesel production

In general, biodiesel is produced by using alkali catalyst so literatures are considered a reactive distillation for biodiesel production using alkali catalyst (He, 2006). However, pure vegetable oil is required to use as raw material due to the limitation of catalyst. Other types of catalysts such as enzyme catalyst and heterogeneous acid catalyst are attractive option for biodiesel production. Although a reactive distillation can be employed for biodiesel production, the energy consumption of reactive distillation for the heterogeneous catalyzed process is large because the high pressure operation is required to increase reaction temperature within the column. Generally, heat integration is investigated when separation of mixture is difficult because of small difference of boiling points, thus large energy consumption is required. A heat-integrated reactive distillation was proposed, including a petlyuk reactive distillation (Gomez-Castro et al., 2010), a thermally coupled reactive distillation (Wang, et al., 2010) and an internal heat integrated reactive distillation (Mali et al, 2010). A multi-effect reactive distillation was another column design for improving energy usage (Lee et al, 2010). There are two types of multi-effect reactive distillation such as feed split multi-effect reactive distillation and multi-effect indirect split arrangement reactive distillation. With this concept, a conventional reactive distillation column was divided into two columns operated at high and low pressures; heat from a top distillate vapor of the high-pressure column is supplied to a reboiler of the low-pressure column. Although feed split multi-effect reactive distillation could reduce energy consumption in a half, it could be carried out in a few cases that the difference of boiling points of key components is not different. Otherewise, heat from the high pressure column was not enough for the low pressure column.

Considering a heat integrated reactive distillation, the capital cost of compressor installation for heat integrated reactive distillation (HIRDC) is high and the column design was performed without concern about a total annual cost. Petyuk reactive distillation column was an alternative option to produce biodiesel production from esterification (Gomez-Castro et al., 2010). Petlyuk reactive distillation also reduced the number of reboiler and condenser. However, petyuk column had a limitation of the range of boiling point of components and bidirectional of vapor and liquid flow. Although heat integration of distillation have been studied, there are a number of studies to propose the selection type of heat integration. For example, Caballero et al, (2008) proposed methodology of the sequence of distillation column and thermally coupled distillation for separation mixtures. To minimize the energy consumption of the reactive distillation, heat integration of distillation could be applied with reactive distillation. Seader et al, (2004) proposed the selection of configuration of distillation for ternary mixtures which based on ease-of –separation index (ESI) but was not included other selection type of heat integration such as internal heat integration and multi-effect distillation . Minimum vapor flow rate was used to determined the type of multi-effect distillation (Engelien, 2005); however, it has been simulated a rigorous model. Furthermore, a few studies have been focused on the implementation of a heat-integrated reactive distillation for a transesterification process to produce biodiesel is quite limited.

2.6 Conclusion

According to literature reviews, a design of biodiesel production integrated with fatty alcohol production involves multi-components system; therefore, the designed methodology is important to determine the suitable economical process and sustainable process. To overcome the limitation of previous methodologies, a systematic screening procedure, applying constraints in a hierarchical manner is proposed. Thermodynamic insights method is also applied to identify feasible separation techniques. Economic analysis is also evaluated to determine the most feasible process in term of profitability indicator such as net present value.

According to literature reviews of combination of reaction task and separation task, reactive distillation has a potential equipment to improve the performance of processes such as esterification. Therefore, reactive distillation also improve the performance of transesterification for biodiesel production. Furthermore, biodiesel production is a special case because of a large different boiling point of components. Design of reactive distillation and heat integration of reactive distillation are important to investigated.

CHAPTER III

THEORETICAL BACKGROUND

3.1 Biodiesel

Biodiesel (fatty acid methyl ester) produced from transesterification of triglycerides in vegetable oils is renewable resources. Therefore, biodiesel is also a renewable fuel that substitutes to petroleum diesel because properties such as cetane number, viscosity and density are similar. Biodiesel offers several advantages over petroleum diesel especially environmental impact such as low emission profile of carbon monoxide and unburned carbon. Methanol is usually used as raw materials for biodiesel production because of low price.

Not only crude vegetable oils contain impurities such as free fatty acids and water content but also minor components such as phospholipids, sterols, aliphatic alcohols and aliphatic hydrocarbons. To produce biodiesel from vegetable oils or consume vegetable oils as edible oils, biorefinarys such as neutralization, bleaching and extraction by solvent are required to meet product specifications and prevent soap formation that occurs from the sponification of free fatty acids.

Vegetable oils that use as feedstock for biodiesel product are soybean oil, coconut oil, palm oil, sunflower oil and jatropha oil. However, palm oil is a usual raw material for biodiesel production in Thailand due to its high availability. Among the various vegetable oils, palm oil has the cheapest price in Thailand. There is 45-50% of oil content in palm fruit. However, since crude palm oil contains high content of free fatty acid (4-5 wt.%), a pretreatment of crude palm oil before feeding to a transesterification process is necessary.

For transesterification, there are different processes to synthesize biodiesel: alkali-catalyzed transesterification, acid–catalyzed transesterification, pre-esterification of free fatty acid with acid catalysts followed by base-catalyzed transesterification, enzyme-catalyzed esterification, transesterification under supercritical condition, etc. In commercial processes, alkali catalyst, i.e., sodium hydroxide or potassium hydroxide, is usually used because of high reaction rate. A amount of catalysts are varied from 0.5-1 wt.% and the standard conditions are 60 ^oC and atmosphere pressure.

3.2 Biodiesel production

3.2.1 Alkali catalyzed process

The transesterification of triglyceride and methanol consists of three reaction steps as shown in Equation 3.1.

$$\begin{aligned} &TG + CH_3OH \xleftrightarrow{k_1 and k_2} DG + RCOOCH_3 \\ &DG + CH_3OH \xleftrightarrow{k_3 and k_4} MG + RCOOCH_3 \\ &MG + CH_3OH \xleftrightarrow{k_5 and k_6} GL + RCOOCH_3 \end{aligned} \quad (3.1)$$

Triglyceride reacts with methanol to form a diglyceride, then a monoglyceride and finally a glycerol byproduct with fatty acid methyl esters. All the reaction steps are reversible reaction. Generally, pure vegetable oil is used as raw material because alkali catalyst is sensitive to free fatty acid contents in vegetable oil. Firstly, methanol and catalysts are mixed together before being fed into a reactor at room temperature. Vegetable oil is heated to 60 ^oC, and reacted with methanol in the reactor (Figure 3.1). The reaction is carried out with 6:1 molar ratio of methanol and oil. Excess methanol is removed from the product by using a distillation column and recycled to the reactor. Crude glycerol is removed from crude biodiesel by using liquid-liquid extractor (water washing). Catalyst that is mixed with product mixture from reactor is neutralized by using acid catalyst such as phosphoric acid before it disposes to environment. The remaining water and methanol are removed from crude biodiesel by a vacuum distillation. This fatty acid methyl ester is finally the biodiesel product with ASTM specifications. Crude glycerol from the washing step is purified by using distillation to remove water and mehanol. The glycerol should have the purity approximately 85% and is typically sold to glycerol refiner. Using a vacuum distillation, the glycerol with the purity up to 99.5% can be acheived.

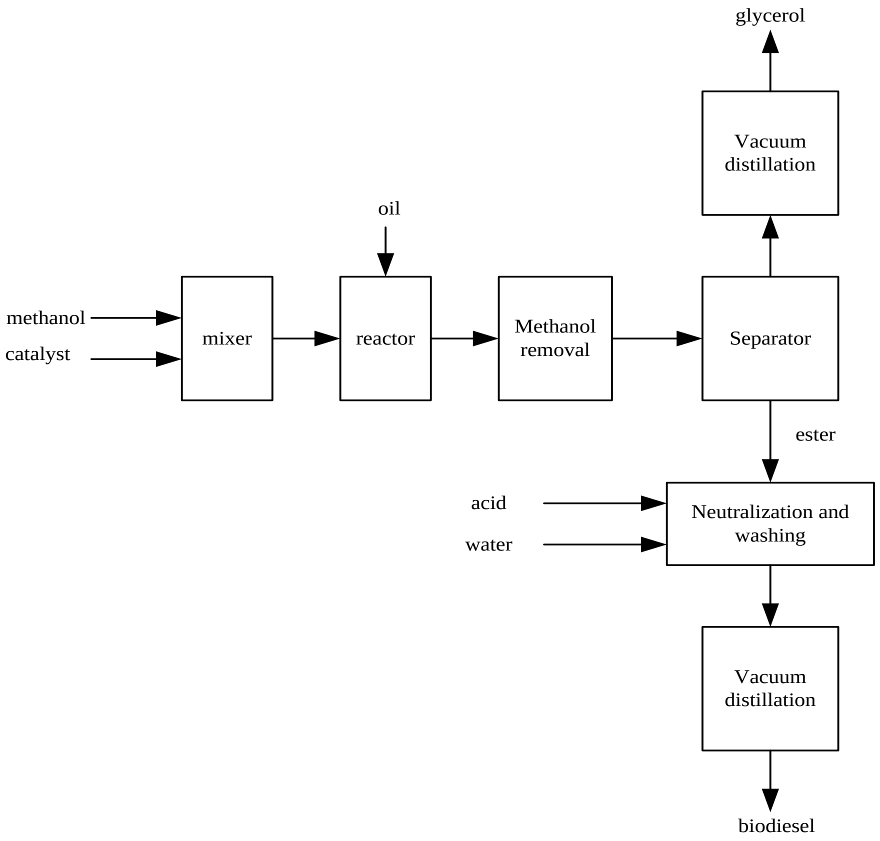

Fig. 3.1 Biodiesel production using an alkali process**,**

3.2.2 Esterification of free fatty acid

The esterification of fatty acid and alcohol alkyl ester is shown in Equation 3.2.

$$R_1 - COOH + R_2OH \leftrightarrow R_2OOCR_1 + H_2O \qquad (3.2)$$

Biodiesel can be also produced from esterification of fatty acid that derived from hydrolysis of triglyceride and free fatty acid in waste cooking oil. Water is obtained as byproduct of this reaction. Although any type of catalysts can be used for esterification, acid catalyst is commonly used. In general, esterification of fatty acid is used for pretreatment of waste cooking oil in case of containing a lot of free fatty acid contents. The reduction of free fatty acid in waste cooking oil can decrease free fatty acid content below 1 wt% then refined vegetable oil can transesterified with methanol by using alkali catalyst. Figure 3.2 shows the reduction of free fatty acid process before vegetable oil is sent to biodiesel production process.

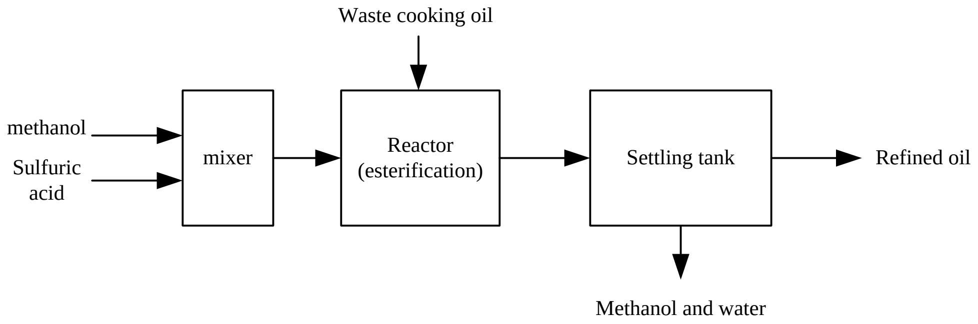

Fig. 3.2 The reduction of free fatty acid in waste cooking oil.

3.2.3 Heterogeneous catalyzed processes for biodiesel production

There are two types of heterogeneous catalyzed processes such as heterogeneous based catalyst and heterogeneous acid catalyst. Operating conditions such as temperature and pressure are depended on catalysts; however, higher operations are required because the reaction rates is low. The advantages of heterogeneous catalysts are reuse and recycle of catalyst. Furthermore, it is not necessary to neutralize the catalyst before disposing to environment. Heterogeneous acid catalyst is preferred than heterogeneous based catalyst because feedstocks consisting of free fatty acid are not sensitive to catalyst. So pretreatment for the reduction of free fatty acid contents in vegetable oil is eliminated. In addition, Biodiesel and glycerol do not contain with catalyst.

3.2.4 Enzyme catalyzed process for biodiesel production

Enzyme catalysts are also developed for biodiesel production to overcome the limitation of conventional process. Enzyme catalyst can be used for biodiesel production from waste cooking oil. Operating conditions are mild conditions such as room temperature and ambient pressure; however, reaction time is quite high in order to achieve high degree of conversion.

3.2.5 Supercritical process for biodiesel production

The advantage of this process is to eliminate the catalysts because the reaction occurs very fast. However, the operating conditions are severe so special equipments are needed. high operating temperature (350^{o}C) and high pressure (19MPa) are required. Then biodiesel is sent to purification process by separation glycerol and unreacted triglyceride using decanter and distillation, respectively.

3.2.6 Hydrolysis of triglyceride and esterification

Two steps biodiesel production involving hydrolysis of triglyceride and esterification of free fatty acid is developed to deal with the problem of conventional biodiesel production process due to high free fatty acid contents in vegetable oil. The first step involves a hydrolysis process. Ttriglycerides in oil are hydrolyzed with water to produce fatty acids and glycerol, whereas all the fatty acids react with methanol via esterification reaction to generate methyl oleate (biodiesel product) and water in the second step (Chen et al., 2010). In general, enzyme catalyst is used for hydrolysis because of high conversion and mild conditions. Glycerol is obtained as a by-product from hydrolysis. It can be separated from free fatty acid by using decanter. For esterification of free fatty acid, biodiesel and water are obtained. Then biodiesel is sent to purification process. The comparison of operating condition of different processes for biodiesel production is shown in table 3.1

Table 3.1 Operating conditions for biodiesel production different processes

process	Temperature (^oC)	Pressure (atm)
Alkali catalyzed process	60	1
Acid catalyzed process	130	1
heterogeneous base catalyzed process	70	1
heterogeneous acid catalyzed process	70	17
Enzyme catalyzed process	30	1
Supercritical methanol	350	40
Hydrolysis	45	1

3.3 Fatty alcohol

Fatty alcohol is aliphatic alcohols that produce from petroleum product such as ethylene by using Ziegler process. However, it can be produced from renewable resources such as palm oil, coconut oil, and palm kernel oil. There are two types of fatty alcohol. Saturated fatty alcohols such as lauryl alcohol and myristyl alcohol commonly produced from coconut oil that contains a lot of saturated fatty acids. Unsaturated fatty alcohol such as oleyl alcohol contains one or two double bonds in fatty alcohol. Saturated fatty alcohol can produce from petroleum product and natural resources while unsaturated fatty alcohol is only produced from natural resources. The properties of fatty alcohol is amphiphatic so it becomes non-ionic surfactant.

The application of fatty alcohol is used as emulsion for cosmetic cream and intermediate substances such as fatty alcohol ethoxylate for producing nonionic detergent, fatty alcohol sulfate for producing anionic detergent. The application of unsaturated fatty alcohol is used for heavy duty detergents, cosmetic creams, textile and leather processing, plasticizers and lubricanting - oil additives.

Typically, fatty alcohol is produced from hydrogenation or hydrogenolysis reaction which is defined as the splitting of a bond of methyl esters and addition of a hydrogen atom. Hydrogenation of fatty acid or fatty acid methyl ester produced from natural vegetable oil is significant pathway to fatty alcohols. The commercial end use of the fatty alcohol or fatty alcohol mixture must have less acid and saponification values (Wilmott et al., 2001). The acid value is a measure of the free fatty acid content of the alcohol product and is defined as the number of mgKOH required to neutralize the free fatty acid in 1 g of the alcohol. The saponification value is a measure of the free ester content of the alcohol product and is defined as the number of mgKOH required to saponify the esters and aids in 1g of alcohol. The ester value is the number of ester obtained by subtracting the acid value from the saponification value. The purity of fatty alcohol is measured by iodine value which is defined as the number of g of I_2 absorbed by 100 g of alcohol. Again, it is generally desirable to have as low an idone value as possible. Table 3.2 shows the specification of fatty alcohol for commercial grade.

Table 3.2 Specifications of fatty alcohol (Heck et al., 2002)

Specification	The maximum value
iodine value	0.05
acid value	0.02
saponification value	0.2
hydroxyl value	230-233
moisture value	0.2
hydrocarbon value	0.2

3.3.1 Route of fatty alcohol production

Figure 3.3 shows the three routes of fatty alcohol production. The first routes is to produce fatty alcohol from direct hydrogenation of triglyceride. Fatty alcohol is main product while glycerol is byproduct. This route can avoid intermediate products such as fatty acid and methyl ester; however, severe conditions and large excess of hydrogen are required. Furthermore, glycerol that is high value added product can be decomposed at high temperature. This route is impractical for the commercial way of fatty alcohol production because of these reasons.

The second route is to produce fatty alcohol from fatty acid that obtained from hydrolysis of triglyceride. This route requires absolutely acid resistant catalyst;

otherwise soap formation from fatty acid is occurred. So a higher catalyst consumption is required. Severe conditions such as temperature and pressure are similar to the direct hydrogenation of triglyceride. High conditions lead to overhydrogenation of ready fatty alcohol resulting in a higher percentage of hydrocarbons. Consequently, he formation of fatty alcohol is limited because the yield of fatty alcohol is decreased.

The third route of fatty alcohol production is tranesterification of triglyceride before hydrogenation of methyl esters. The transesterification of triglyceride or esterification of fatty acid produce methyl esters that it is raw material for fatty alcohol production. This route is commercial way because less conditions are required when compare with other routes.

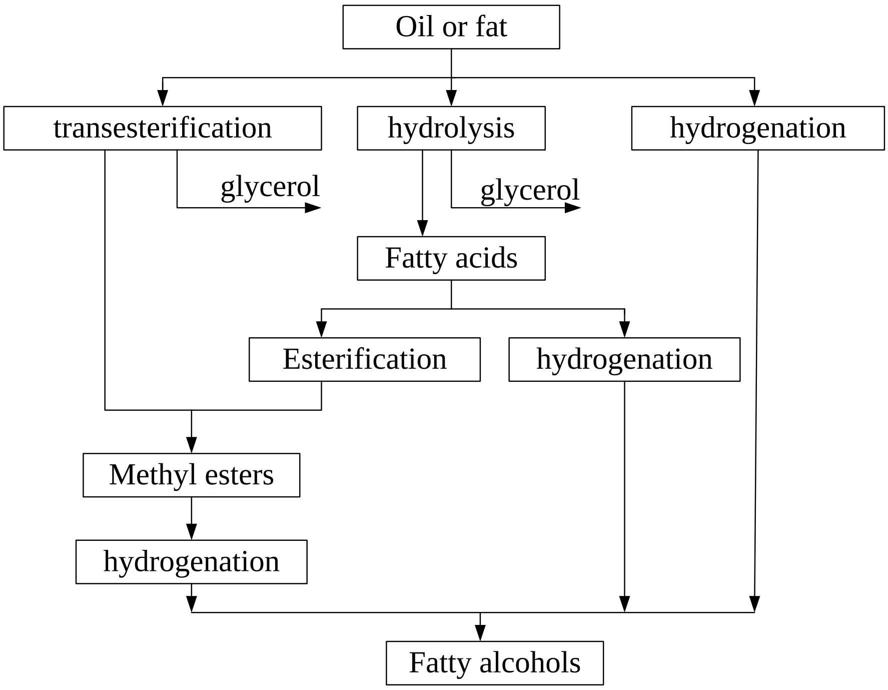

Fig. 3.3 Route of fatty alcohol production (Krutzer et al, 1985).

The hydrogenation reaction of methyl ester with hydrogen is shown in Equation 3.3.

$$RCOOCH_3 + 2H_2 \rightarrow RCH_2OH + CH_3OH \qquad (3.3)$$

Undesired side reactions are the hydrogenation of the fatty alcohol to a hydrocarbon and the saturation of unsaturated alcohols as follows:

$$\mathrm{RCH_2OH + H_2 \rightarrow RCH_3 + H_2O} \tag{3.4}$$

$$\mathrm{RCH = CHR'CH_2OH + H_2 \rightarrow RCH_2 - CH_2R'CH_2OH} \tag{3.5}$$

In addition, methyl ester can be hydrogenated to form aldehyde and then fatty alcohol. Wax ester is another major byproduct. It is formed by esterification of methyl ester with fatty alcohol. Regarding the fatty alcohol production, the main side products are wax ester and alkane; therefore, the separation of side products and the selection of catalyst are important for fatty alcohol production.

3.3.2 Fatty alcohol production process

Esters of fatty acid are converted into fatty alcohols via a hydrogenation process in the presence of heterogeneous catalysts. Figure 3.4 shows a fatty alcohol production process. Methyl ester is compressed and heated until the pressure is 200-300 bar and the temperature is 250-300 ^{o}C, then it is hydrogenated with compressed hydrogen in a packed reactor. Since the hydrogenation is an exothermic reaction, the reaction temperature is increased, causing the formation of hydrocarbons, as an undesired side reaction. The products are cooled down to separate light components from liquid product phase. Excess hydrogen which is separated can be recycled into the hydrogenation reactor while the liquid products are sent to methanol separation. After removal of the methanol, the crude fatty alcohol still contain 2-5% of unreacted ester. It can be removed by addition of alkali to form soap, which remains in the bottom of the distillation column. Soap formation can be separated from unreacted methyl ester by water washing. The specification of fatty alcohol is 99.5 wt.% of purity (Lurgi, 2001).

In general, the hydrogenation of methyl ester can be carried out by different approaches such as gas phase hydrogenation, suspended hydrogenation and fixed bed hydrogenation. For gas phase hydrogenation, methyl ester is vaporized and reacted with compressed hydrogen in gas phase under the presense of catalyst (0.3 wt.%.) at temperature of 250-300 ^{o}C and pressure of 200-300 bar. This process requires the high ratio of hydrogen to methyl ester (500:1) to obtain the 99% yield of fatty alcohol.

For suspended hydrogenation, methyl ester and hydrogen are fed into a catalyst-suspended reactor. Operating conditions are similar to the gas phase hydrogenation; however, the amount of catalyst used is about 0.4-0.7 wt.%. The feed stream of methyl ester is mixed with catalyst in form of powder. In this process, the final crude fatty alcohol contains 2-5% of unreacted methyl ester. Due to the over hydrogenation of the fatty alcohol, hydrocarbons up to 2-3% are formed.

For fixed bed hydrogenation, the conversion of the methyl ester into fatty alcohol is almost quantitative with a very low formation of hydrocarbons; therefore, the quality of the crude fatty alcohol obtained from the fixed bed hydrogenation is better, with a lower hydrocarbon and lower saponification values. The catalyst consumption of the fixed bed hydrogenation is 0.2-0.3 wt.%, which is lower than the suspended hydrogenation process.

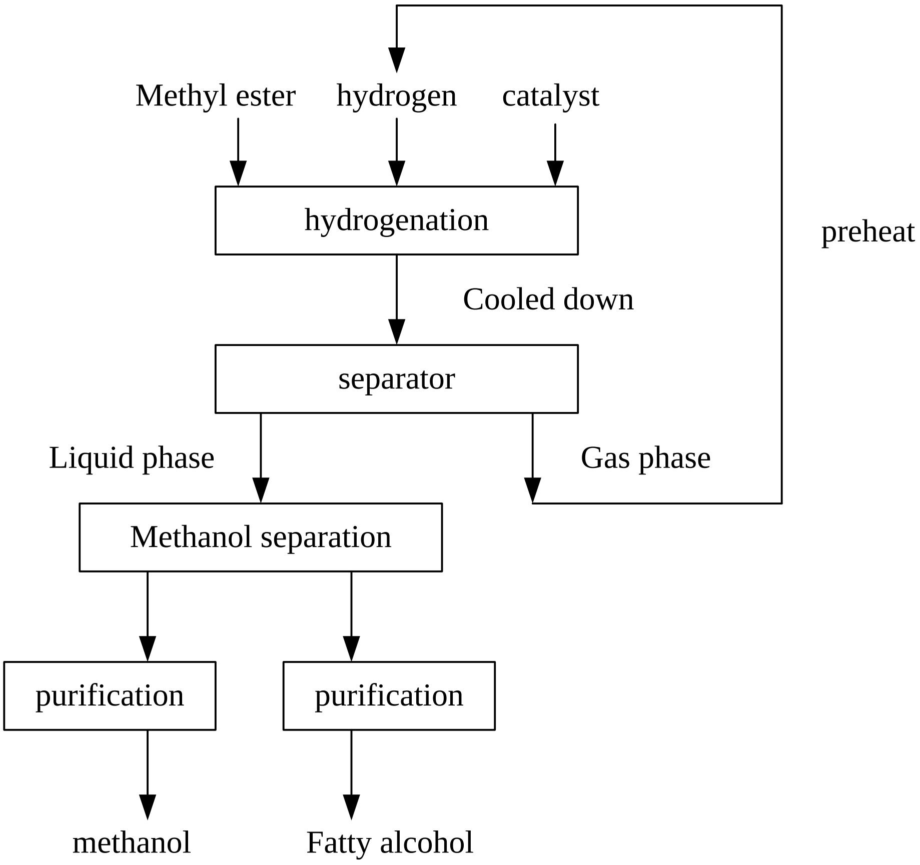

Fig. 3.4 Fatty alcohol production process.

3.4 Process design synthesis (Dimain et al., 2008)

Process design synthesis is an important design to determine the optimal design such as technic, economic and sustainable process. Therefore, there are many approach that proposed for design an optimum chemical process. The starting point of all approaches is to define problem that produce to desire a product. Then flowsheet structure given by reactor and separation systems is drawn. The optimal design is determine in terms of criteria such as economic indicators (Value added, net present value and pay-back period), and sustainable indicators (Material intensity, energy intensity, water comsumption).

The classification of approaches are roughly as:

- Heuristic-based methods
- Thermodynamic analysis methods
- Optimization methods

3.4.1 Heuristic based methods

Most of heuristic approach are the results of fundamental studies rather than mathematic algorithm. For example, process synthesis by hierarchical approach.

The classical hierarchcal approach have been proposed by Douglas (1988) in step by step as followed such as input information, number of plants, input/output structure and connection of plants, recycle structure, separation systems of simple plants and energy integration.

For separation system, phase split between vapor phase and liquid phase is consider first. For example, flash drum is used to remove the vapor stream from liquid streams. Centrifuge or filter is used in case of the separation of mixture liquid and solid. While decanter separates two liquid phase. Mass separation agent is sometimes needed for phase split; however, it is difficult to recover and treatment. Then vapor and gases are recovered to the system. The purpose of vapor recovery is to recycle valuable components from exit gas by using gas absorber, adsorption and membrane.

Liquid-separation system by separating products from liquid mixtures is further considered. For example, if relative volatility is greater than 1.5, distillation column is suitable for separation. However, if relative volatility is less than 1.1, other equipments should be considered. Distillation column is not suitable for separation in case of azeotrope formation. The classical approach is shown in fig. 3.5

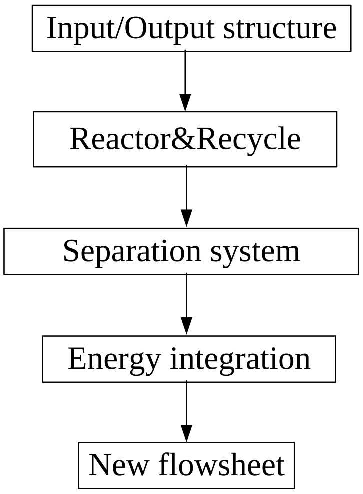

Fig. 3.5 methodology for heuristic method

However, Dimian et al. (2008) proposed the improvement of classical approach which have more efficient. This approach focused on reactor/separation and recycle structure. It is the most important of conceptual design because side reactions or formation of impurities are considered. Bifurcation analysis is used for rigorous analysis. Excess reactants should be recovered because there are several advantages. For example, conversion is improved for equilibrium reactions. The rate of heat and mass transfer inside reactor are increased. The formation of undesired byproducts is eliminated. Energy saving should be considered without affecting neither the chemical reactor nor the structure of recycle. For separation system, near optimum sequencing of separation is determined. The ranking of separation techniques is based on characteristic property amoung the components of a mixture.

3.4.2 Optimization methods

A process synthesis problem can be formulated through mathematical problem. The objective of this method is the optimization of an objective function such as economic cost, waste and energy consumption with subject to constaints. The problem may include non-linear system.

$$F_{obj} = \min\ f(x) \tag{3.6}$$

s.t.

$$h_1(x) = 0 \tag{3.7}$$

$$h_2(x) = 0 \tag{3.8}$$

$$l_1 \le g_1(x) \le u_1 \tag{3.9}$$

Where x is variables such as flowrates, conditions and design variables. $h_1(x)$and $h_2(x)$ are equality constraints such as mass balance, energy balance $g_1(x)$is inequality constraints such as process design specification.

3.4.3 Thermodynamic methods (Jakland and Gani, 1995)

Chemical properties and physical properties are important to select separation techniques. The information of properties such as chemical formula, molecular weight, normal boiling point, freezing point, liquid density, water solubility and critical properties are needed because properties of components related to separation. For example, boiling point and vapor pressure are related to flash operator and distillation column. For thermodynamic insight approach, Jakland and Gani (1995) have been developed. A separation task involves a binary separation or multicomponent separation. The important concept of this method is the properties of key components; therefore, information of pure components properties and separation techniques should be available. Binary azeotrope and ratio of properties of all binary pairs shown in equation (3.10).

$$r_{ij} = \frac{p_{A,j}}{p_{B,j}} \tag{3.10}$$

When subscript A and B is two components of all binary pairs.The binary ratio will show the possible of separation technique. $p_{A,j}$ is the properties of component A that is higher value than the properties of component B

3.5 Distillation design based on driving force technique

The driving force as defined by Gani and Bek-Pederson (2004) is given in equation 3.11,

$$F_{ij} = y_i - x_i = \frac{x_i \beta_{ij}}{1 + x_i(\beta_{ij} - 1)} - x_i \qquad (3.11)$$

Where F_{ij} is driving force for component i

β_{ij} is the relative separablility factor for component i with respect to property (or separation technique)

x_i is the liquid phase composition of component i

y_i is the vapor phase composition of component i

According to the equation 3.11, driving force is defined as the difference in composition. Note that all the component indices are in principle with respect to component k in the binary pair. The relative separablility factor depends on temperature, pressure and external factors such as resistance to mass transfer and heat transfer. From equation 3.11, it is clear that as relative separablility approaches 1, the driving force approaches zero; therefore, separation by distillation becomes easier as the driving force moves towards 1 while it becomes more difficult as driving force moves towards 0. For azeotropic mixtures, the driving force becomes zero at the azeotropic point; therefore, separation beyond the azeotropic point is infeasible in a conventional distillation column. For non-azeotropic mixtures, the driving force approaches zero only at the pure component. The plot of driving force versus x_i or y_i is shown in figure 3.6. According to the figure 3.6, as the location of the feed point on the D_x-D_y line is determined at the largest driving force, the corresponding minimum reflux and reboil ratios are also determined from slope BD. Gani and Bek-Pedersen (2004) have already shown how the driving force diagrams with respect to relative volatility. Driving force diagrams can be used for near optimal of single distillation column design and sequence of distillation columns. The driving force technique can be also applied with azeotropes in the multi-component mixtures by combining with other separation techniques.

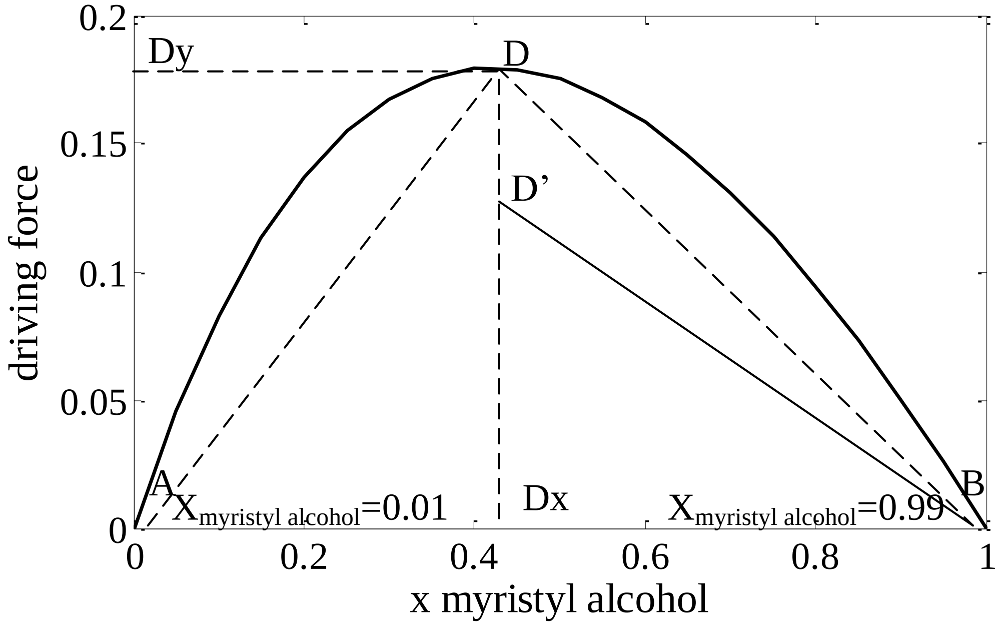

Fig 3.6 Driving force diagram of myristyl alcohol and cetyl alcohol

This algorithm solves the mixture of two products in a distillation column with the optimal N stage. The stepwise is following:

(1) Select the two key components as a binary key component, then generate vapor – liquid diagram of this key component.

(2) Compute the driving force curve by using the equation and plot driving force as a function of x_i.

(3) Locate the point D_x on the x-axis in the figure that corresponds to the largest driving force. In case of an azeotrope, rescale the x-axis and locate the point D_x between the two points (two points are azeotopic point and the bottom/top product point)

(4) Specify composition of products at driving force diagram (point A and B)

(5) Calculate the minimum reflux ratio from slope BD

(6) Determine whether rescaling needs to be applied. If condition 1 or 2 is satisfied, scaling is needed and go to (7) otherwise go to (8). The both conditions are followed in table 3.3.

(7) If condition 1 is satisfied go (7.1) else go (7.2).

(7.1) If condition 1a is satisfied, relocated N_F by 10% up in the column. Else condition 1b is satisfied, relocated N_F by 10% down in the column.

(7.2) If condition 2a is satisfied, relocated N_F by 10% down in the column.

Else condition 2b is satisfied, relocated N_F by 5% down in the column.

Else condition 2c is satisfied, relocated N_F by 5% up in the column.

Else condition 2d is satisfied, relocated N_F by 10% up in the column.

(8) Determine the feed stage from equation 3.12

$$N_F=(1-D_x)N \tag{3.12}$$

Where N_F is feed stage location

D_x is the point Dx in driving force diagram

N is total stage

Table 3.3 Condition to design the single distillation column (Bek-Pederson and Gani, 2004)

Condition 1	Condition 2
(a) $x_{HK,F} \rangle 0.8$ and $D_x \langle 0.7$	(a) $[(1- x_{LK,D})/(1- x_{HK,B})] \langle 0.01$ and $D_x \langle 0.7$
(b) $x_{LK,F} \rangle 0.8$ and $D_x \rangle 0.3$	(b) $[(1- x_{LK,D})/(1- x_{HK,B})] \langle 0.1$ and $D_x \langle 0.7$
	(c) $[(1- x_{LK,D})/(1- x_{HK,B})] \langle 0.1$ and $D_x \rangle 0.3$
	(d) $[(1- x_{LK,D})/(1- x_{HK,B})] \langle 0.01$ and $D_x \rangle 0.3$

3.6 Economic analysis

The economic calculation based on total capital investment and total production cost is used to determine the suitable process which minimizes total capital investment and total production cost. For economic assessment of each process, the price of chemicals, utilities and materials is necessary to calculate the total capital cost. To calculate the sizes of all the equipment and to estimate the amounts of utilities are first calculated then capital cost is further computed. Then the other cost factors are added and finally economic analysis is carried out.

3.6.1 Total capital investment

Total capital investment is the sum of the fixed capital investment and the working capital which is followed in equation (3.13).

$$\text{Tot. Inv.} = \text{Fixed Cap} + \text{Work Cap} \tag{3.13}$$

Fixed capital cost is divided in two parts which consist of total module cost and auxiliary facility cost. Total module costs are the equipment cost in each process and contingency fee which is 18% of total module cost. Auxiliary facility costs are purchase of land, installation of electrical and water system. Auxiliary facility cost is 30% of total module costs.

For preliminary design calculations, equipment cost is included in total module cost. Guthrie proposed a typical cost module in term of free on board equipment as shown in equation 3.14 to equation 3.15.

For pressure vessel $$BC = C_0\left(\frac{L}{L_0}\right)^{\alpha}\left(\frac{D}{D_0}\right)^{\beta} \tag{3.14}$$

For process equipment $$BC = C_0\left(\frac{S}{S_0}\right)^{\alpha} \tag{3.15}$$

Bare module cost is defined as equipment cost multiply with module factor (MF). Furthermore, total installed cost, updated bare module cost are defined in equation 3.16. Equipment cost and module factor is shown in appendix D.

Total installed cost = BC(MPF+MF-1) (3.16)

Updated bare module cost = UF(BC) (MPF+MF-1) (3.17)

Working capital cost is the capital required to actually operate the plant. Working capital cost consists of raw material, finished products in stock, accounts receivable. Working capital is estimated as 15% of fixed capital cost.

3.6.2 Total production cost

Total production cost is the sum of manufacturing cost (MC) and general expenses (GE) which followed in equation 3.18. Total manufacturing cost is the cost of day to day operation of a chemical plant which consists of direct manufacturing cost, fixed charges and plant overhead.

Tot. Prod. = MC + GE (3.18)

Direct manufacturing cost are raw material costs, operating labor, direct supervision labor (about 10% of operating labor), utilities cost, maintenance (about 6% of fixed capital cost) laboratory charges (about 15% of operating labor), patent and royalty.

Fixed charges are depreciation (about 10% of fixed capital cost), local taxes (about 1.5% of fixed capital cost), insurance (about 0.5% of fixed capital cost). Plant overheads are packaging, medical service, safety and protection, restaurants, salvage, and storage facilities. In this work, plant overhead is neglected.

General expenses consist of administrative costs (about 15% of operating labor or 5% of total product cost), including costs for executive salaries, clerical wages, legal feeds, office supplies and communications, distribution and selling costs (about 10% of total manufacturing cost) and research and development (about 5% of total manufacturing cost).

3.6.3 Profitability Indicators

There are several profitability indicators such as payback period (PBP), return on investment (ROI) and discounted cash flow rate of return (DCFR). In this work, return on investment and net present value are considered while other profitability indicators are not mentioned.

Return on investment is the annual profit divided by the total capital investment which follows in equation 3.19

$$\text{\% ROI} = (\text{Annual Profit/ Tot. Inv.}) \times 100 \tag{3.19}$$

Return on investment does not include time value of money. High return on investment means that this process is better.

Net present value (NPV) or net present worth (NPW) is another criteria for selection the feasible project by estimating project life year. Net present value is computed by summary the each net cash flow at the fixed interest rate (MARR). Net present value equation is shown in (3.20) to equation 3.22

$$PW(i) = \frac{A_0}{(1+i)^0} + \frac{A_1}{(1+i)^1} + \frac{A_2}{(1+i)^2} + \ldots + \frac{A_N}{(1+i)^N} \tag{3.20}$$

$$= \sum_{n=0}^{N} \frac{A_n}{(1+i)^n} \tag{3.21}$$

$$= \sum_{n=0}^{N} A_n (P/F, i, n) \tag{3.22}$$

Where PW(i) is NPV calculated at i

A_n is net cash flow at end of period n

i is interest rate

N is economic life of the project

A_n can be revenue, depreciation and operating costs; therefore, A_n will be positive for revenue and will be negative for depreciation and operating costs. A positive NPV means that income is higher value than outcome; therefore a project that has positive value of NPV is a feasible project while a project is rejected when NPV is a negative value.

3.7 Reactive distillation

Generally, continuous stirred tanked reactor followed by a sequence of distillation column can be used in esterification and transesterification reaction. The flowsheet of this process consists of a reactor followed by a sequence of distillation columns. Ordinary distillation column is required to purity the products. Fig. 3.7 shows the traditional process which consists of a reactor and distillation column.

Process intensification such as reactive distillation has a potential to improve the conventional process because it combines unit operations between reactor and distillation column. Therefore, reactive distillation can be applied for chemical reactions especially, esterification reaction.

Reactive distillation involves simultaneous chemical reaction and distillation in a single vessel. The term reactive distillation is also used for such systems where a catalyst (homogeneous or heterogeneous) is used to accelerate the reaction. Reactive distillation is suitable for the reaction that is equilibrium- limit because products can be removed continuously from the reactants. This is advantage when recovery excess reactant is difficult. In addition, the reduction of investment and operating cost are directed result in this approach.

Both exothermic reaction and endothermic reaction can be used in reactive distillation. The reactive distillation is attractive when exothermic reaction occurs because the heat reaction releases. Furthermore, the reactive distillation is very attractive when the reactants are less volatile than products. If the reactants are very volatile, the large internal flow is needed to keep the reactant in liquid phase. The reactive distillation is still attractive option for endothermic reaction because the products are removed. It overcomes the unfavorable reaction equilibrium.

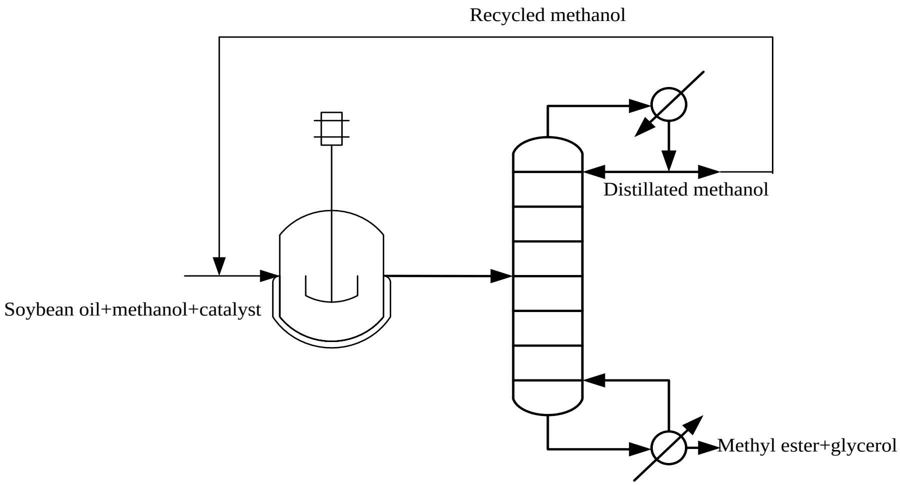

Fig.3.7 conventional process of biodiesel production

3.7.1 Reactive distillation configuration

A conventional process configuration involves two steps of chemical reaction, and subsequent separation. In the chemical reaction step, reactants are brought into one or more reactors. The stream leaves the reactor, then goes into separation step. This step separates unconverted reactant from the products. The unconverted reactants can be recycled to the reaction step to reduce the amount of fresh reactants. At least two separation units are required to separate high purity products. Distillation is used for the separation step.

A conventional process configuration is presented in Fig.3.7 where a distillation is used for separation. The reactive distillation is double-feed reactive distillation configuration as shown in fig. 3.8. The reactive distillation divides into three sections. The first section is reactive section, which is in the middle section of the reactive distillation column. Other sections are rectifying section, and stripping section. Rectifying section locates above reaction section. Stripping section locates below reaction section. Rectifying stages prevent loss of products, and recycle unconverted reactants back to the reaction section. The stripping stages remove the products from the reaction to shift the reaction forward, and purify the products.

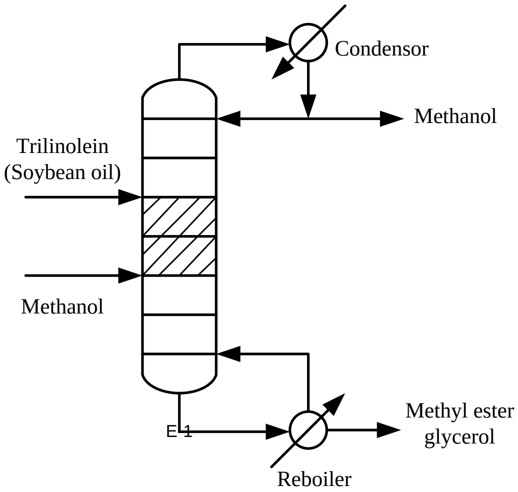

Fig.3.8 Double-feed reactive distillation

3.7.2 Advantage of reactive distillation

There are many advantages in the reactive distillation by following

1. Reactive distillation technology is a reduction in capital investment because two process steps can be carried out in one unit. Reactive distillation technology leads to lower costs in piping, pumps and instrumention.

2. Reactive distillation increases the conversion by removing the products and recycling the reactants. Increasing conversion gives benefit in reduce recycle cost.

3. It is appropriate for exothermic reaction, because the heat generated by the reactions reduces the reboiler duty. Although endothermic reaction requires more reboiler duty, and exhibit no large energy saving. There are no restrictions to the application of reactive distillation.

4. Selectivity for desire product is improved because reactive distillation removes one product and reduces side reactions. The sequential reactors are lowered.

5. The reaction can be carried out completely and achieve a high conversion. This is advantageous when recovery of the excess reagent is difficult because of azeotrope formation.

6. Reactive distillation avoids azeotrope. When the products are a mixture of species form several ordinary azeotropes in nonreactive mixtures. Reactive distillation conditions can allow the azeotropes to be reacted away in a single vessel.

7. Amount of catalyst is significantly reduced.

3.7.3 Application of reactive distillation

The production of methyl acetate by using reactive distillation is a classical example. Many researchers develop for the design, synthesis and control. Experimental data is reported in many configurations. Huss et al. (2003) developed the synthesis of methyl acetate and compared the experiment and math model. The design was provided two feed where was acetic acid is fed near the top of column, and methanol is fed the bottom of column. The effect of reflux ratio on the number of reactive stages was studied in different column pressure to find the optimum reflux ratio.

Steinigeweg et al. (2002) were investigated the synthesis of normal-butyl acetate by using reactive distillation. They were compared the result of experiment and simulation. From the experiment, the conversion could be reached 98.5% with normal-butyl acetate purity of 96.9%. The operating conditions such as reboiler duty and total feed rate were varied to find the affection. The simulation was used to determine the influence of design parameters such as feed location, the number of reactive and non reactive stages. In addition, the design of butyl acetate production was developed. The reactive distillation with pre reactor can make higher conversion than reactive distillation without pre reactor.

3.7.4 Design of reactive distillation

There are three types of design of reaction distillation. The first way is heuristic method that is based on Fenske-Underwood equation. The second type is optimization method and the last type is element based method.

3.7.4.1 Heuristic method

Heuristic method is based on Fenske-Underwood equation to determine the number of stages and reflux ratio. Fenske equation is used to determine the minimum number of stages. Underwood equation is used to determine the reflux ratio that divided into 2 classes. The first class is that all components distribute at the top and bottom of column. The second class is that one component or other components can be obtained at the top of column. When reactive stages are located at the middle of column. The stages that below the feed stream is stripping stages while the stages that above the feed stream is rectifying stages. Reactive zone height is depended on catalyst mass, catalyst density and column diameter. In this method, the bottom product and top product are specified and reflux ratio is 20% of minimum reflux ratio. Fenske-Underwood equation are shown in equation 3.23-3.26.

Fenske equation for theoretical stages

$$N_{\min} = \frac{\log\{[(x_{i,N+1})/x_{i,1}][x_{j,i}/(x_{j,N+1})]\}}{\log \alpha_{i,j}} \tag{3.23}$$

Underwood equation

Class 1

$$L_{\infty,\min} = \frac{L_F[(Dx_{LK,D})/(L_F x_{LK,F}) - (\alpha_{LK,HK})_F (Dx_{HK,D})/(L_F x_{HK,F})]}{(\alpha_{LK,HK})_F - 1} \tag{3.24}$$

$$R_{\min} = L_\infty / D \tag{3.25}$$

Class 2

$$\sum_i \frac{(\alpha_{i,r}) Z_{i,F}}{(\alpha_{i,r}) - \theta} = 1 - q \tag{3.26}$$

$$\sum_i \frac{(\alpha_{i,r}) x_{i,D}}{(\alpha_{i,r}) - \theta} = 1 + R_{\min} \tag{3.27}$$

3.7.4.2 Optimization method

Optimization method is based on mixed-integer nonlinear programming (MINLP). Objective function can be the minimization of total annual cost as shown in equation 3.28.

$$F_{obj} = \min\ f(x) \tag{3.28}$$

When $f(x) = OperatingCost + \frac{CapitalCost}{3}$ (3.29)

Subject to

$$h_1(x) = 0 \tag{3.30}$$

$$h_2(x) = 0 \tag{3.31}$$

$$l_1 \langle g_1(x) \langle u_1 \tag{3.32}$$

Where x is variable such as flow rates, conditions and design variables. $h_1(x) = 0$ is equality constraint that is mass balance. $h_2(x) = 0$ is equality constraint that is energy balance, $l_1 \langle g_1(x) \langle u_1$ is inequality constraint that is product specification.

3.7.4.3Element based method

Element based method such as Mccabe-Thele methods and Lewis Methason's method is used to design reactive distillation and helpful to understand the fundamental insights of reactive distillation columns. In case of multi-component, Lewis Methason's method is preferred to design reactive distillation column. Lewis Methason's method is shown in fig. 3.9 Element in this method is defined as a combination of atom in compounds such as CH_2 or the smallest compound such as

CH_3OH so that atomic balance is satisfied. In addition, element can be defined as the atoms, fragments or radical of molecule. (Perez Cisneros et al., 1996). Components in reactions can be defined in term of element, then element fraction can be determined. The advantage of element based method is that kinetic constants are not required for the simulation.

The selection of the elements

It has been known that element is the partial of molecule or the smallest molecule. The equation 3.33 is to determined the number of element in the system.

$$M = NC - NR \tag{3.33}$$

Where M is the number of element. NC is the number of components. NR is the number of reactions.

The elements are preferably chosen in an identity matrix (AI) that is a lower triangle matrix of dimension MxM. While the rest of formula matrix is matrix AII. The rank of matrix AI is equal to the number of element.

Example 1 $\mathrm{iC_4H_8 + CH_3OH \rightarrow MTBE}$

The number of component is 3. The number of reaction is 1. Therefore, the number of element is 2. The element A is defined as isobutene while the element B is defined as methanol. So the equation in the example is become (3.34).

$$\mathrm{A + B \rightarrow AB} \tag{3.34}$$

Formula matrix A consisting of matrix AI and AII is writen as table .3.4 .

Table 3.4 Formula matrix of example 1

	iC_4H_8	CH_3OH	MTBE
A	1	0	1
B	0	1	1

AI AII

Example 2 $CH_3COOH + C_2H_5OH \rightarrow CH_3COOC_2H_5 + H_2O$

The number of component is 4. The number of reaction is 1. Therefore, the number of element is 3. The element A is defined as CH_2CO while the element B is defined as ethanol. The element C is defined as H_2O. So the equation in the example is become (3.35).

$$AC + B \rightarrow AB \tag{3.35}$$

Formula matrix A consisting of matrix AI and AII is writen as table 3.5.

Table 3.5 Formula matrix of example 2

	CH_3COOH	C_2H_5OH	H_2O	$CH_3COOC_2H_5$
A	1	0	0	1
B	0	1	0	1
C	1	0	1	0

AI AII

Element balance is analogous with mass balance in ordinary distillation column. Element balance around rectifier and stripper is shown in eq 3.36-3.41.

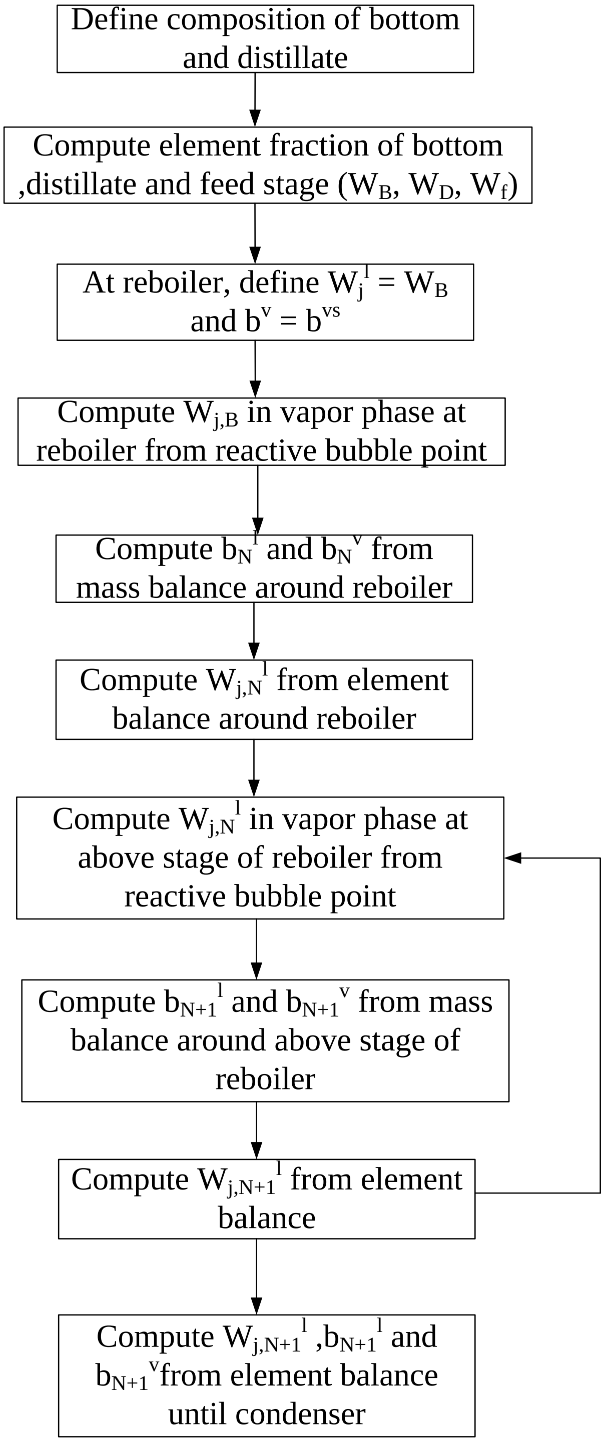

Fig 3.9 Lewis Methason’s method

Element balance

Around column

$$b^F = b^B + b^D \tag{3.36}$$

$$b^F W_j^F = b^B W_j^B + b^D W_j^D \tag{3.37}$$

Rectifying section

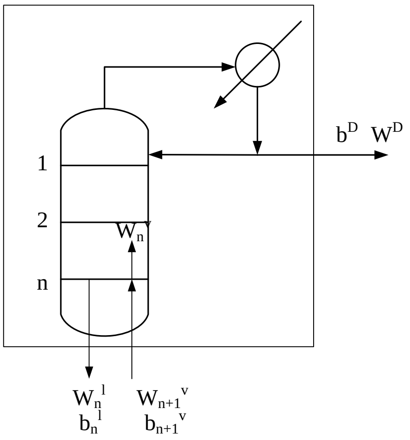

Fig 3.10 Rectifying section

$$b_{n+1}^v = b_n^l + b^D \tag{3.38}$$

$$b_{n+1}^v W_{j,n+1}^v = b_n^l W_{j,n}^l + b^D W_j^D \tag{3.39}$$

Stripping section

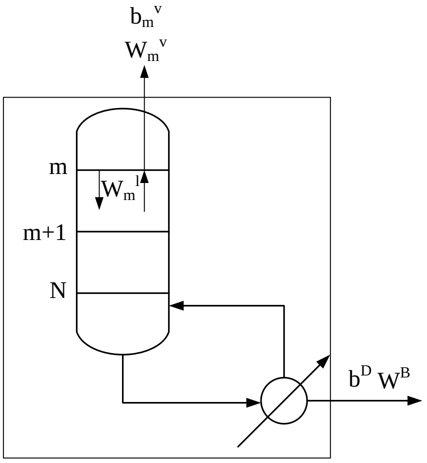

Fig 3.11 Stripping section

$$b_m^l = b_{m+1}^v + b^B \tag{3.40}$$

$$b_m^l W_{j,m}^l = b_{m+1}^v W_{j,m+1}^v + b^B W_j^B \tag{3.41}$$

Where $b^l = L\sum\sum A_{ji}x_i$, $b^v = V\sum\sum A_{ji}y_i$

3.8 Heat integration of reactive distillation

Generally, heat integration is investigated when separation of mixture is difficult because of small difference of boiling points, thus large energy consumption is required. In addition, heat that supplys to reboiler and heat that sinks from condenser are not be reused. Heat integration of distillation can be applied for heat integration of reactive distillation because the configuration is similar. There are several methods to improve thermal efficiency such as thermally coupling reactive distillation column, multi-effect reactive distillation, heat internally thermal coupling reactive distillation, petlyuk reactive distillation, etc.

3.8.1 Multi-effect reactive distillation

There are three types of multi-effect reactive distillation depending on the sequence of column such as feed split multi-effect column, multi-effect direct sequence and multi-effect indirect sequence. The concept is that the difference of pressure within individual column results in different temperature of overhead and bottom of column. Vapor from high pressure column is used as heat source for reboiler of the low pressure of column. For feed split multi-effect column, feed is splitted in a half and sent to each column, The pressure of one column is increased to enhance higher temperature in the top of column. It is necessary to increase temperature of vapor stream at the top of column to be greater than reboiler temperature of low- pressure column. From this concept, the heat is supplied to one reboiler and sinked to one condenser. Heat exchanger between two columns is represented to be condenser for high- pressure column and to be reboiler for low-pressure column. Because feed is cut in a half, vapor stream at the top of high-pressure column is also cut in a half that results in the reduction of heat duty at reboiler. Configuration of feed split multi-effect reactive distillation is shown in fig. 3.12

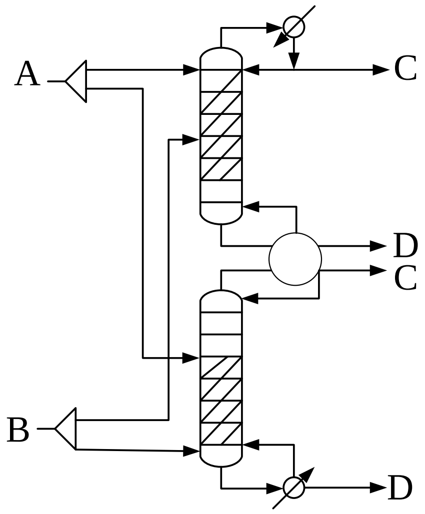

Fig. **3.12** Multi-effect reactive distillation

3.8.2 Thermally coupled reactive distillation

To reduce the energy consumption, thermally coupled column is an alternative heat integration because vapor stream that is higher temperature will transfer heat to liquid stream by direct contact. In addition, the number of reboiler or condenser can be reduced that leads to lower capital cost. Thermally coupled direct sequence column is the thermal coupling of direct sequence of column. That is reboiler of the first column is replaced by thermal coupling of liquid stream from bottom of the first column and vapor stream of the second column. Thermally coupled direct sequence column can become the column with side rectifier. Configuration of thermally coupled direct sequence is shown in fig. 3.13

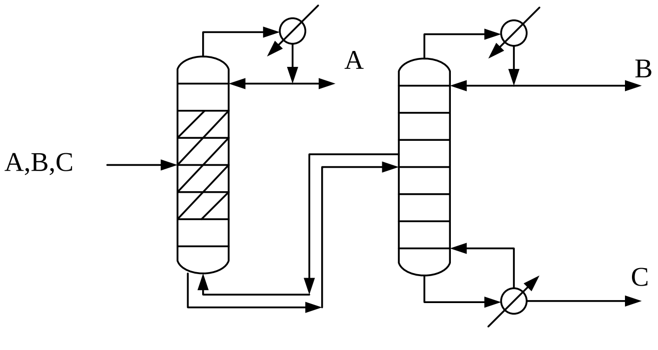

Fig. 3.13 Thermally coupling direct sequence reactive distillation

While thermally coupled indirect sequence is that condenser of the first column is replaced by thermal coupling of vapor stream of the first column and the liquid stream of the second column. Thermally coupled indirect sequence column can be become the column with side stripper. Configuration of thermally coupledindirect sequence is shown in fig. 3.14

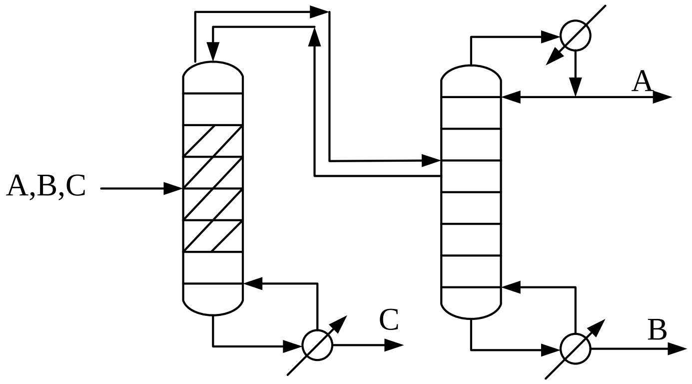

Fig. 3.14 Thermally coupling indirect sequence reactive distillation

Petlyuk column is thermal coupling of prefractionator and main column. Both prefractionator and petlyuk column, the total heat duties and cooling duties are the same. However, petlyuk column requires extra plates to replace condenser and reboiler. According the configuration of petlyuk column, vapor flow at the top of column of prefractionator is sent to the main column. Similarity, vapor flow from the main column is sent to prefractionator at the bottom of column. Liquid flow from main column is sent to prefractionator at the top of column. Liquid flow from prefrationator is also sent to main column. Configuration of petlyuk column is shown in fig. 3.15

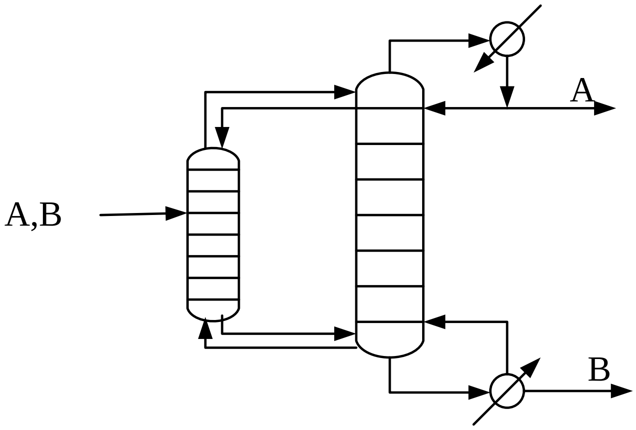

Fig. 3.15 Petlyuk reactive distillation

CHAPTER IV

METHODOLOGY

This chapter is divided into 3 parts. The first part is to propose the methodology for producing two main products plus side products. The methodology will show the step for design and the number of alternative processes is systematically reduced through a screening procedure until only feasible alternatives are obtained. The overview of methodology including synthesis steps such as gathering information (search literatures in Step 2), alternative generation (generation superstructure from available data in Step 3), evaluation of performance from criteria (Screening of alternative in Step 4) is based on Biegler et al., (1997). Then, a simulation of biodiesel production integrated with fatty alcohol production is performed under steady state condition. Economic evaluation is analyzed for the remaining alternatives to determine the best economical process in term of profitability indicator. The second part is to design reactive distillation that combines between chemical reaction task and separation task. An element based method is an interesting design methodology for reactive distillation involving a multi-component system because it spends less computational time. The last part of this chapter involves heat integration of reactive distillation such as internally heat integrated reactive distillation, muti-effect reactive distillation and thermally indirect sequence reactive distillation. The application of the methodology is presented through a case study involving biodiesel and fatty alcohol production in chapter 5.

4.1 Methodology for producing two main products plus side product

The objective of the methodology is to design a chemical process to convert a renewable source to multiple main products with associated side products. The main-steps of the methodology are shown in Fig. 4.1 and fig. 4.2, where the work-flow is structured in terms of steps (0-7) after problem definition. Step by step is following:

Step 1: Define problem

The starting point is problem definition, where the number of available renewable sources, the number of desired main products, the number of side product, the qualities of the main products and the performance criteria for the desired process, among others, is defined as:

Objective:

$$\text{Max and Min} \sum_{i=0}^{n} w_n(F(X,Y)) \tag{4.1}$$

Subject to constraints:

$$h(X) = 0 \tag{4.2a}$$

$$g(X) \geq 0 \text{ (or } < 0) \tag{4.2b}$$

$$\sum_{i=N1_k}^{N2_k} Y_{ik} = 1 \qquad , k = 1, NS \tag{4.3}$$

where F is the performance criteria, X are the design variables (e.g., temperature, pressure and compositions), Y are the binary integer (decision) variables corresponding to the existing streams, h(X) are the set of equality constraints, such as process models (i.e., mass balance equations and energy equations), g(X) indicates the set of process design specifications, $N1_k$ and $N2_k$ indicate the decision variable numbers involved in section k, and, NS is the total number of sections.

Step 2: Search literatures/database

At this step, search of available data (in a database as well as open literature) is made. Information on raw materials, main products, side products, reactions, catalysts, reaction conversion and operating conditions is gathered. The chemical and physical properties of substances existing in the process, such as solubility, vapor pressure, azeotropes, heat of vaporization, boiling point, critical properties and molar volume, are also important for generation of the process superstructure. Information of all available flowsheets are included in the superstructure generation (step 3).

Step 3: Generate superstructure from available data (Jaksland et al., 1995)

Based on all available data from Step 2, the generic superstructure is created as follows:

Step 3.1: Identify all components from reactions

All components in the reaction systems using different types of catalysts are listed. Side products and impurities are also identified.

Step 3.2: Identify the properties of all components

The properties of all components, such as vapor pressure, heat of vaporization, boiling point, critical properties, etc., as well as formation of binary azeotropes between them are collected and used to select unit operations for separation tasks (Jaksland et al., 1995). When the needed component properties are not available or found in databases, the ProPred tool in the ICAS software (Diaz-Tovar et al., 2011) is employed to predict them. For known binary azeotropic mixtures, if information about solvents is available, this is also included in the collected data.

Step 3.3: Find azeotrope of binary mixtures

For the binary pairs of components that may form azeotropes, the azeotrope temperature and composition are determined through VLE based calculations. When the azeotrope is found, use of solvent to separate the desired product is also considered. In general, selection of solvents depends on type of azeotropic mixture, i.e., minimum or maximum boiling azeotropes. In addition, the mixed feed of solvent and the binary mixture should be located in the same distillation region of the desired product (Hostrup et al., 1999) for extractive distillation. Various methods for solvent selection have been reported, for example, Hostrup et al. (1999), Skouras et al. (2005), and, Mitrofanov et al. (2012). In this work, the method and tool of Mitrofanov is employed. For solvent-less alternatives, changing operating pressure to shift the azeotrope is considered.

Step 3.4: Calculate binary ratio of properties

All components are ranked in increasing order for each property and the binary ratios of any property for adjacent components is computed. Repeating this for all properties, the binary ratio matrix of properties for all components is generated. The rows are the binary pairs of components and the columns are the property ratios.

Step 3.5: List the feasible separation techniques of all components

Separation techniques are selected by considering the adjacent binary ratios of properties (Jaksland et al., 1995). Table 1 shows the relationship of the separation technique and component properties.

Step 3.6: Superstructure generation

Based on the information collected, the superstructure is created together with the list of decision variables that will need to be determined. It is noted that process alternatives are generated by considering all separation techniques found feasible through the binary ratio matrix of properties and/or collected data (such as catalyst based reactions).

Table 4.1 Key pure component properties used to select the separation technique (Jaksland et al., 1995)

Separation technique	Separation type	Pure component properties
Absorption	Gas separation	Solubility parameter
Azeotropic distillation	Vapor-liquid separation	Vapor pressure, formation of azeotropes, solubility parameter
Crystallization	Solid-liquid separation	Melting point, heat of fusion at melting point
Distillation	Vapor-liquid separation	Vapor pressure, heat of vaporization, boiling point
Extractive distillation	Vapor-liquid separation	Vapor pressure, heat of vaporization, boiling point, solubility parameter
Flash operation	Vapor-liquid separation	Vapor pressure, heat of vaporization, boiling point
Gas separation membrane	Gas separation	Critical temperature, van der Waals volume
Ion exchange	Liquid separation	Ion charge
Liquid liquid extraction	Liquid-liquid separation	Solubility parameter
Liquid membrane	Liquid separation	Solubility parameter, molar volume, radius of gyration, affinity to carrier
Molecular sieve adsorption	Gas separation Liquid separation	Kinetic diameter, van der Waals volume, polarizability, dipole moment
Partial condensation	Vapor-liquid separation	Vapor pressure, heat of vaporization, boiling point

Table 4.1 Key pure component properties used to select the separation technique (Jaksland et al., 1995) (Cont)

Separation technique	Separation type	Pure component properties
Pervaporation	Vapor-liquid separation	Molar volume, solubility parameter, dipole moment
Stripping	Vapor-liquid separation	Solubility parameter
Supercritical extraction	Liquid-liquid separation	Solubility parameter, critical temperature, critical pressure

Step 4: Screen of alternatives

This step involves screening of alternatives, where process design constraints (see Eq. 2b) are ordered in a hierarchical manner; the computationally easier constraints are considered first. Consequently, as the number of alternatives reduces, computationally more intensive constraints are considered. This step is divided into seven sub-steps as follows:

Step 4.1: Screen the processes by considering only selected raw materials

Criteria for selection of raw materials are availability locally together with the lowest price.

Step 4.2: Screen and reduce the number of synthesis pathway based on phase of feed

If phase of feeds in the reaction is similar, this reaction pathway is selected to avoid the limitation of mass transfer of different phase such as liquid phase/vapor phase.

Step 4.3: Screen and reduce the number of synthesis pathway based on productivity of catalyst(Pham and El-Halwagi, 2012)

In this step, the pathway of reaction is selected when catalyst of each pathway is different. However, if desired products are obtained in different pathway. This step is skipped. For example, the reactions, A can converted to B and B converted to C in the first reaction when catalyst x is used. While A can also converted to D in the second reaction when catalyst y is used. If desired product is C, only one pathway that provides the highest productivity is selected. However, if desired products are B and D, this step is skipped. The selection of pathway in this case, is selected by using other criterias.

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \tag{4.4}$$

$$A \xrightarrow{k_3} D \xrightarrow{k_4} C \tag{4.5}$$

Step 4.4: Screen and reduce the number of synthesis routes based on productivity for each catalyst (Pham and El-Halwagi, 2012)

Since the productivity depends on the used catalysts and operating conditions, this step involves a fast screening process. The processes that give the highest productivity of main products for each catalyst type are only retained; thereby reducing the number of alternatives. In this step, the tasks involving reactions are considered.

Step 4.5: Screen and reduce the number of synthesis routes based on attainable region (AR) (Biegler et al., 1997)

If there are complex reactions (parallel reactions or series reactions) for one catalyst and a desired product is obtained in the complex reactions, a route of reaction is selected by construction attainable region. This step requires kinetic parameter (k constant). For example, the reactions, B is desired product. However, B can continuously converted to C. Amount of maximum B is obtained from attainable region.

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \tag{4.6}$$

The step of construction attainable region is below:

- Write mass balance for Plug flow reactor and CSTR.

- Provide the concentration of desire product as a state variable.
- Generate graph between concentration of raw material and desired product with space time for PFR and CSTR.
- At the same space time, data of concentration of raw material and desired product are collected.
- Generate graph between concontration of raw material and desire product for PFR and CSTR.
- Combine the graph between concontration of PFR and CSTR.
- Find the highest concentration of desired product. It means that concentration of raw material is required at the highest concentration of desired product. If amount of raw material is too much, the divider is required.

This step is eliminated when kinetic equations are ignored.

Step 4.6: Reduce the alternatives with respect to the highest driving force of separation process (Jaksland et al., 1995)

Separation techniques for various separation tasks are screened. For further reduction of alternatives, the adjacent binary pair corresponding to the highest ratio of properties computed in Step 3 is selected for the first separation task (Jaksland et al., 1995). Alternatively, the separation task could also be selected by considering the largest driving force of separation process from the further adjacent binary ratio. This step is repeated until the desired products are obtained. At the end of this step, the number of alternatives is reduced and the reduction of superstructure for the highest separation task is carried out. It is noted that when the binary ratios for vapor pressures and boiling points are the highest but the binary pairs also form azeotropes, solvent-based separation tasks are included in the list of feasible alternatives.

Step 4.7: Screen the alternatives in terms of limitations of the separation technique (Hostrup et al., 1999)

In this step, the limitation of the separation technique is taken in account to reduce the process alternatives. For example, for an azeotropic binary pair, conventional distillation is removed because it cannot separate azeotropic mixtures. Separation by adsorption is removed if the temperature of operation is too high for the known adsorpbents that are usually quite sensitive to the temperature, or, a suitable adsorbent could not be found. Membrane-based separation is limited by limited flux and fouling problems.

4.1.5 Step 5: Process simulation

A large number of alternatives are eliminated from the above screening steps. The remaining alternatives that include feasible unit operations, such as reactor, flash operator, distillation and decanter within flowsheets, are simulated by using an appropriate process simulator (such as, ASPEN, PRO/II, HYSYS, ChemCAD or ICAS). Operating conditions, such as reaction temperature and pressure (determined in Steps 3-4), and other information, such as the reaction conversion, the amount of catalyst and the desired product specification (collected in Step 2), are used for these simulations. Table 4.2 lists the variables to be specified for each unit operation. A rigorous simulation is required in this step; therefore, thermodynamic model selection is also important.

In this study, a driving force based technique is used to design distillation columns by considering the energy consumption and total capital cost and using the reverse approach, the number of stages and the feed location that matches the driving force target are determined. The driving force of the two key components is defined as (Bek Pederson & Gani, 2004):

$$F_{ij} = y_i - x_i = \frac{x_i \beta_{ij}}{1 + x_i\left(\beta_{ij} - 1\right)} - x_i \tag{4.7}$$

where F_{ij} is the driving force, y_i is the composition in the vapor phase, x_i is the composition in the liquid phase and β_{ij} is the relative volatility of components *i* and *j*.

Table 4.2 Process variables and specifications needed for simulation

Unit operation	Process variables	Specification
Reactor (stoichiometric conversion)	Temperature, Pressure, Flow rate	Reaction conversion
Flash separator	Temperature, Pressure, Flow rate	Recovery of light key product (0.9)
Distillation (one feed, two products)	Reflux ratio, Feed composition, Number of stage, Feed stage, Flow rate	Recovery of light key (0.99) and heavy key (0.99) products
Decanter	Temperature, Pressure, Flow rate	

Step 6: Analyze process (two dimensional metric)

4.1.6.1 Perform economic analysis (Blank and Tarquin, 2012)

Remaining processes are analyzed based on an economic indicator. Since a net present value (NPV) gives the present value of all payments and provides a basis for process comparison, it is used as an economic criterion to find the best economic process. The Guthrie’s modular method is used to evaluate the capital costs of equipment.

It is noted that the proposed design methodology is generic in nature (can handle any number of main products); flexible (method of solution can be changed through another order of constraints, including all at the same time). Note, however, in this paper the option for two main products and a fixed hierarchical order for constraints is used.

4.1.6.2 Determine environment indicator (El-Halwagi, 2012)

Mass intensity is the use of feedstock that impact on feedstock consumption and discharge of waste.

$$MassIntensity = \frac{kg_{raw} - kg_{product}}{kg_{product}} \qquad (4.9)$$

From sub-step 6.1 and 6.2, weight of objective function between economic and environmental should be fixed. If weight of objective function of economic is equal to 1, it means that only economic is concerned. While weight of object function of enviromental is equal to 1, it implies that only enviromental is concerned. In this work, multi-objective optimization between economic and environment are aggregrated into a single objective optimization by using AHP (Analytic Hierarchy Process). The index of net present value (NPV) and mass intensity are normalized so they can compare at the same scale. However, it has been known that high NPV give better performance while low mass intensity give better performance. AHP score is shown in equation 4.10

$$AHP = P_{econ} \times weight + P_{env} \times weight \tag{4.10}$$

Where P_{econ} is normalization of NPV, P_{env} is normalization of environment. In this work, the weighting of economic and environement is 0.82 and 0.18, respectively. These values are suggested by Chen et al. (2002)

Step 7: Combine the reaction task and separation task

For the best alternative process that is obtained from Step 6, a process intensification option involving the reaction and separation tasks is further considered. In general, there are many types of process intensification, such as reactive crystallization, reactive flash, reactive distillation, reactive absorption, etc. The objective here has been to consider process intensification only when reaction followed by separation could be combined into one operation. It is beyond the scope of this paper to develop a comprehensive intensified process. However, integration of the method proposed by Lutze et al. (2012) with this methodology could be considered in future work. In this study, a reactive distillation in which the reaction and separation occur at the same time is employed to improve the designed process by shifting the equilibrium reactions (Georgiadis et al., 2002). Fig. 2 shows the criteria used to determine whether a combination of separation and reaction tasks should be performed by using the reactive distillation. Table 4.3 summarizes tools and methods that are employed in each step of the design methodology.

Table 4.3 Summary of tools and methods used in the design methodology

Step	**Tools**	**Methods**
1. Define problem	-	Define the objective function of problem
2. Search literatures/database	Available data reported in journals and open sources	
3. Generate superstructure from available data	- Thermodynamic insights - CAPEC databases of oil - ProPred - Simple mass balance	- Calculate adjacent binary properties ratio - Azeotrope information - List the alternative separation techniques - List the possible biodiesel production with different catalysts and fatty alcohol production - Generate superstructure
4.1 Screen the processes by considering only selected raw materials	Price of raw materials	Select interesting raw material
4.2 Screen and reduce the number of synthesis pathway based on phase of feed	Phase of feed at pressure and temperature	Select the pathway that same phase of feed
4.3 Screen and reduce the number of synthesis pathway based on productivity of catalyst	Simple mass balance	Calculate productivity (kg of mass product/kg of mass oil)

Table 4.3 Summary of tools and methods used in the design methodology

Step	**Tools**	**Methods**
4.4 Screen and reduce the number of synthesis routes based on productivity for each catalyst	Simple mass balance	Calculate productivity (kg of mass product/kg of mass oil)
4.5 Screen and reduce the number of synthesis routes based on attainable region (AR)	Kinetic rate, mass balance of PFR and CSTR	Generate attainable region
4.6 Reduce the alternatives with respect to the highest driving force of separation process	Thermodynamic insight	Choose the separation technique with the highest driving force.
4.7 Screen the alternatives in terms of limitations of the separation technique	LLE	
5. Process simulation	- Driving force diagram - Process simulator	Use the driving force method to obtain the optimum conditions of separation process such as reflux ratio, optimum total stages and feed location which minimize the energy consumption

Table 4.3 Summary of tools and methods used in the design methodology

Step	**Tools**	**Methods**
6.1 Perform economic analysis	- Cost of raw materials, capital cost and operating cost - Product prices	- Calculate the profitability (NPV) - Perform sensitivity analysis of NPV with respect to raw material price and product prices. - Determine the fraction of product one to produce product two which gives the highest profitability.
6.2 Determine environment indicator	- total mass of raw material	- Calculate mass intensity
7 Combine reaction task and separation task		

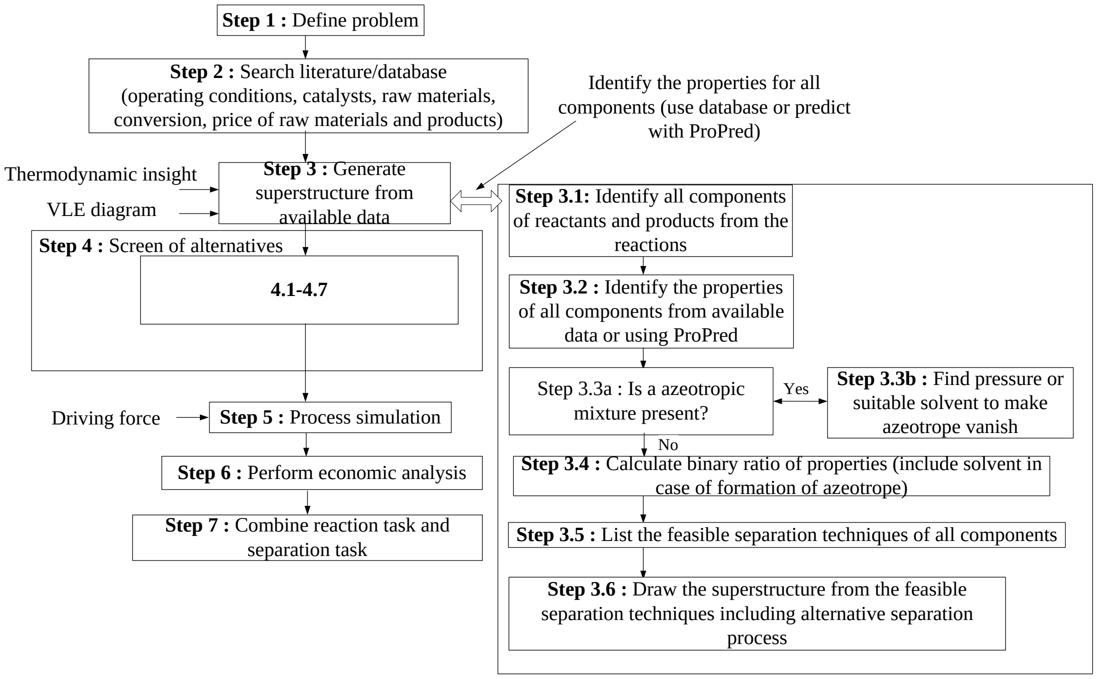

Fig 4.1 Design methodology of the process producing two main products plus side products.

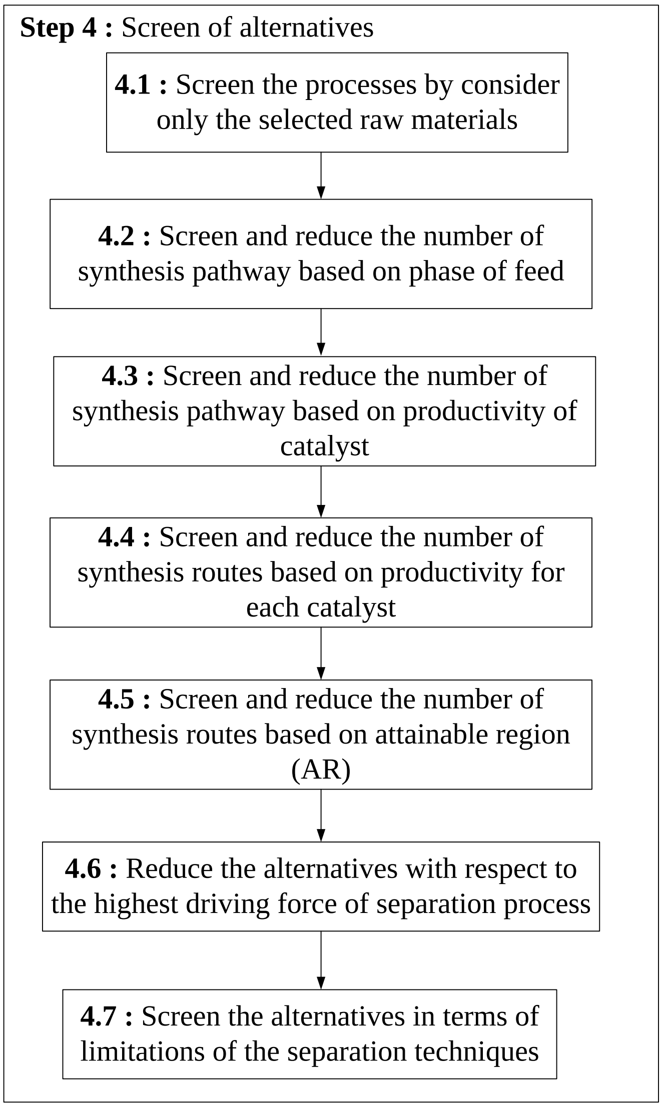

Fig 4.2 Detials of screening step of design methodology of the process producing two main products plus side products.

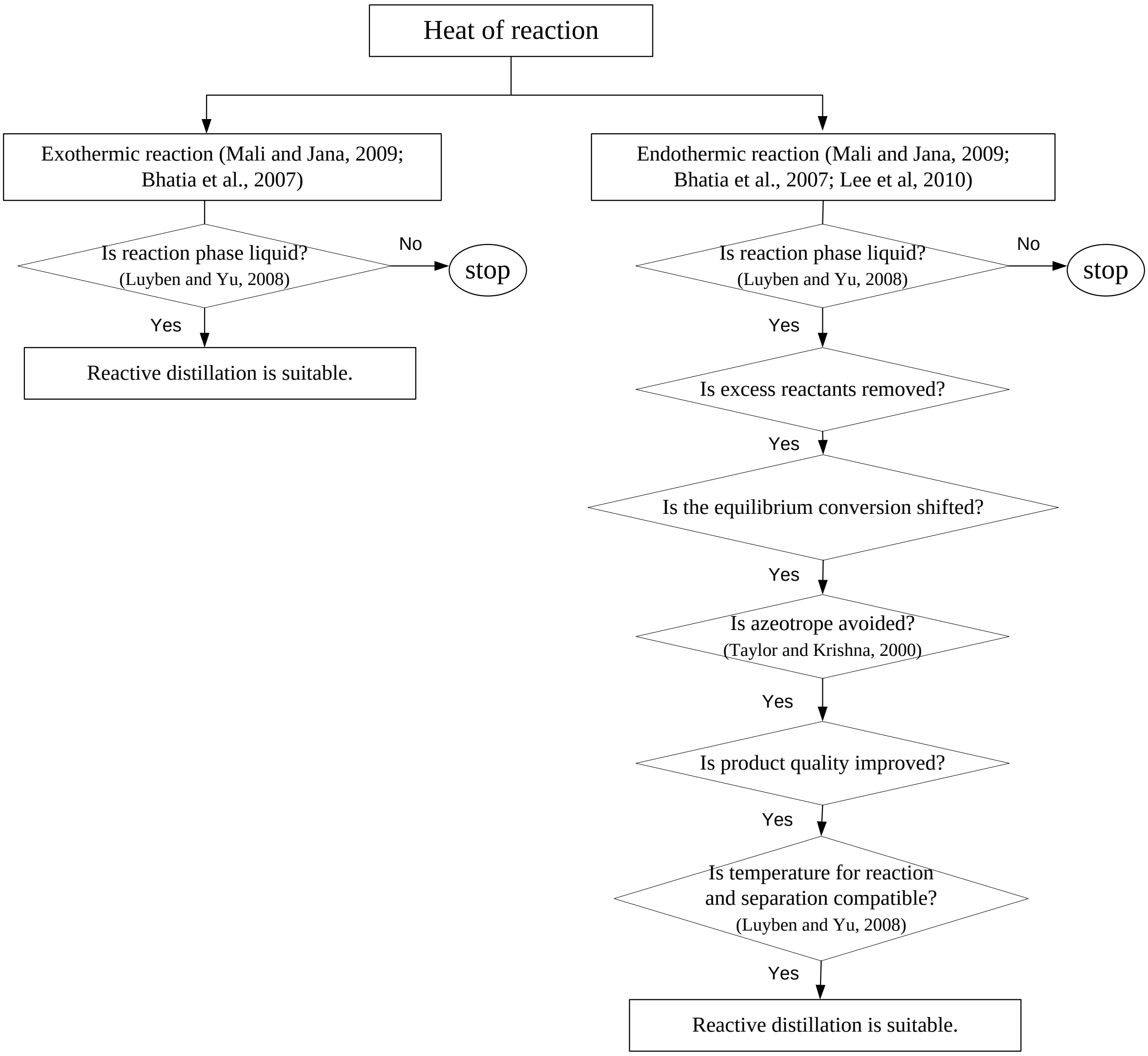

Fig 4.3 Criteria for choosing a reactive distillation.

4.2 Design of reactive distillation

In this part, a new methodology based on hybrid method between element based method and heuristic method is proposed for a synthesis and design of reactive distillation. The element-based method is modified and implemented to design the reactive distillation. A reactive phase diagram is constructed and used to design and analyze the reactive distillation with a multi-component mixture. This methodology is flexible in any case of design reactive distillation. The application of design methodology is presented through a case study involving biodiesel production from pure palm oil and waste cooking palm oil. Because biodiesel production is a special case so some steps of the design need to be added. The reactive distillation is flexible for biodiesel production that is different feed resource. Further, the effect of various operating parameters on the performance of the reactive distillation for biodiesel production is investigated. Fig 4.4 shows the methodology to design reactive distillation based on element method.

Step1: List all components and define product specification.

The first step is to define the reactions, components in the system and quality of products such as mole fraction at the top of column and at the bottom of column. Information on product bottom flow rate boiling point of components and reflux ratio is gathered. This information is important for further analysis.

Step 2: Calculate binary ratio of boiling point

The boiling point of all the components is ranked increasing order and then, the boiling point ratios of adjacent components are computed. This step can find the component at the top and bottom of reactive distillation. The adjacent binary pairs with the highest ratio of boiling point is key components such as light key component and heavy key component. Reactive distillation removes light key component from heavy key component by driving light key component at the top of column.

Step 3: Define element and compute the element fraction in vapor phase

Next, the smallest compound of substances in the system, called element, is defined from formula matrix. The element fraction in vapor phase is computed to identify the separation task. Element fraction can obtained from ICAS-PDS (Daza et al., 2003).

Step 4: Identify the separation task

The criteria for selection the separation task is element fraction in vapor phase. Reactive distillation depends on separation task such as separation of products and separation of excess reactants. The criteria for selection the separation task is element fraction in vapor phase that is computed in Step 3. This step divides into 2 separation tasks.

Separation task is to separate excess reactant

In this case, element fraction in vapor phase is closed to one. The separation task is to separate excess reactant. It means that the reactive distillation cannot separate light product from heavy product so only excess reactant is removed in the distillate stream. Reactive flash operator is preferred to use instead of reactive distillation. However, amount of desire product can be lost in excess reactant stream due to percentage of recovery. Reactive distillation with lower the number of stages is preferred.

Separation task is to separate products

In this case, element fraction in vapor phase is less than 0.99. It means that the reactive distillation can separate light products from heavy products. The suitable number of reactive stages depends on operating conditions that increase the performance of reaction task and separation task. Therefore, the suitable number of reactive stages can be determined from Lewis Methason’s method that is specified composition of bottom product when reflux ratio molar flow rate of distillate and bottom column are known.

Step 5: Determine operating parameters (Pérez- Cisneros et al., 1997)

The number of reactive stages is determined by using Lewis - Methason’s method. The starting point of this method is to define mole fraction at the bottom of column from a ternary phase diagram. Overall mass balance and element mass balance are computed. Reactive bubble point algorithm is also computed to determine mole fraction of all components in all stages from the bottom of column to the top of column until product specification is met.

Step 6 : Process simulation

A rigorous simulations using a process flowsheet simulator such as, ASPEN, PRO/II, HYSYS, ChemCAD or ICAS) are performed to determine suitable design and operating parameters.

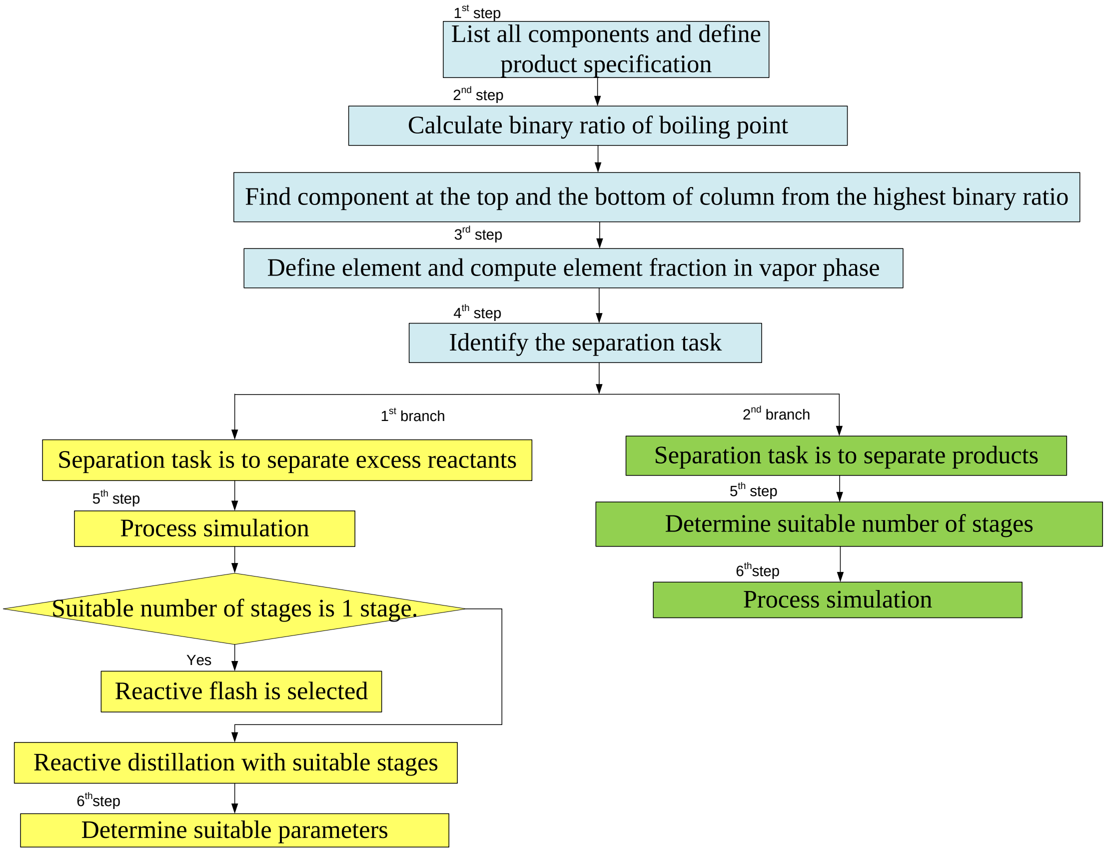

Fig 4.4 methodology for design reactive distillation.

4.3 Design of Heat integration of reactive distillation

Not only heat integration is investigated when separation of mixture is difficult because of small difference of boiling points, but also high operating conditions such as temperature and pressure are operated. Thus large energy consumption is required. Although the heat integration of conventional and reactive distillation columns has been studied, a limited works have focused on a systematic design of the heat-integrated reactive distillation. This study presents a systematic design of a heat integrated reactive distillation through a case study, biodiesel production from waste cooking oil. The selection criteria for different configurations of reactive distllation with heat integration is also considered. In the proposed methodology, a full set of alternatives of the heat integrated reactive distillation is generated. The number of alternatives is reduced by considering a sequence of contraints, such as purity, properties of the product mixture, and total annual cost, until a feasible one is obtained.

Step 1 : Define problem for heat integrated reactive distillation

The starting point is problem definition, where the number of available renewable sources, the number of desired main products, the qualities of the main products and the performance criteria for the desired process is defined. Here, the minimization of a total annual cost is set as a target for process design.

$$\min F_{obj} = f\left(X, Y, d\right) \tag{4.11}$$

Subject to

Operational constraint

$$g,_{LB} \leq g(X) \leq g,_{UB} \tag{4.12}$$

Process model

$$h_1(X) = 0 \tag{4.13}$$

Product specification

$$P = 99.5\% \tag{4.14}$$

Where X is vector of process variable, d is equipment parameter

The step of methodology is shown in fig. 4.5 that is to design heat integrated reactive distillation. Full sets of alternatives in problem formulation that is a complex problem. It is decomposed through the constraints in sequential manners when the easier constraint is considered first while more intensive constraints are considered later. The methodology includes algorithm and sub algorithm. For the first step, objective function is defined to improve the reactive distillation process by decreasing the heat duty of reboiler and condenser when product specifications such as molar flowrate and composition are fixed at the specified value. Operational constraints are defined for example, operating pressure should be higher than 1 atm.

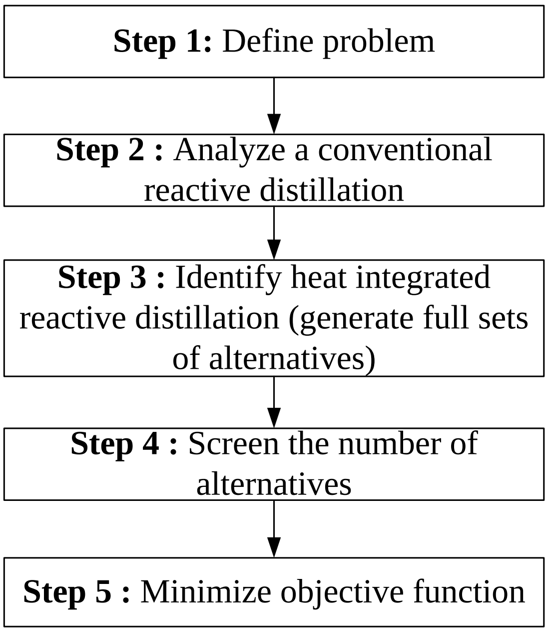

Fig. 4.5 Methodology for design heat integrated reactive distilllation

Step 2 : Analyze conventional reactive distillation

In this step, a conventional reactive distillation is analyzed in order to determine the limitation of the reactive distillation. This step divided in to 6 sub-steps as shown in fig. 4.6.

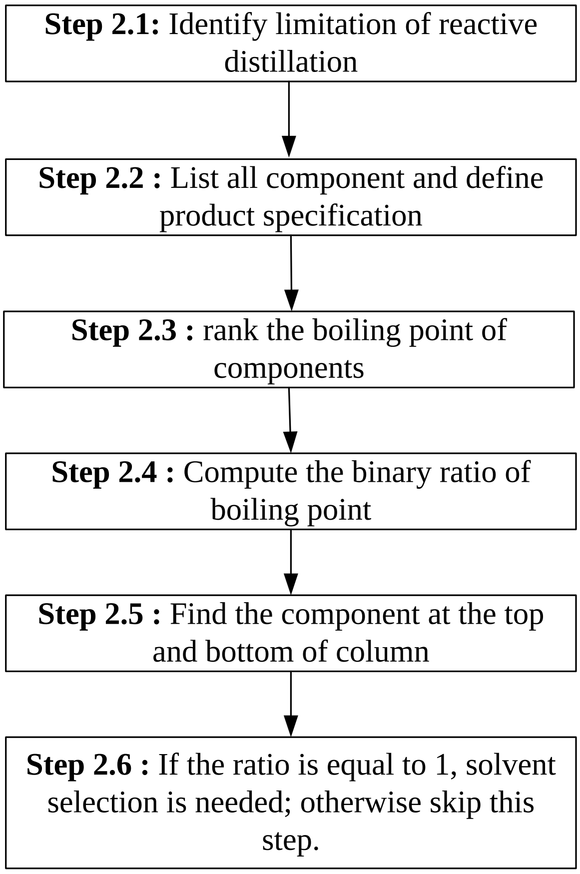

Fig. 4.6 methodology for design heat integrated reactive distillation in step 2

Step 2.1 : Identify the limitation of conventional reactive distillation

In this step, the suitable parameters such as the number of reactive stages, stripping stages, rectifying stages, feed location and operating pressure are determined before the limitation is identified. Then the energy data is collected from simulation results. Conventional reactive distillation is compared with conventional process (i.e. alkali catalyzed process). If operating pressure and heat duty of conventional reactive distillation are higher than the commerial process in the literature reviews. Otherwise the heat integration of reactive distillation is stopped.

Step 2.2 : List components and define product specification

All components from reactions and product specification are defined such as molar flow rate and product purity at the bottom of column.

Step 2.3 : Rank the boiling point of components

Components are listed in order of increasing of boiling point.

Step 2.4 : Compute the binary ratio of boiling point

The boiling point ratio of all adjacent components is computed as shown in equation 4.15.

$$r_{ij} = \frac{T_{b,j}}{T_{b,i}} \tag{4.15}$$

When r_{ij} is binary ratio of boiling point of adjacent component

$T_{b,i}$ is the boiling point of component i (^{o}C)

$T_{b,j}$ is the boiling point of component j(^{o}C)

Step 2.5 : Find the component at the top and bottom of column

From Step 2.4, the boiling point ratio of adjacent components is used to find top and bottom products. If ratio of boiling point of adjacent components is the highest value, adjacent components are represented as key components consisting of light key component and heavy key component. The light key component is component which is lower boiling point while other component is the heavy key component. These two key components are adjacent in order of boiling point. (Seader and Henley, 2006). A sharp separation between key components is indicated. Therefore, the light component is removed to the top of column while other components are remained at the bottom of column.

Step 2.6 : If the ratio is equal to 1, solvent selection is needed.

From step 2.5, if the ratio of boiling point is equal to 1, it means that the separation is difficult. Therefore the suitable solvent is selected by using residue curve map that the desire product should be unstable node or stable node (Dimian et al., 2008).

Step 3 : Identify heat integrated reactive distillation

The objective of this step is to generate a full set of heat integrated reactive distillation column. This step is divided into two sub-steps according to the type of key components.

Key components are the lightest key component and the light key component

In this case, the lightest component is removed at the top of column while other components are removed at the bottom. There are several types of heat integrated reactive distillation such as heat integrated reactive distillation with heat exchanger, heat integrated reactive distillation without heat exchanger, multi-effect reactive distillation, reactive distillation with intercooler, reactive distillation with heat pump, petlyuk reactive distillation, vapor recompression reactive distillation, reactive distillation with side-rectifier.

Key components are the light key component and the heavy key component

In this case, separation task of reactive distillation is to separate products. The heat integrations of this type is divided into 2 cases. The first case is that a reactive distillation divides into two smaller reactive distillation that is integrated each other. In this case, the configurations of the first case are heat integrated reactive distillation (with/without heat exchanger) , petyuk reactive distillation, reactive distillation with side stripper, reactive distillation with rectifier and feed split multi-effect reactive distillation. The second case is the heat integration between reactive distillation and distillation column. The heat integration of this type are heat integrated reactive distillation (with/without heat exchanger), multi-effect direct split arrangement of reactive distillation, multi-effect indirect split arrangement of reactive distillation, thermally coupled direct sequence of RD, thermally coupled indirect sequence of RD.

Step 4 : Screen the number of alternatives

The objective of this step is to decompose the number of alternatives through the constraints such as purity of key component, ratio of boiling point, type of key components and limitation of separation techniques. Only a few feasible alternatives are retained for further analysis. This step divided in 3 sub-steps.

Step 4.1 : Fast screen the number of alternatives.

First, the number of alternatives is reduced through the easier constraints that perform by the purity of components. If high purity of key component is required (95%), the multi-effect indirect split arrangement reactive distillation, heat integrated reactive distillation with distillation column are eliminated because there is no reboiler at distillation in order to recycle the boilup stream. Figure 4.8 shows the configuration of multi-effect indirect split arrangement reactive distillation when the rank of boiling point are B, C, D, A.

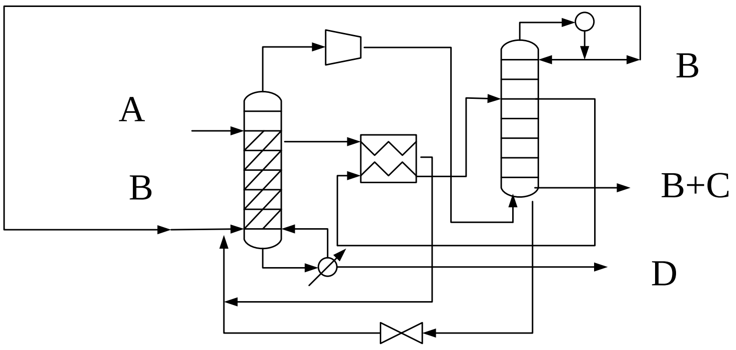

Fig. 4.7 . multi-effect indirect split arrangement reactive distillation when the rank of boiling point are B, C, D, A

Step 4.2 : Screen and reduce the number of alternatives from ratio of boiling point of key components

Secondly, the boiling point ratio of key components is considered. Barroso-Muñoz et al., 2007 investigated the production of ethyl acetate by using petlyuk reactive distillation. The binary ratio of key component in for ethyl acetate production is 1.28; therefore, if the ratio of boiling point of key components is more than 1.28, a petyuk reactive distillation is a feasible alternative. If the ratio of boiling point of key components is between 1.3 and 1.56, feed split multi-effect reactive distillation is a feasible alternative. Whileas heat integrated reactive distillation that divided into two smaller column with/without heat exchanger are eliminated. Figure 4.8 shows the configuration of petlyuk reactive distillation. Figure4.9 shows the configuration of feed split multi-effect reactive distillation. Figure 4.10 shows Heat integrated reactive distillation without heat exchanger (HiRDC without heat exchanger). Figure 4.11 shows Heat integrated reactive distillation with heat exchanger (HiRDC with heat exchanger).

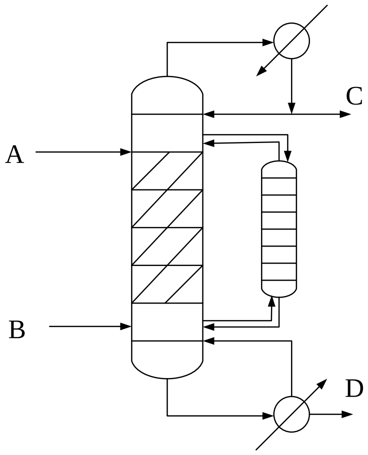

Fig. 4.8 Petlyuk reactive distillation when the rank of boiling point are B, C, D, A

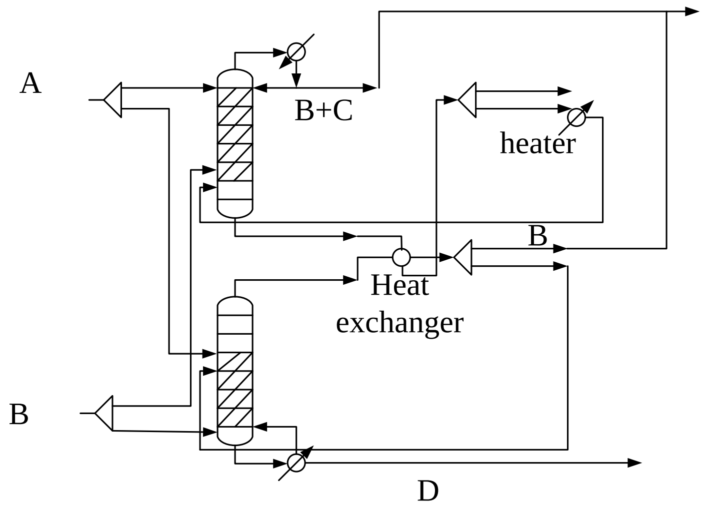

Fig. 4.9 Feed split multi-effect reactive distillation when the rank of boiling point are B, C, D, A

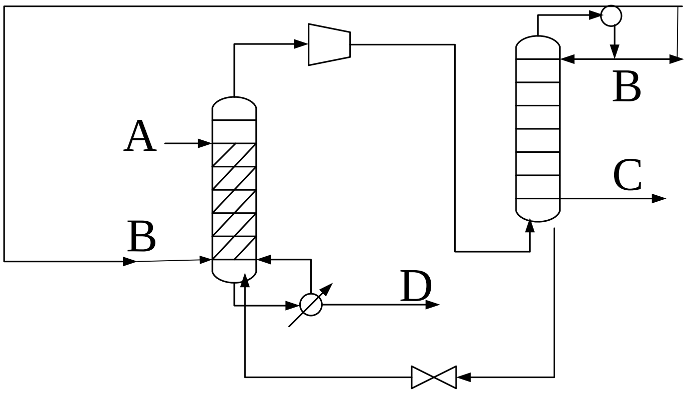

Fig. 4.10 Heat integrated reactive distillation without heat exchanger (HiRDC without heat exchanger) when the rank of boiling point are B, C, D, A

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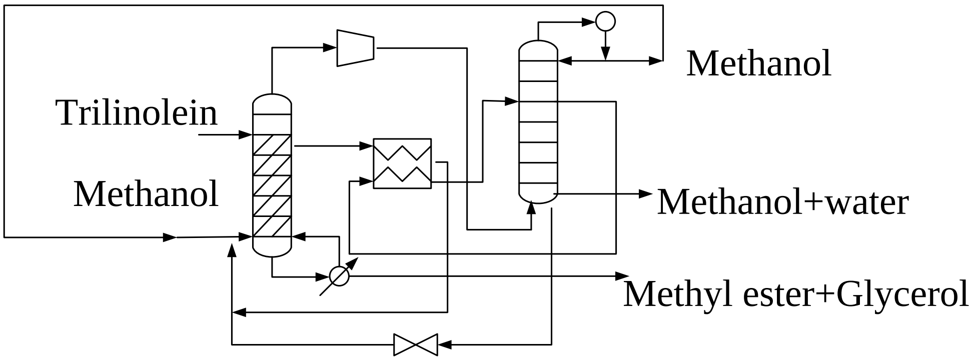


Fig. 4.11 Heat integrated reactive distillation with heat exchanger (HiRDC with heat exchanger) when the rank of boiling point are B, C, D, A

Step 4.3 : Reduce the alternatives with respect to the type of key components

Finally, the key component is taken into account.This step is divided into 3 cases.

- *Key component is the lightest component and the light component*

In this case, the heat integration of reactive distillation that divided into two smaller column is not feasible alternative. This is because large reboiler heat duty is required for the contaction of raw materials. Vapor recompression reactive distillation is also eliminated as unfeasible alternative. However, a thermally coupled direct sequence of RD is chosen as a preferable option. Figure 4.12 shows the configuration of thermally coupled direct sequence of RD.

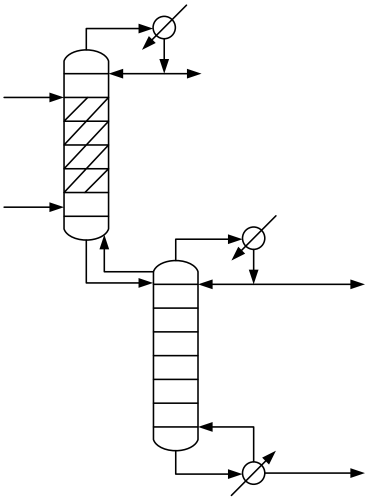


Fig. 4.12 Thermally coupled direct sequence of RD

- *Key component is the light component and the heavy component*

If key component is light component and the heaviest component, thermally coupled indirect sequence of RD, reactive distillation with side-rectifier, multi-effect indirect split arrangement of reactive distillation and heat integrated reactive distillation with distillation column (with/without heat exchanger) are preferable options.

- *Other cases*

Otherwise, a heat integrated reactive distillation with distillation column (with and without heat exchanger between the two columns) is chosen. The table 4.4 and figure 4.13 show the step to select or eliminate the type of heat integrated reactive distillation through the criterias.

Table 4.4 Screening alternatives of heat integrated reactive distillation

Step	Criteria	Value	Suitable configurations	Eliminated configurations
4.1	Purity of key component	Higher than 0.95%		multi-effect indirect split arrangement reactive distillation, heat integrated reactive distillation with distillation column (with/without heat exchanger)
4.2	Binary ratio of key components	Lower than 1.28		Petlyuk reactive distillation
4.2	Binary ratio of key components	1.3-1.56	feed split multi-effect reactive distillation	heat integrated reactive distillation with distillation column (with/without heat exchanger)

Table 4.4 Screening alternatives of heat integrated reactive distillation

Step	Criteria	Value	Suitable configurations	Eliminated configurations
4.3	Type of key component	The lightest component/ the light component	thermally coupled direct sequence of RD with distillation column	heat integrated reactive distillation with distillation column (with/without heat exchanger), multi-effect reactive distillation, vapor recompression reactive distillation
4.3	Type of key component	The light component/the heavy component	thermally coupled indirect sequence of RD, reactive distillation with side-rectifier multi-effect indirect split arrangement of reactive distillation, heat integrated reactive distillation with distillation column	

Table 4.4 Screening alternatives of heat integrated reactive distillation

Step	Criteria	Value	Suitable configurations	Eliminated configurations
4.4	limitations of the separation technique			Petlyuk reactive distillation

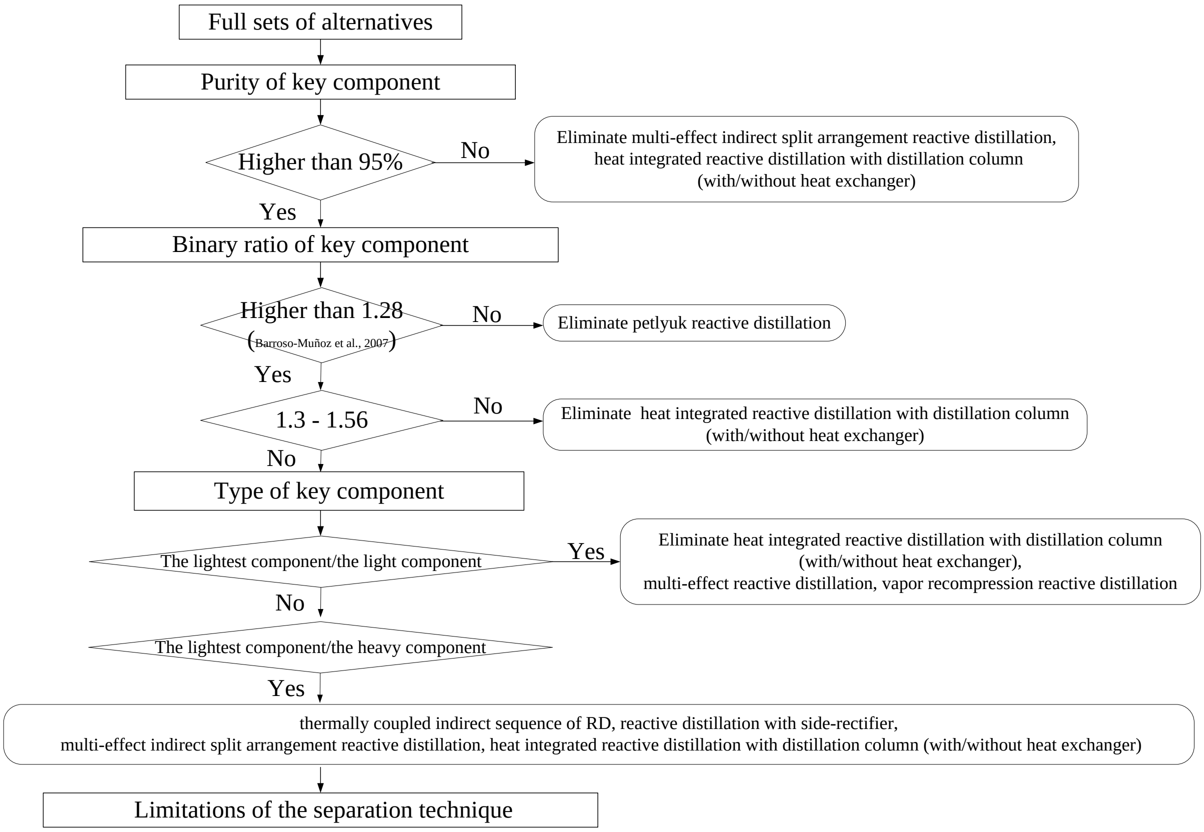


Fig 4.13 Diagram to eliminate the type of heat integrated reactive distillation

Step 5 : Minimize objective function

Objective function such as total annual cost, energy consumption is minimized in order to find a feasible one and suitable parameters such as the number of reactive stages, the number of stripping stages, the number of rectifying stages and feed location are obtained.

CHAPTER V

APPLICATION OF METHODOLOGY FOR PRODUCING TWO MAIN PRODUCTS PLUS SIDE PRODUCT

Application of proposed the methodology for producing two main products plus side product is presented through a case study, biodiesel production integrated with fatty alcohol production. This chapter is divided into 2 case studies. The first study is involving the production of biodiesel integrated with fatty alcohol. Glycerol is regarded as a major by-product of the biodiesel production process. Another option to use glycerol as a fuel to produce hydrogen for fatty alcohol production is also considered.

5.1 Case study : biodiesel production integrated with fatty alcohol production, Glycerol is regarded as a major by-product of the biodiesel production process.

5.1.1 Scenario 1: single objective funtion (to maximize NPV)

Step 1: Define problem

Here, the defined problem is to produce biodiesel and fatty alcohol from methyl esters (biodiesel) at a purity of 99.5 wt.%. Cetane number should be a minimum of 51 (EN 14214) and Iodine value should be higher than 120 g of I_2/100g of biodiesel. Cetane number and iodine value are the linearly function of the degree of unsatuation (Ramos et al., 2009). Glycerol is considered the by-product. The performance criterion is to maximize the net present value (NPV) of the process. Thus, the problem can be mathematically described as follows:

Objective function

$$\text{Max NPV} = f(X,Y) \tag{5.1}$$

$$\begin{aligned} \text{NPV} = [&(F_{bio}P_{bio}+F_{fat}P_{fat}+F_{gly}P_{gly})(P/A,i,n) \\ &- (F_{oil}P_{oil}+F_{met}P_{met}+F_{cat}P_{cat}+F_{H2}P_{H2})(P/A,i,n) \\ &- (Q_{reactor}P_{steam}+Q_{r,i}P_{steam}+Q_{c,i}P_{steam}+Q_{elec}P_{elec}+S)(P/A,i,n) \\ &- D(P/A,i,n) - \Sigma Y_i C(X,a)] \end{aligned} \tag{5.2}$$

subject to

$$h(X) = 0 \tag{5.3}$$

$$g(X) = 0 \tag{5.4}$$

$$p_1 = 99.5 \text{ wt.\%} \tag{5.5}$$

$$p_2 = 99 \text{ wt.\%} \tag{5.6}$$

$$\sum_{i=N_j}^{N_k} Y_i = 1 \qquad \text{where } i = N_j \text{ to } N_k \tag{5.7}$$

$$DU = (monounsaturatedC:1, wt\%) + 2(polyunsaturatedC:2,3, wt\%)$$

(5.8)

where X is the vector of process variables, such as flow rate, pressure and temperature, h(X) is the mass balance, g(X) is the energy balance, Y are the binary integer (decision) variables, a is the equipment size, such as diameter, height and heat exchanger area, S are the costs of maintainance, insurance and laboratory, P are the material and energy prices, such as biodiesel, fatty alcohol, glycerol and catalyst, Q is the heat duty, F is the flow rate, C is the capital cost of equipment, P/A is the present worth factor, *i* is the interest rate and n is the project life. DU is degree of unsturation parameter.

The NPV includes the total capital investment, revenues, and depreciation (D) and operating costs and is determined based on the interest rate of 15% and the lifetime of 20 years.

Step 2: Search literatures/database

At this step, the properties of chemicals involving the biodiesel and fatty alcohol productions are collected. These chemicals include protriglycerides (e.g., trilaurin (C12), trimyristin (C14), tripalmitin (C16), tristearin (C18), triolein (C18 with single double bond), trilinolein (C18 with two double bonds), trilinolenin (C18 with three double bonds)), methanol, free fatty acids (e.g., lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, linoleninc acid), methyl esters (e.g., methyl laurate, methyl myristate, methyl palmitate, methyl stearate, methyl oleate, methyl linoleate, methyl linolenate). The missing data are estimated based on thermodynamic models.

According to a literature review, there are 3 pathways for producing fatty alcohol from vegetable oil. The first pathway is to produce fatty alcohol by direct hydrogenation of vegetable oil. The second pathway is to produce fatty alcohol from hydrogenation of fatty acid that derive from hydrolysis of vegetalble oil. The third pathway is to product fatty alcohol from hydrogenation of methyl ester that obtained from biodiesel production. The pathway of fatty alcohol production is shown in fig. 5.1 and reactions for each pathway are shown in equation 5.9 to 5.14 .

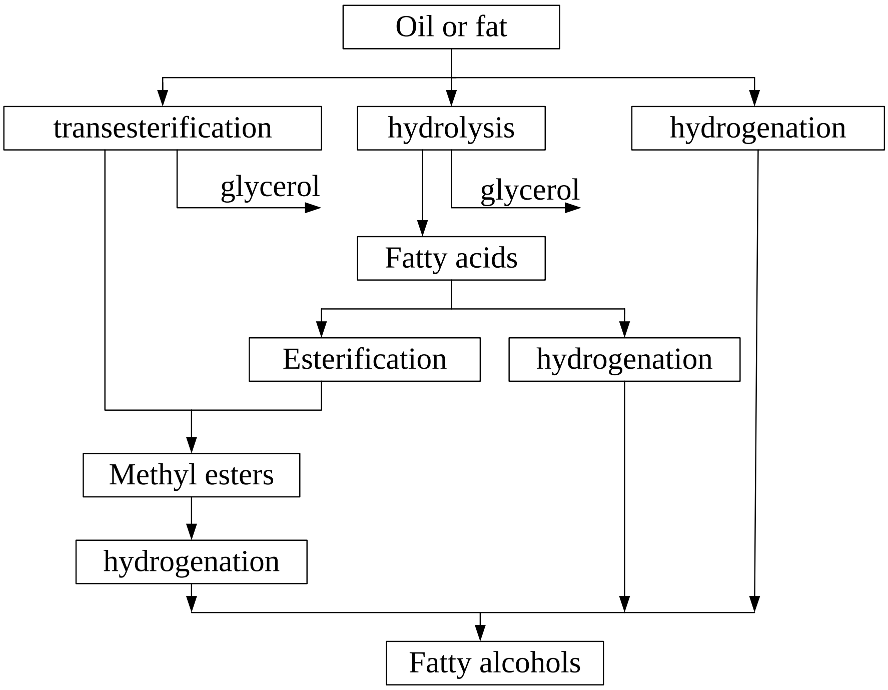


Fig. 5.1 The pathways of fatty alcohol production (Krutzer, 1984)

1st reactions

Pathway 1: $\text{Triglyceride} + H_2 \rightarrow RCH_2OH + CH_3OH$ (5.9)

Pathway 2: $\text{Triglyceride} + H_2O \rightarrow RCOOH + \text{Glycerol}$ (5.10)

Pathway 3: $\text{Triglyceride} + CH_3OH \rightarrow RCOOCH_3 + \text{Glycerol}$ (5.11)

2nd reactions

Pathway 1: -

Pathway 2: $RCOOH + H_2 \rightarrow RCH_2OH + CH_3OH$ (5.12)

$RCOOH + CH_3OH \rightarrow RCOOCH_3 + H_2O$ (5.13)

Pathway 3: $RCOOCH_3 + 2H_2 \rightarrow RCH_2OH + CH_3OH$ (5.14)

However, objective is to produce fatty alcohol from biodiesel. So the desire reactions are shown

1st reactions

Pathway 3: $\text{Triglyceride} + CH_3OH \rightarrow RCOOCH_3 + \text{Glycerol}$ (5.15)

2nd reactions

Pathway 3: $RCOOH + CH_3OH \rightarrow RCOOCH_3 + H_2O$ (5.16)

According to a literature review, it is found that there are 54 different catalysts applied for biodiesel production using different types of vegetable oils and they can be classified in terms of alkali catalyst, acid catalyst, solid base catalyst, solid acid catalyst, enzyme catalyst. The main reaction for biodiesel production consists of the three-step transesterification of triglyceride, diglyceride and monoglyceride with methanol. In addition, biodiesel can be produced under methanol supercritical condition. In case of using vegetable oils with high free fatty acid content, a two-step biodiesel production consisting of the hydrolysis and esterification processes is considered; 13 different catalysts used in the hydrolysis process are reported. For fatty acid production, there are two approaches; firstly, the mixed methyl esters from biodiesel production are hydrogenated and the mixed fatty alcohol produced is then separated (Approach 1), and secondly, the mixed methyl esters are separated before hydrogenation (Approach 2).

Information on the operating conditions and reaction conversion is also collected at this step as shown in appendix B.

Step 3: Generate superstructure from available data

Step 3.1: Identify all components of reactants and products from reactions

A mixture of triglycerides in vegetable oils, such as trilaurin, trimyristin, tripalmitin, tristearin, triolein, trilinolein and trilinolenin, are identified. Diglycerides and monoglycerides including dilaurin, dimyristin, dipalmitin, distearin, diolein, dilinolein, dilinolenin, monolaurin, monomyristin, monopalmitn, monostearin, monoolein, monolinolein and monolinolenin are intemediates generated from the biodiesel production process. In addition to triglycerides, vegetable oils also contain free fatty acids (e.g., lauric acid, myristic acid, palmitic acid, oleic acid, linoleic acid and linolenin acid). Biodiesel product consists of a mixture of methyl esters, such as methyl laurate, methyl myristate, methyl palmitate, methyl stearate, methyl oleate and methyl linoleate. Methyl esters can be produced via the hydrogenation process to produce fatty alcohols, e.g., lauryl alcohol, myristyl alochol, cetyl alcohol, stearyl alcohol, oleyl alcohol, linoleyl alcohol and linolenyl alcohol. Other substances in the biodiesel integrated with fatty alcohol production are methanol, glycerol, water, and hydrogen.

Step 3.2: Identify the properties of all components from available data or using ProPred

In this step, information on the properties of all components in the biodiesel and fatty alcohol production systems, as previously mentioned, are collected.

Step 3.3: Find azeotrope of binary mixture by using VLE diagram

The UNIQUAC model is used to describe thermodynamic properties and VLE diagrams for all binary systems are generated. Fig. 5.2 shows an example of the VLE diagram between methyl myristate and methyl palmitate at 4kPa. In this figure, the model prediction is also compared with experimental data (Silva et al., 2011) to indicate the reliability of the thermodynamic model used in this study. Figs 5.3 and 5.4 show the VLE diagrams between glycerol/methyl laurate and glycerol/lauric acid, respectively, and indicate a formation of azeotropic mixtures. Thus, these mixtures cannot be separated by using an ordinary distillation. For this case, the solubility is the key parameter and a decanter is used for separating these mixtures.

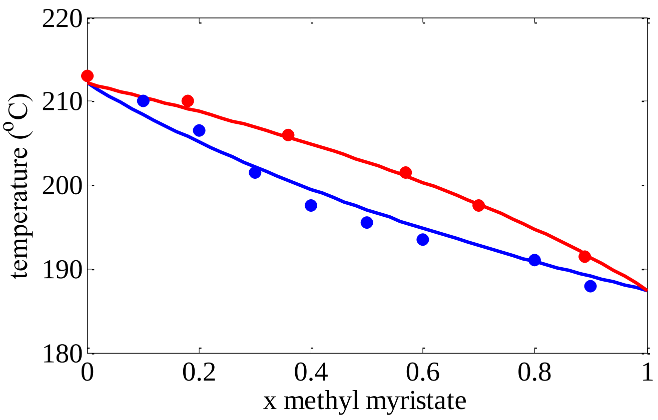


Fig. 5.2 VLE diagram between methyl myristate and methyl palmitate**.**

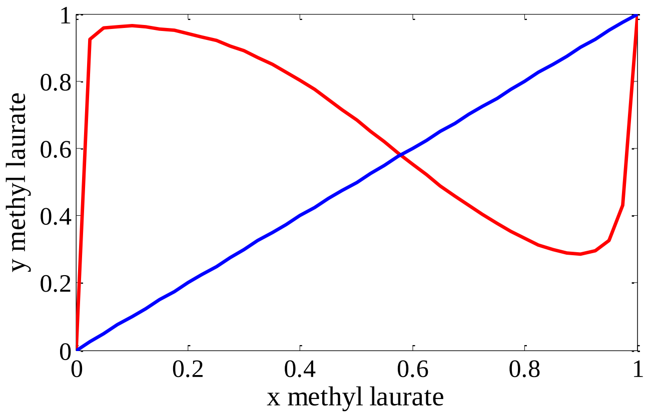


Fig. 5.3 VLE diagram between glycerol and methyl laurate.

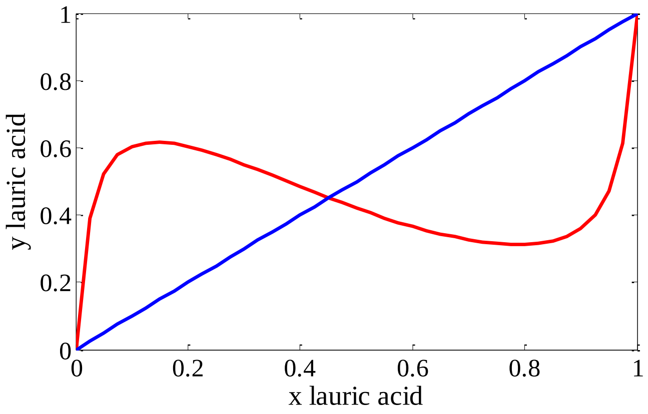


Fig. 5.4VLE diagram between glycerol and lauric acid.

Step 3.4: Calculate binary ratio of properties

For the identified chemicals present in the system, binary ratios of properties, such as vapor pressure, melting point, boiling point, solubility and molecular weight, for all components are computed.

Step 3.5: List the feasible separation techniques of all components

From the binary ratio of properties, feasible separation techniques of all components are listed as shown in Table 5.1 (for biodiesel production) and Table 5.2 (for fatty alcohol production).

Table 5.1 Identification of separation technique for biodiesel production (bold letter means feasible separation techniques)

Task	Separation technique
1. Methyl laurate/water (adjacent binary ratio) Methyl oleate/water	**Flash drum, distillation, Azeotropic distillation, membrane, pervaporation,** absoption, LL extraction, stripping, supercritical extraction
2. Methyl myristate/water Methyl palmitate/water Methyl stearate/water Methyl linoleate/water	**Flash drum, distillation, membrane, pervaporation,** absoption, LL extraction, stripping
3. Glycerol/methyl linoleate (adjacent binary ratio) Glycerol/methyl laurate Glycerol/methyl myristate Glycerol/methyl palmitate Glycerol/methyl oleate Glycerol/methyl linoleate	**Membrane, centrifuge, extractive distillation,** liquid adsorption, supercritical extraction, distillation with decanter, flash separation
4. Water/methanol (adjacent binary ratio)	**Distillation, flash separation,** pervaporation, membrane

Table 5.1 Identification of separation technique for biodiesel production (bold letter means feasible separation techniques) (cont.)

Task	Separation technique
5. Fatty acids/glycerol	**Azeotropic distillation**, **extractive distillation**, liquid membrane, **LL extraction**, Pervaporation, Crystalization, distillation, suplimation
6. Water/fatty acids	**Distillation**, **extractive distillation**, absorption, flash operation, membrane
7. Water/triglycerides	**LL extraction, membrane, pervaporation, distillation**
8. Methanol/methyl esters	**LL extraction, membrane, pervaporation, distillation**
9. Methanol/glycerol	**Distillation**, **membrane**, LL extraction, stripping
10. Methanol/triglyceride	**LL extraction, Distillation, membrane**, **stripping**
11. Water/glycerol	**Distillation, membrane**, stripping, liquid adsorption
12. Glycerol/triglycerides	**LL extraction, membrane, distillation, stripping**
13. Methyl esters /triglycerides	**Distillation**

Table 5.1 Identification of separation technique for biodiesel production (bold letter means feasible separation techniques) (cont.)

Task	Separation technique
14. Methyl laurate/ methyl esters	**Distillation,** flash separation, liquid membrane, pervaporation
15. Methanol/fatty acids	Flash separation**, distillation, membrane, pervaporation,** crystallization
16. Glycerol/ lauric acid	**Membrane, centrifuge, extractive distillation,** liquid adsorption, supercritical extraction, distillation with decanter, flash separation
17. Fatty acid/methyl esters	Flash separation**, liquid membrane,pervaporation, distillation**

Table 5.2 Identification of separation technique for fatty alcohol production (bold letter means feasible separation techniques)

Task	Separation technique
1. H_2/liquid product	**Flash separation**
2. Methanol/methyl ester	**Flash separation, distillation, LL extraction, membrane, pervaporation, liquid adsorption**
3. Methanol/lauryl alcohol Methanol/myristyl alcohol Methanol/palmityl alcohol Methanol/oleyl alcohol	**Flash separation, distillation**, **LL extraction, membrane, pervaporation, stripping**, liquid adsorption**,** crystallization
4. methyl ester /lauryl alcohol methyl ester /myristyl alcohol methyl ester /palmityl alcohol methyl ester /oleyl alcohol	**Flash separation, distillation**, **azeotrope distillation, extractive distillation, LL extraction, membrane, pervaporation**, liquid adsorption**,** crystallization
5. lauryl alcohol /myristyl alcohol lauryl alcohol /palmityl alcohol lauryl alcohol /oleyl alcohol	**Liquid membrane, distillation, Pervaporation**
6. myristyl alcohol /palmityl alcohol myristyl alcohol /oleyl alcohol	**Liquid membrane, distillation, Pervaporation**
7. palmityl alcohol /oleyl alcohol	**Liquid membrane, distillation, Pervaporation**

Step 3.6: Draw the superstructure from the feasible separation techniques including alternative separation process

Using the collected data, a superstructure for the production of biodiesel integrated with fatty alcohol is generated (Fig. 5.5). The superstructure contains six separation operation types (such as flash separator, decanter, distillation, stripper and absorber) and conversion reactors (transesterification reactor, esterification reactor and hydrolysis reactor - one for each type of catalyst considered; seven types of catalysts have been considered). The binary integer variable (Y_i), as shown in Fig. 5.5, indicate the available alternatives. It is noted that when Y_i is zero, it means that the alternative is not considered. The full set of alternatives is 342,144. Tables 5.3 and 5.4 show the feasible set of alternatives for biodiesel and fatty alcohol productions, respectively. The select type of the reaction task and separation task are related to the rules.

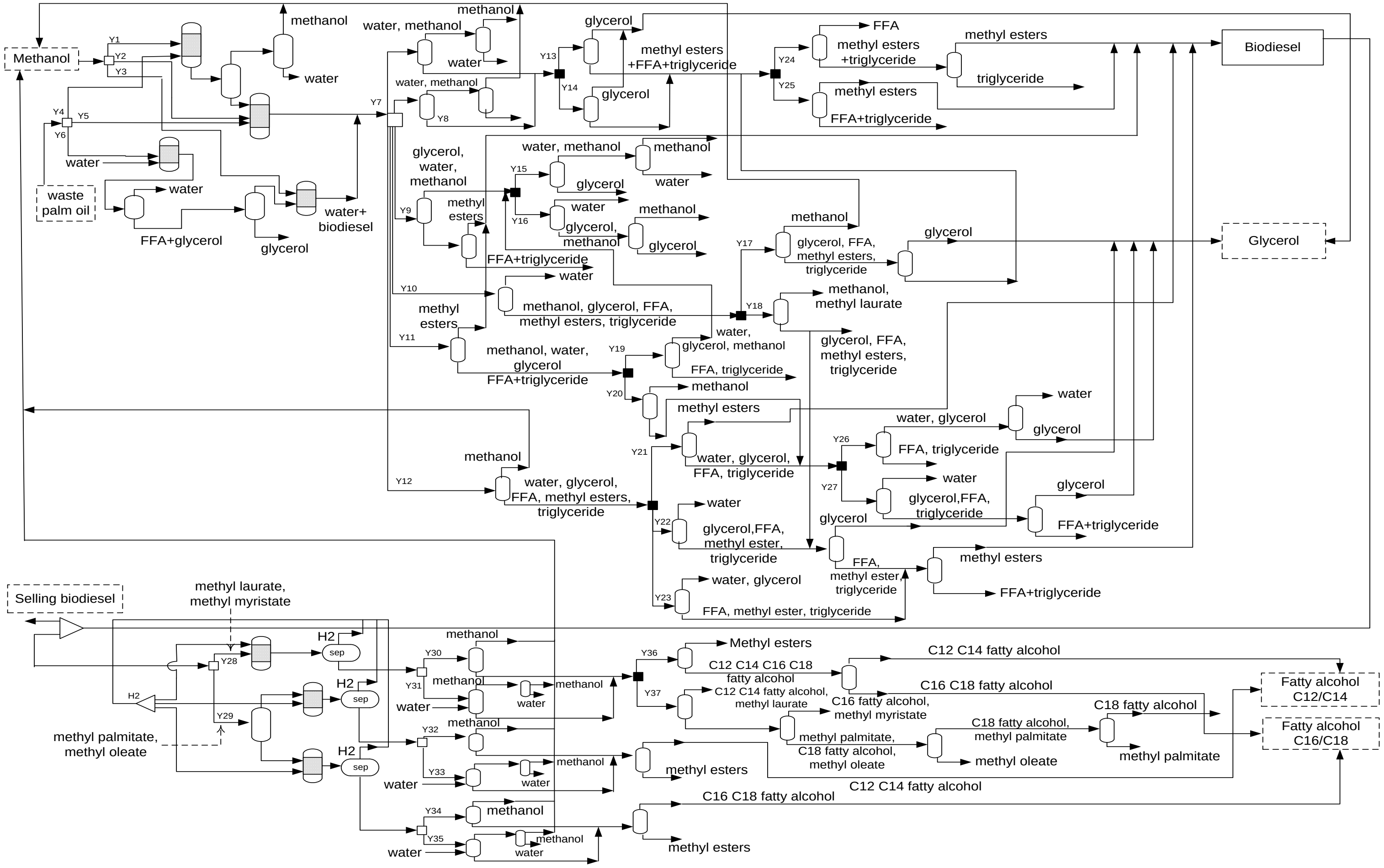


Fig. 5.5 The superstructure for biodiesel production integrated with fatty alcohol production

Table 5.3 Separation superstructure alternative for biodiesel production

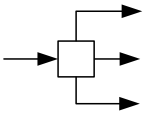
	reactor						Separation1						Separation2											Separation3			
	Y1	Y2	Y3	Y4	Y5	Y6	Y7	Y8	Y9	Y10	Y11	Y12	Y13	Y14	Y15	Y16	Y17	Y18	Y19	Y20	Y21	Y22	Y23	Y24	Y25	Y26	Y27
reactor (alkali and solid base)	1	1	0	0	0	0																					
reactor (acid, enzyme, supercritical)	0	1	0	0	0	0																					
reactor (hydrolysis)	0	0	1	0	0	0																					
reactor (alkali and solid base for waste oil)	0	0	0	1	1	0																					
reactor (acid, enzyme, supercritical for waste oil)	0	0	0	0	1	0																					
reactor (hydrolysis for waste oil)	0	0	0	0	0	1																					
LL extractor	0	0	0	0	0	0	0	0	1	0	0	0															
Membrane2	0	0	0	0	0	0	0	0	0	1	0	0															
Liquid adsorption	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	1	0	0	1	0	0				
Decanter	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0				
Flash	0	0	0	0	0	0	1	0	0	0	0	0	0	0	1	0	1	0	0	1	0	1	0	0	0	0	1
distillation	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	1	0	0
Membrane1	0	0	0	0	0	0	0	0	1	0	0	0	0	1	0	1	0	0	0	0	0	0	0	1	0	0	0
pervaporation	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	1	0

Table 5.4 Separation superstructure alternative for fatty alcohol production

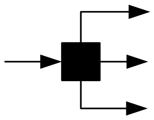
	Reactor or separation		Separation1						Separation2	
	Y28	Y29	Y30	Y31	Y32	Y33	Y34	Y35	Y36	Y37
reactor	1	0								
spliter	0	1								
Flash	0	0	1	0	1	0	1	0		
LL extractor	0	0	0	1	0	1	0	1		
Distillation	0	0	0	0	0	0	0	0	0	1
Liquid adsorption	0	0	0	0	0	0	0	0	1	0

Rules

- Tor selection reaction for biodiesel production, To select the route of reaction , If alkali is used, Y1=1 and Y2=1 else Y3=1 for biodiesel production from crude oil
- To select the route of reaction , If alkali is used, Y4=1 and Y5=1 else Y6=1 for biodiesel production from crude oil
- To select the route of separation, $\sum_{i=7}^{12} Y_i = 1$(biodiesel production) and $\sum_{i=28}^{29} Y_i = 1$, $\sum_{i=30}^{31} Y_i = 1$, $\sum_{i=32}^{33} Y_i = 1$, $\sum_{i=34}^{35} Y_i = 1$ (fatty alcohol production) for the white box



- To select the route of separation, $1 \le \sum_{i=7} Y_i \le 2$ for the black box



Step 4: Screen of alternatives

Step 4.1: Screen the processes by considering only selected raw materials

In this study, waste cooking palm oil is selected as a renewable source for biodiesel production. Thus, the number of alternatives is reduced at this step to 95,040.

Step 4.2: Screen and reduce the number of synthesis pathway based on phase of feed

Step 4.3: Screen and reduce the number of synthesis pathway based on productivity of catalyst

Step 4.4: Screen and reduce the number of synthesis routes based on productivity for each catalyst

Productivities of biodiesel and fatty alcohol productions is used as the criteria to reduce the number of alternatives. It is noted that seven biodiesel production processes based on different catalysts and two fatty alcohol production processes as mentioned earlier have been considered. Table in appendix A shows the biodiesel and fatty alcohol productivities obtained from different biodiesel processes. At the end of this step, the number of alternatives is reduced to 7,392.

Step 4.5: Screen and reduce the number of synthesis routes based on attainable region (AR)

For biodiesel production, main reactions consist of three-steps of transesterification of triglyceride while the reduction of free fatty acid contents is esterification reaction. Desired reactions are transesterification and esterification; however, there is no undesired reactions. The number of alternatives for biodiesel production is still remaining.

For fatty alcohol production, there are side reactions such as wax ester formation, saturation and hydrocarbon formation depending on type of catalysts. However, only one catalyst that gives the highest productivity is selected. In this work, CuCr is selected as a catalyst because undesired product is only hydrocarbon (alkane) and amount of undesired product is very low. The main reactions and side reaction of fatty alcohol production are shown in eq 15 to eq.16.

$$RCOOCH_3 + 2H_2 \rightarrow RCH_2OH + CH_3OH \qquad (5.15)$$

$$RCH_2OH + H_2 \rightarrow RCH_3 + H_2O \qquad (5.16)$$

Side reaction (equation 5.16) is occurred. The concentration of methyl esters are determined to obtain high concentration of desire product (fatty alcohol) and low concentration of undesire product (hydrocarbon). However, high conversion is obtained for fatty alcohol production by using CuCr as catalyst. In addition, concentration of hydrocarbon is low (0.03%). Therefore, this step can be skipped.

Step 4.6: Reduce the alternatives with respect to the highest driving force of separation process

Most preferable separation technique is selected based on the highest value of binary ratio of properties, indicating the highest driving force of a separation task and the lowest energy consumption required for this separation technique. The reduced superstructure of biodiesel production integrated with fatty alcohol production is shown in Fig. 5.6. The number of alternatives is reduced to 14 at this step.

Step 4.7: Screen the alternatives in terms of limitations of the separation technique

At this step, the limitations on separation tasks are taken into account in the screening process. For example, when considering the separation of glycerol from biodiesel, it is found that a decanter is a suitable process due to a high binary ratio of their solubility. However, methanol has a negative effect on this phase separation. For this case, methanol should be first removed from the biodiesel product before separating glycerol. At the end of this step, the number of alternative is reduced to seven.

According to the generated superstructure, the waste palm oil consisting of mixed triglycerides with free fatty acids are sent to the pre-reactor (if alkali catalyst and heterogeneous base catalyst are used) or sent to the main reactor (if acid catalyst, heterogeneous acid and enzyme catalysts, supercritical methanol are used) to produce the mixed methyl esters (biodiesel) and glycerol. Alternatively, the waste palm oil is first hydrolyzed with water and the product obtained (mixed fatty acids) is sent to the esterification reactor to produce the mixed methyl esters. In this case, all the products and unreacted raw materials are sent to the flash separator. The light products including water and methanol are separated by a distillation column while the heavy products (methyl esters) are sent to the decanter to separate the light phase (mixed methyl ester and methanol) and the heavy phase (water, glycerol and methanol). The purified mixed methyl esters are obtained from the distillation column. The mixed methyl esters are split into two streams: one for biodiesel product and the other for fatty alcohol production. To produce fatty alcohol, the methy esters are sent to the hydrogenation reactor. Excess hydrogen is separated by flash separator. The final products are C12-C14 fatty alcohol and C16-C18 fatty alcohol.

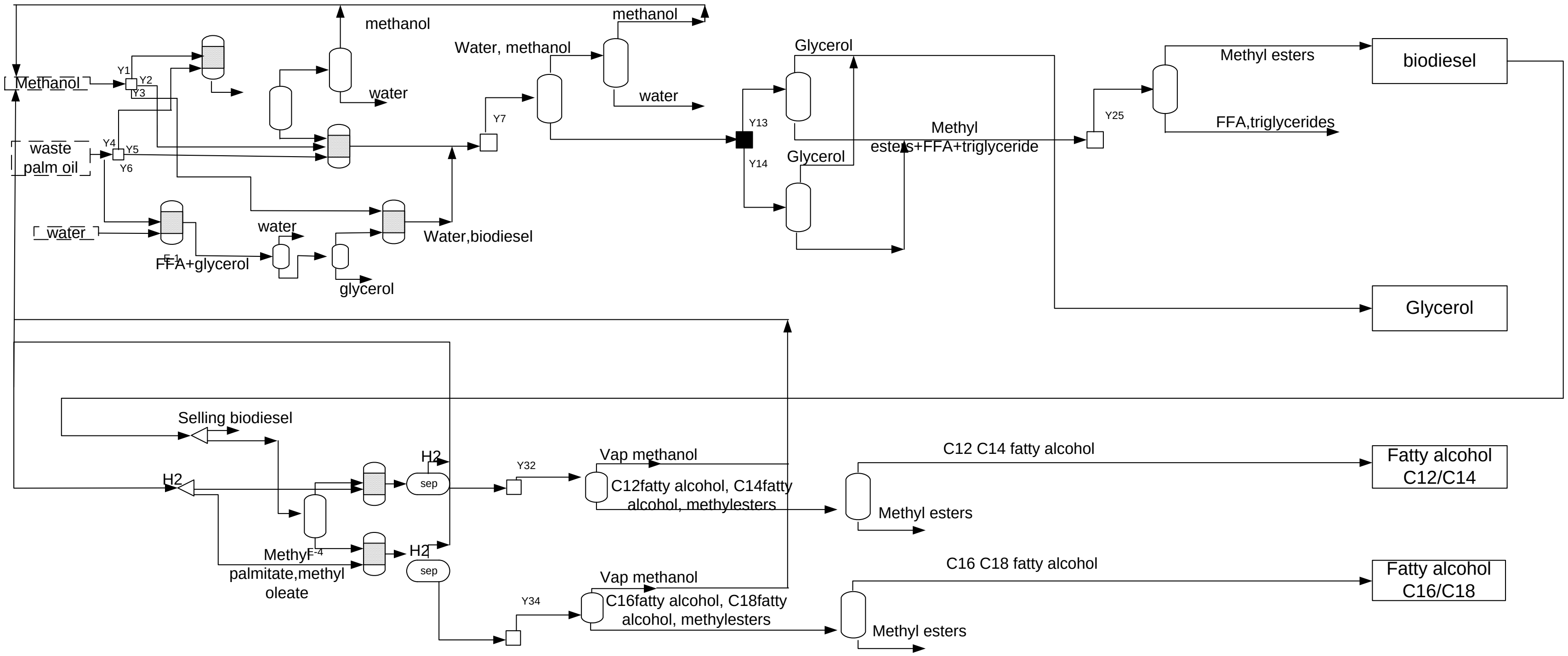


Fig. 5.6 The flowsheet of alternative processes for biodiesel production integrated with fatty alcohol production (based on the largest driving force).

Step 5: Process simulation

Rigorous steady state process simulations of all remaining feasible process alternatives are performed before their corresponding performance criteria are computed in Step 6 for economic analysis and final selection. In the process simulation step, a waste palm oil consisting of a mixture of triglycerides (e.g., trilaurin, trimyristin, tripalmitin, tristearin, triolein, trilinolein and trilinolenin) and free fatty acid (e.g., lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid and linolenin acid) is used as a feedstock to produce biodiesel. The UNIQUAC model is used for the phase equilibrium calculations, while the percentage recoveries of flash separators and distillations are specified at 90% and 99%, respectively. Reaction conditions for the biodiesel and fatty alcohol production processes are shown in Table 5.5. The driving force technique is used to design distillation columns by considering the energy consumption and total capital cost and using the reverse approach, the number of stages and feed location that match the driving force target are determined. The optimum number of stages and feed stage of the distillation column for separating binary mixtures (methanol/water, methyl oleate/palmitic acid, methyl myristate/methyl palmitate, methanol/myristyl alcohol, methanol/cetyl alcohol) under the highest driving force condition is shown in Figs. 5.7 and 5.14, respectively. It can be seen that a minimum total cost can be achieved when the optimum feed stage and total stage are selected due to the tradeoff between the capital cost and the energy cost.

Table 5.5 Operating conditions and performance of the transesterification reactor using different catalysts

Catalyst	T (°C)	P (atm)	Conversion (%)
Biodiesel production	60	1	94.3
NaOH (base cat.) (Narva´ez et al., 2007)			
H_2SO_4 (acid cat.) (Wang et al., 2006)	130	1	90
KOH/Al_2O_3 (heterogeneous base cat.) (Noiroj et al., 2009)	70	1	91.7
DTPA/Clay (heterogeneous acid cat.) (Bokade et al., 2009)	70	17	94
κ-carrageenan (enzyme) (Jegannathan et al., 2011)	30	1	99
Supercritical methanol (Song et al., 2008)	350	40	95
Hydrolysis (Serri et al., 2008)	45	1	95
Fatty alcohol production			
CuCr (Fleckenstein et al., 1991)	250	50	99

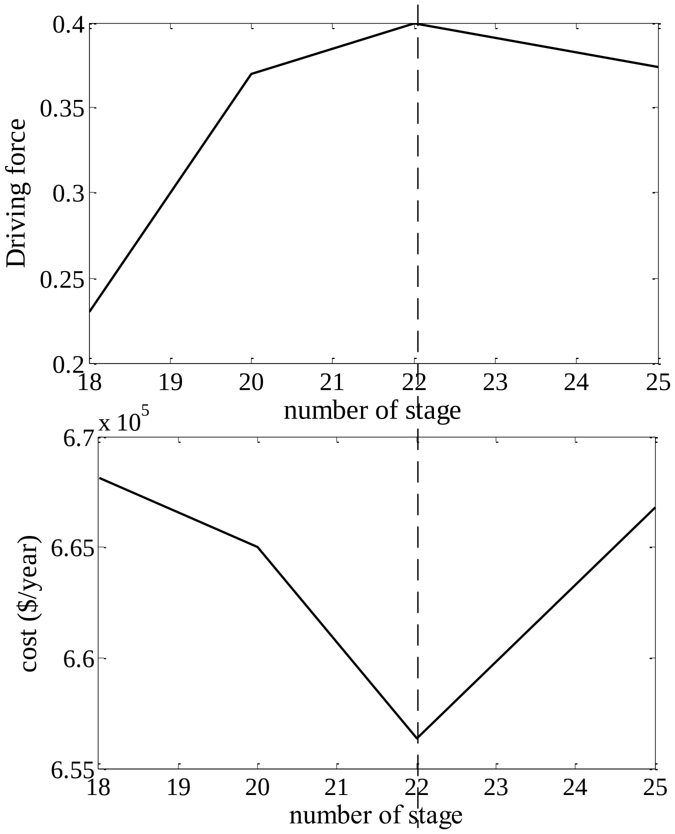


Fig. 5.7 Effect of the number of total stages of distillation for separating methanol from water on the total annual cost ($/year).

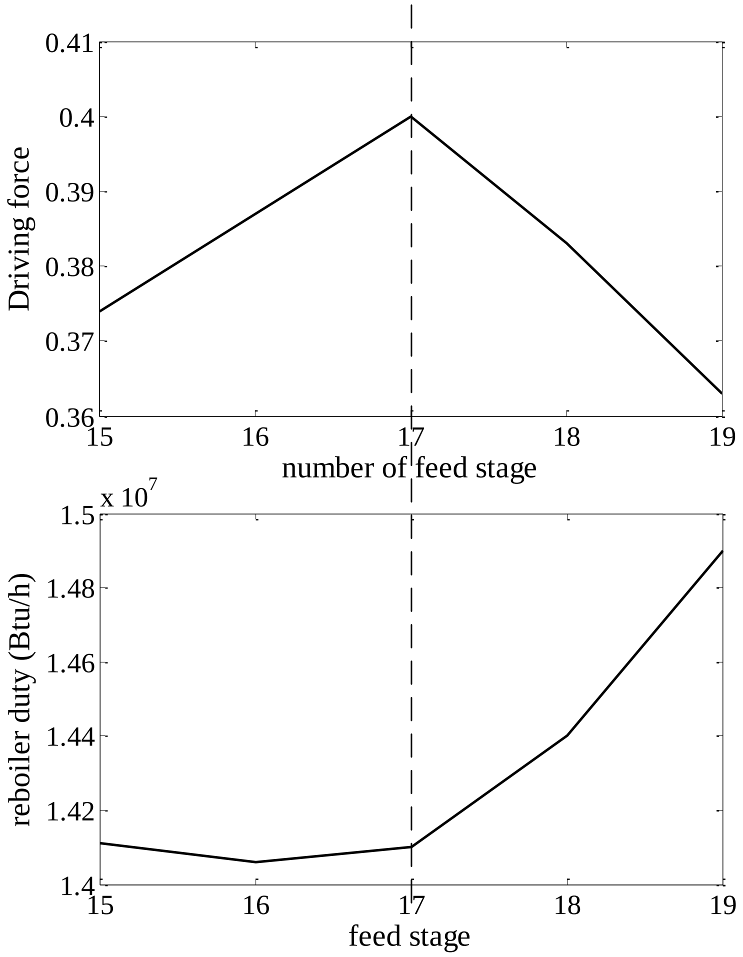


Fig. 5.8 Effect of the feed stage location of distillation for separating methanol from water on the reboiler heat duty (Btu/h).

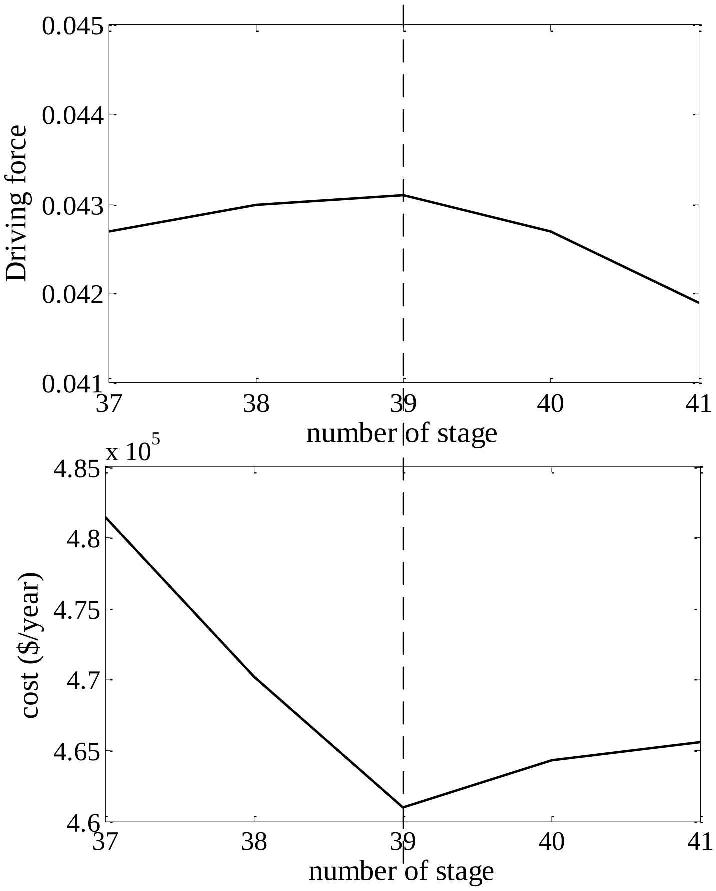


Fig. 5.9 Effect of the number of total stages of distillation for separating methyl oleate from palmitic acid on the total annual cost ($/year)

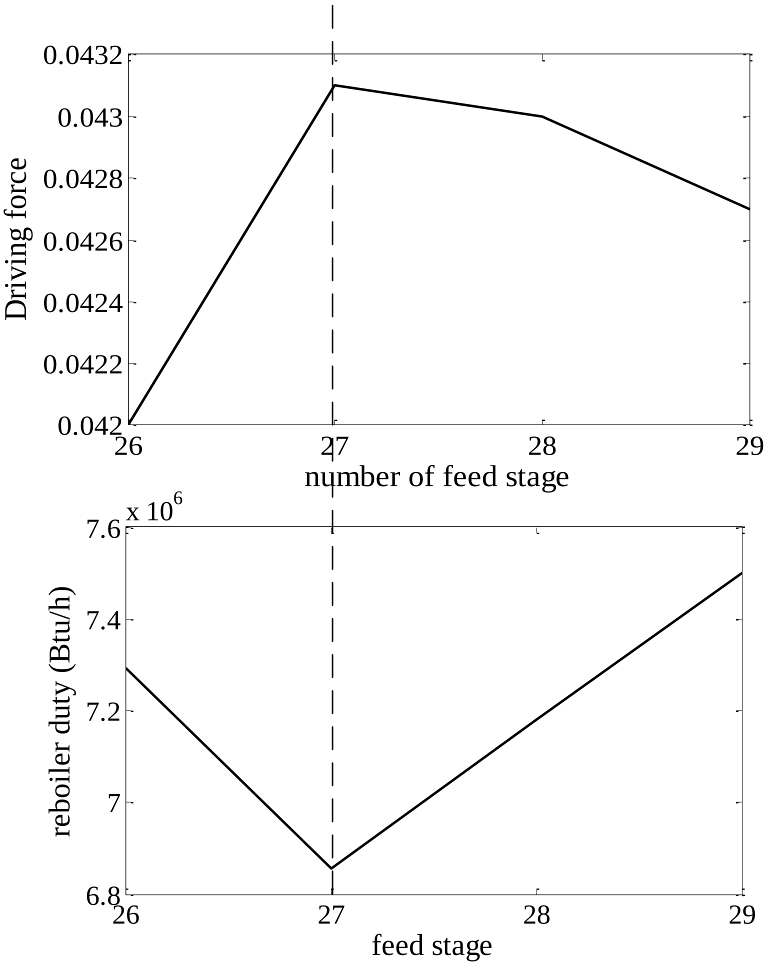


Fig.5.10 Effect of the feed stage location of distillation for separating methyl oleate from palmitic acid on the reboiler heat duty (Btu/h).

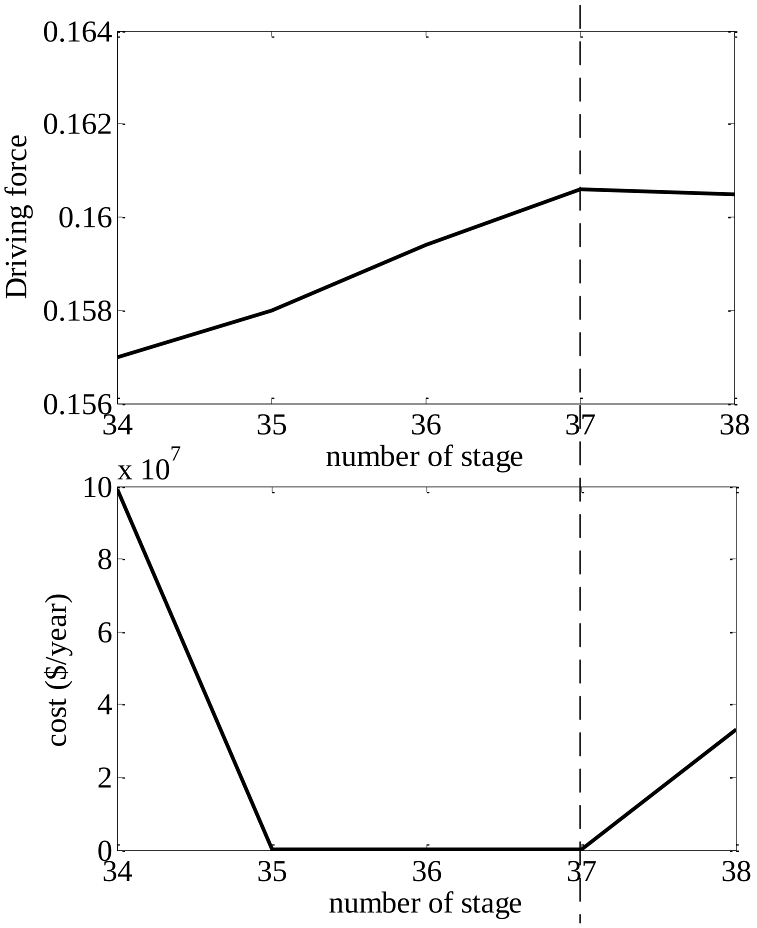


Fig. 5.11 Effect of the number of total stages of distillation for separating methyl myristate from methyl palmitate on the total annual cost ($/year).

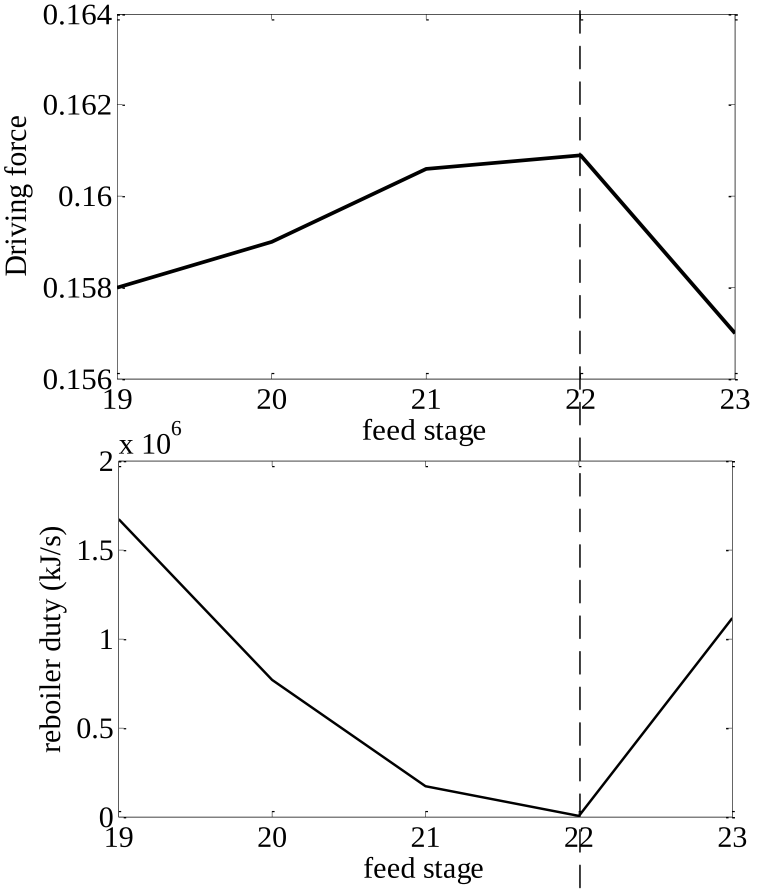


Fig. 5.12 Effect of the feed stage location of distillation for separating methyl myristate from methyl palmitate on the reboiler heat duty (Btu/h).

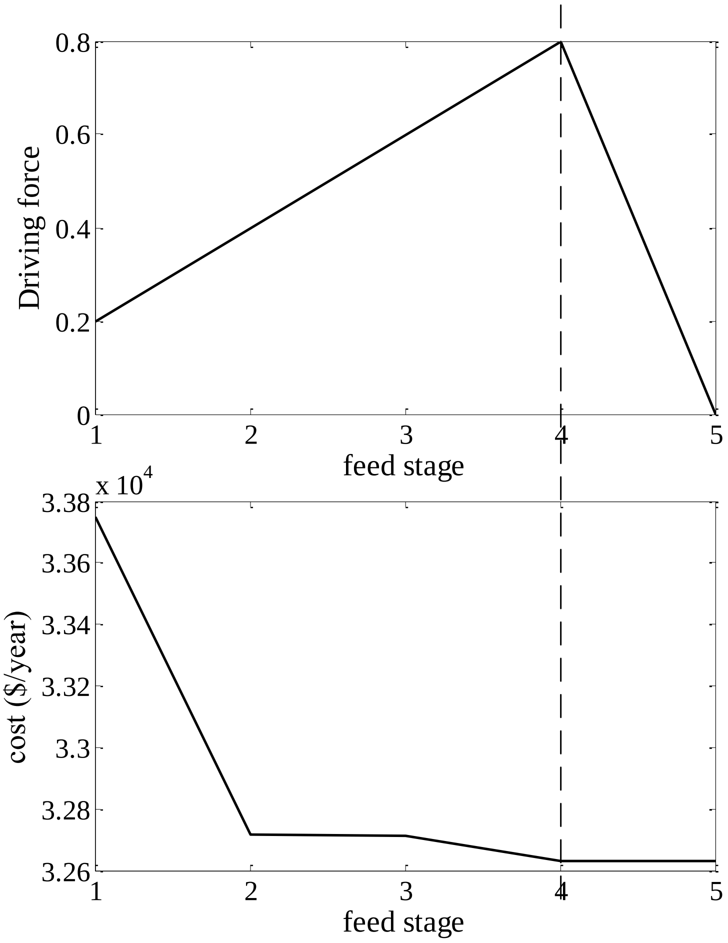


Fig. 5.13 Effect of the feed stage location of distillation for separating methanol from myristyl alcohol on the total annual cost ($/year).

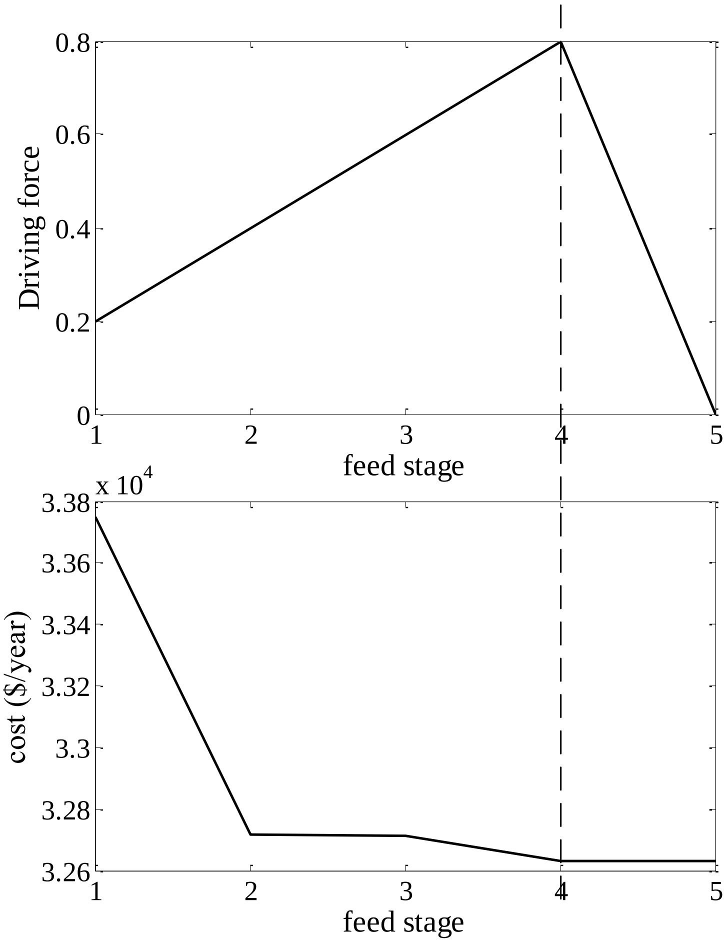


Fig. 5.14 Effect of the feed stage location of distillation for separating methanol from cetyl alcohol on the total annual cost ($/year).

Step 6: Perform economic analysis

Seven processes are analyzed through profitability indicators such as a net present value (NPV). The following assumptions were made to determine the NPV; interest rate is 15%, a straight line depreciation and no discount payback period are assumed, salvage value is neglected and project life is 20 years.

The results show that all the processes are feasible because of the positive NPV. In addition, the NPV increases with increasing fraction of biodiesel to produce fatty alcohol. The heterogeneous acid process for biodiesel production shows the highest NPV value due to its high revenue and low total production costs, whereas the alkali catalyzed process has low total investment cost. The effect of the fraction of biodiesel to produce fatty alcohol on the NPV is shown in Fig. 5.15. At the end, the best process is found to be the heterogeneous acid catalyzed process and the suitable fraction of biodiesel to produce fatty alcohol is 1. That is, most of biodiesel should be diverted to fatty alcohol because the price of fatty alcohol is higher than biodiesel (note that this is a constrained optimal solution and by adding a maximum amount of allowed diversion of biodiesel, both main products can be obtained).

Fig. 5.16 shows the effect of productivity on NPV. The NPV increases with increasing the productivity and reaches its maximum value; there is a trade-off between the productivity and the NPV. When considering the fraction of biodiesel to produce fatty alcohol, it is found that the suitable fraction can be changed when the biodiesel price increases higher than 20% (Fig. 5.17).

Table 5.6 summarizes the results for screening procedure in the proposed design methodology.

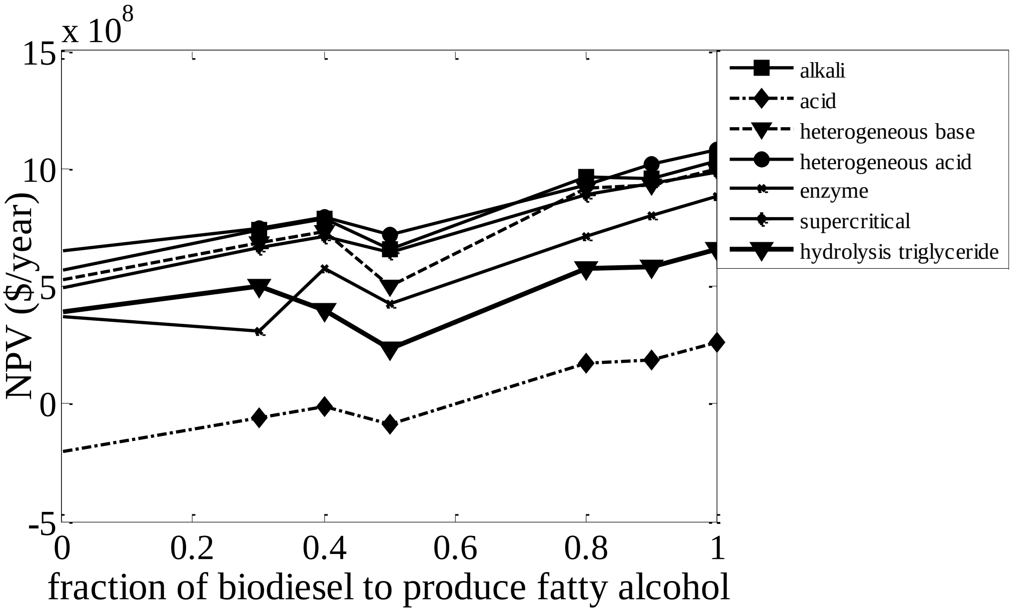


Fig. 5.15 Effect of the fraction of biodiesel to produce fatty alcohol on NPV($/year).

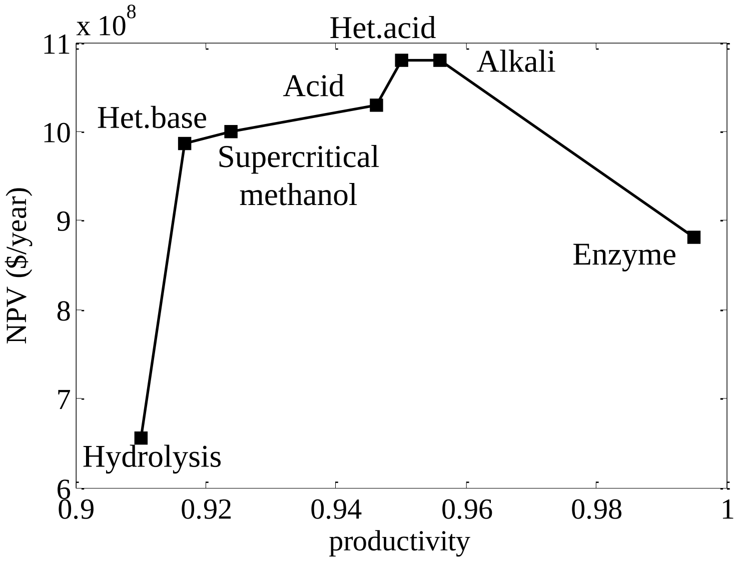


Fig. 5.16 Effect of biodiesel productivity on NPV ($/year) when the fraction biodiesel to produce fatty alcohol is 1.

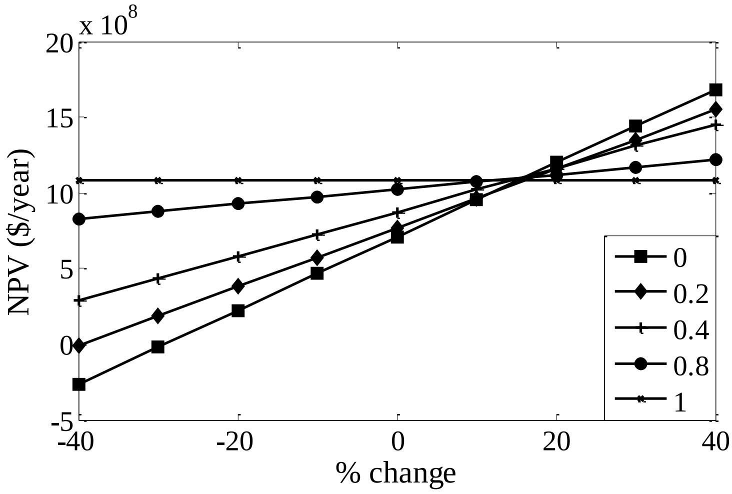
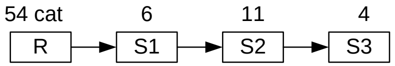
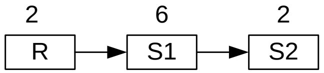
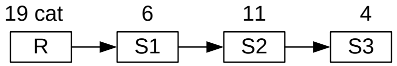
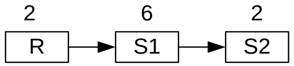
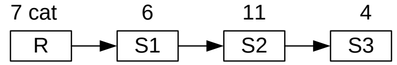
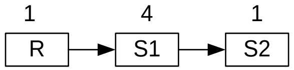
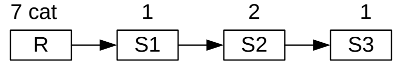
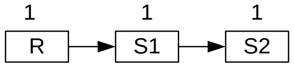
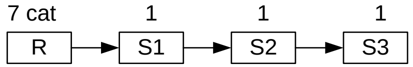
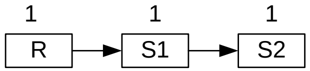
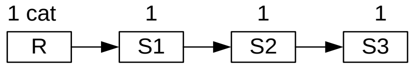
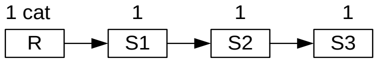


Fig. 5.17 Effect of changes in the biodiesel price on NPV with different fraction of biodiesel to produce fatty alcohol.

Table 5.6 Screening alternative for biodiesel production integrated with fatty alcohol production

	Criteria	Method	Remaining processes	Reduced step	
				Biodiesel production	Fatty alcohol production
1	-	Review literature then generate the overview superstructure	342,144	 14,256 processes	 24 processes
2	Waste palm oil is considered as raw material	Interesting raw material	95,040	 5,016 processes	 24 processes
3	Highest productivity	Calculate the kg product/kg oil	7,392	 1,848 processes	 4 processes
4	Highest driving force	Calculate the adjacent properties ratios	14	 14 processes	 1 process
5	Limitation of separation task	Consider LLE diagram	7	 7 processes	 1 process
6	Highest NPV	Perform economic analysis	1		

Step 7: Combine the reaction task and separation task

In the last step of the methodology, a process intensification of the best biodiesel production process obtained from the previous step is considered to improve its performance. In this study, a reactive distillation where reaction and separation tasks are carried out in a single unit is applied to the biodiesel process. Combining separation of water and methanol from biodiesel with the reaction step to improve the conversion of equilibrium-limited reaction has been considered. It is assumed that as the reaction reaches equilibrium condition, the number of total stages is five (including condenser and reboiler), feed location of the mixed triglycerides and methanol is the second stage and the feed ratio of methanol to triglycerides is 4.5. Methanol and water are obtained at the top of the column, while methyl esters and glycerol are obtained at the bottom. The results with and without process intensification are compared in Table 5.7. Due to its low fraction, water derived from the esterification process (the pre-treatment section of waste palm oil) is assumed to be an inert component. The details of reactive distillation are shown in further chapter. The separation task of the reactive distillation cannot separate excess reactant from the product; therefore, biodiesel product is mixed with methanol and glycerol. Other separation techniques, such as distillation and flash, are required for purification of biodiesel. Although the reactive distillation cannot separate the light product (methanol and glycerol) from the heavy product (methyl esters), it can improve the biodiesel process by increasing the biodiesel production rate.

Table 5.7 Comparison of design with and without process intensification for heterogeneous acid catalyzed process for biodiesel production (not including fatty alcohol production)

Parameters	Process with intensification	Process without intensification
Amount of biodiesel (kmol/h)	153.1	137.6
Heating duty (kJ/h)	7.798×10^{7}	9.307×10^{7}
Cooling duty (kJ/h)	6.87×10^{7}	7.806×10^{7}

5.1.2 Scenario 2: multi- objective funtion (to maximize NPV and to minimize mass intensity)

As previous section, only economic is concerned for biodiesel and fatty alcohol production. To produce sustainable process, the disposal waste in term of mass intensity should be included. Therefore, multi-objective function is considered. The process design problem is startly defined to produce biodiesel and fatty alcohol at a purity of 99.5 wt.%. The performance criterion is to maximize the net present value (NPV) of the process and minimize the mass intensity, defined as:

Objective function

$$\text{Max NPV} = f(X,Y) \tag{5.17}$$

$$\begin{aligned}\text{NPV} = [&(F_{bio}P_{bio}+F_{fat}P_{fat}+F_{gly}P_{gly})(P/A,i,n)\\ &- (F_{oil}P_{oil}+F_{met}P_{met}+F_{cat}P_{cat}+F_{H2}P_{H2})(P/A,i,n)\\ &- (Q_{reactor}P_{steam}+Q_{r,i}P_{steam}+Q_{c,i}P_{steam}+Q_{elec}P_{elec}+S)(P/A,i,n)\\ &- D(P/A,i,n) - \Sigma Y_iC(X,a)]\end{aligned}$$

$$\text{Min mass intensity} = f(X,Y)$$

$$MassIntensity = \frac{F_{raw}(X) - F_{product}(X,Y)}{F_{product}(X,Y)} \tag{5.18}$$

subject to

$$h(X) = 0 \tag{5.19}$$

$$g(X) = 0 \tag{5.20}$$

$$p_1 = 99.5 \text{ wt.\%} \tag{5.21}$$

$$p_2 = 99 \text{ wt.\%} \tag{5.22}$$

$$\sum_{i=N_j}^{N_k} \mathrm{Y}_i = 1 \qquad \text{where } i = N_j \text{ to } N_k \tag{5.23}$$

$$DU = (monounsaturatedC:1, wt\%) + 2(polyunsaturatedC:2,3, wt\%) \tag{5.24}$$

In this case, the superstructure is similar to the scenario 1. The number of full sets alternatives and the number of alternatives at the screening step are also similar to the scenario 1, except the step 6. The alternative processes are analyzed in two dimensional metric (economic and environment). For economic analysis, the optimal fraction biodiesel to produce fatty alcohol is 1 and the best process is heterogeneous acid catalyzed process.

To determine environmental indicator, mass intensity of acid catalyzed process is the highest value while mass intensity of enzyme catalyzed process and heterogeneous acid catalyzed process is low. Low mass intensity means that raw material is less dispose to environment. Fig. 5.18 shows that increasing fraction of biodiesel to produce fatty alcohol enhance a decreasing of mass intensity for different biodiesel production process except acid catalyzed process. The fraction of biodiesel to produce fatty alcohol of 0.2 of enzyme catalyzed process leads to the lowest mass intensity. It implies that enzyme catalyzed process at this fraction is an alternative option when the waste is minimized.

Based on sustainability metric (economic and environment), AHP is used to aggregrate mutiple objective function into single objective function. NPV and mass intensity are normalized so they can compare in the same scale. Fig. 5.19 shows the effect of fraction of biodiesel to produce fatty alcohol on AHP. It presents that acid catalyzed process is not suitable process for economic and environment because AHP is zero value. The suitable fraction of biodiesel to produce fatty alcohol is changed. The AHP increases with increasing fraction of biodiesel to produce fatty alcohol first and then it is slightly decrease. However, it cannot predict the trend of the curve because economical score and environmental score are changed. From fig. 5.19, it concluded that heterogeneous acid catalyzed process with the fraction of biodiesel to produce fatty alcohol of 0.5 is a sustainable process because AHP score is 0.995. The sustainability metric for biodiesel production integrated with fatty alcohol production is shown in fig. 5.21. Heterogeneous acid catalyzed process with the fraction of biodiesel to produce fatty alcohol of 0.5 (B) is satisfied the multiple objective function (to maximize NPV and to minimize mass intensity). While heterogeneous acid catalyzed process (A) with the fraction of biodiesel to produce fatty alcohol of 1 is satified the single objective function in terms of NPV. And The fraction of biodiesel to produce fatty alcohol of 0.8 of enzyme catalyzed process (C) is satisfied the single object function in terms of mass intensity.

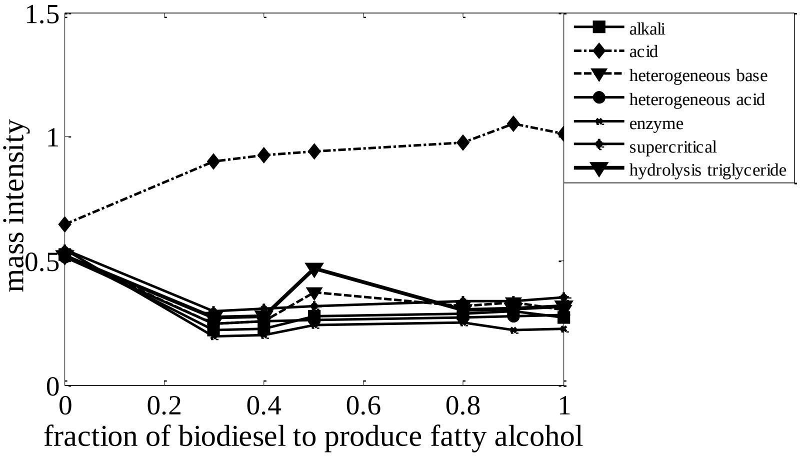


Fig. 5.18 Effect of the fraction of biodiesel to produce fatty alcohol on mass intensity

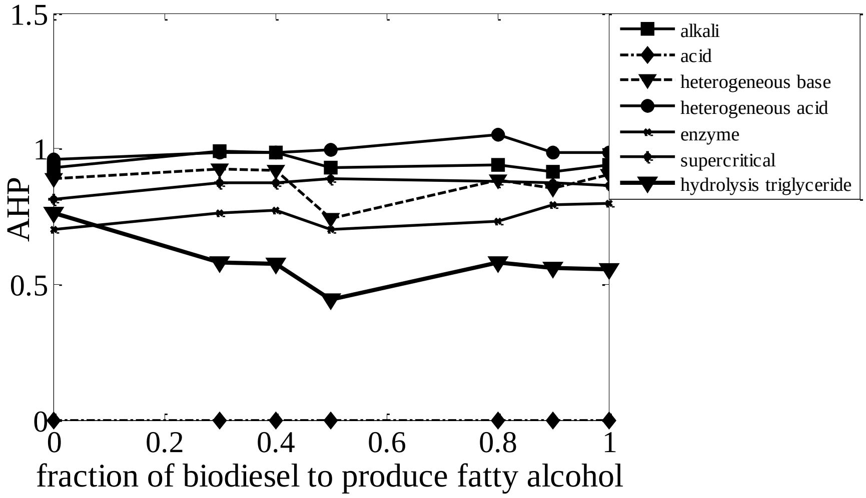


Fig. 5.19 Effect of the fraction of biodiesel to produce fatty alcohol on AHP

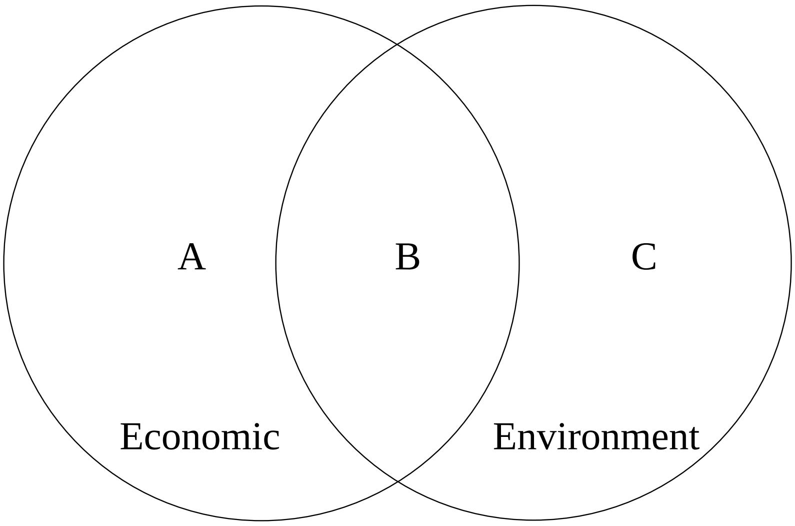


Fig. 5.20 Sustainability metric

5.2 Case study : biodiesel production integrated with fatty alcohol production, glycerol as a fuel to produce hydrogen for fatty alcohol production

As previously mentioned, glycerol can be used for the production of hydrogen, which is used in the synthesis of fatty alcohol, instead of specifying it as a by-product of the biodiesel production. This option of using the glycerol is also considered and the developed design methodology is applied. Thus, the process design problem is re-defined as to produce biodiesel and fatty alcohol at a purity of 99.5 wt.%. In this option, glycerol is used as a fuel to produce hydrogen through a reforming process and the obtained hydrogen is used in the fatty alcohol production. The performance criterion is to maximize the net present value (NPV) of the process, defined as:

Objective function

$$\text{Max NPV} = f(X,Y) \tag{5.11}$$

$$\begin{aligned}\text{NPV} = [&(F_{bio}P_{bio}+F_{fat}P_{fat})(P/A,i,n)\\ &- (F_{oil}P_{oil}+F_{met}P_{met}+F_{cat}P_{cat})(P/A,i,n)\\ &- (Q_{reactor}P_{steam}+Q_{r,i}P_{steam}+Q_{c,i}P_{steam}+Q_{elec}P_{elec}+S)(P/A,i,n)\\ &- D(P/A,i,n) - \Sigma Y_i C(X,a)]\end{aligned} \tag{5.12}$$

subject to

$$h(X) = 0 \tag{5.13}$$

$$g(X) = 0 \tag{5.14}$$

$$p_1 = 99.5 \text{ wt.\%} \tag{5.15}$$

$$p_2 = 99 \text{ wt.\%} \tag{5.16}$$

$$\sum_{i=N_j}^{N_k} Y_i = 1 \qquad \text{where } i = N_j \text{ to } N_k \tag{5.17}$$

When the methodology is implemented step by step to design the process, it is found the superstructure of the process is similar to the previous one except that the hydrogen production process from glycerol is included (Fig. 5.21). The number of process alternatives for this option is 1.8×10^8. For the screening step by using the highest productivity as a criteria and the easiest separation, the number of alternatives is reduced to 42. The reduced superstructure is shown in Fig. 5.22

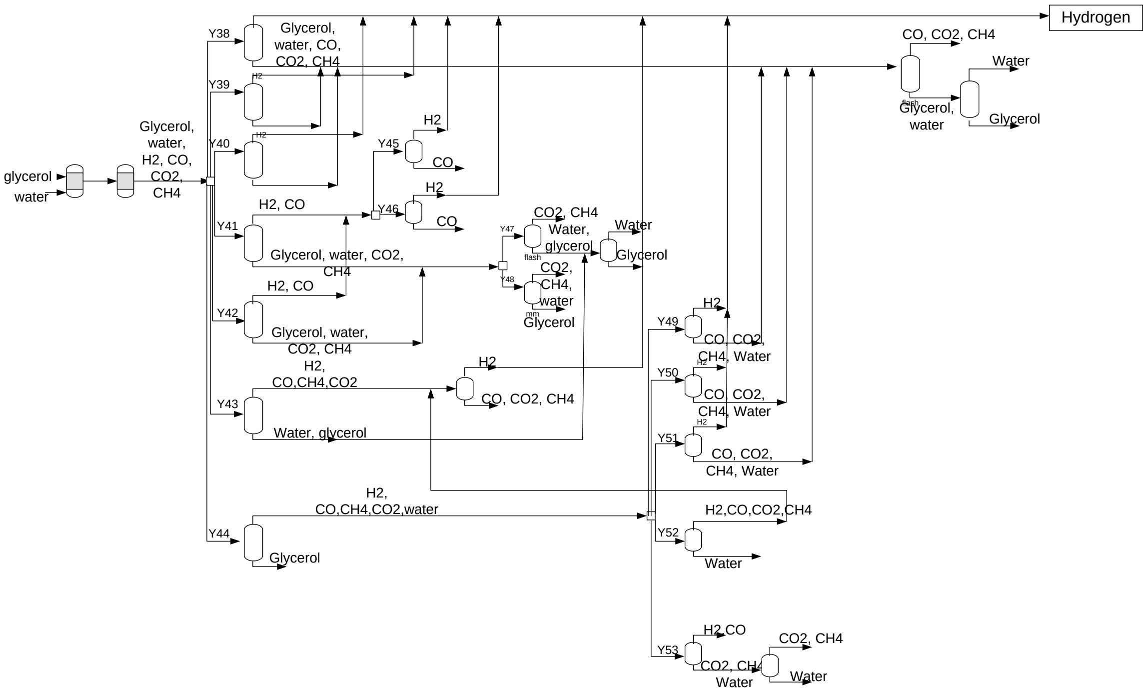


Fig. 5.21 The superstructure for hydrogen production.

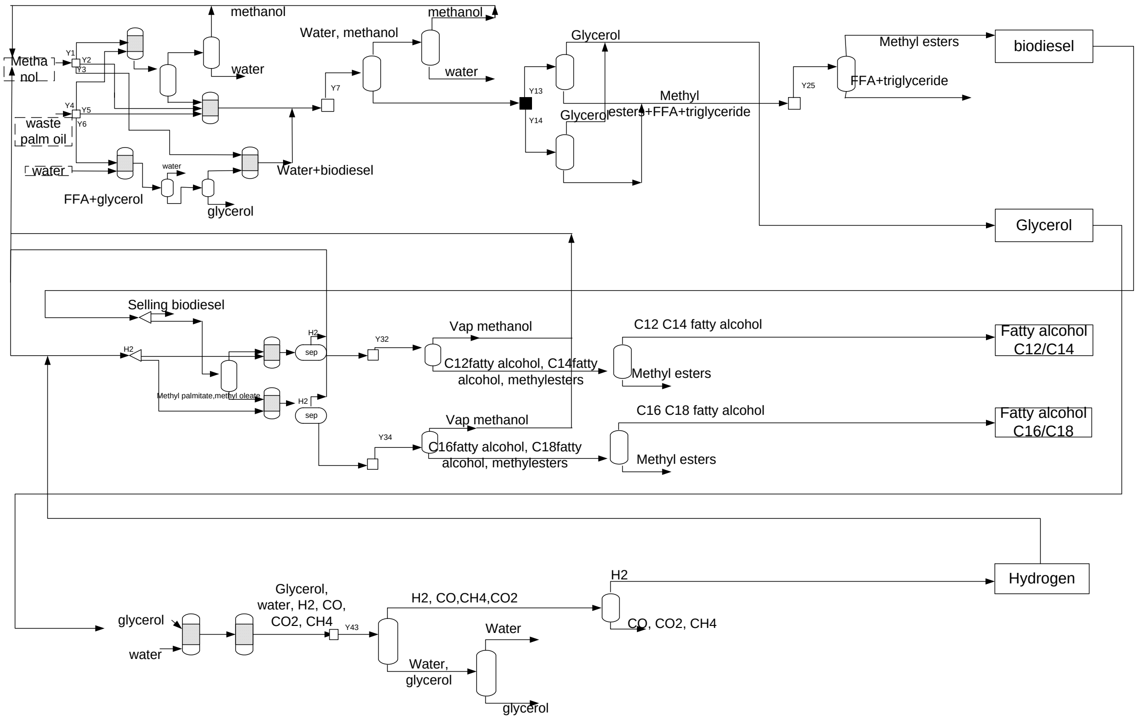


Fig. 5.22 The flowsheet of alternative processes for biodiesel production integrated with hydrogen and fatty alcohol productions.

Unit operations for biodiesel and fatty alcohol productions are the same as the previous process design. For the hydrogen production process, flash separator is used to separate steam from other gaseous components in the first separation task while in the second separation task, membrane is employed to purify hydrogen. The remaining process alternatives are further analyzed through the economic analysis. It is noted that the fraction of biodiesel to produce fatty alcohol is assumed to be 0.4 because of the availability of glycerol to produce hydrogen. The results show that the alkali catalyzed process for biodiesel production integrated with hydrogen and fatty alcohol productions is the best economical process. The results of the screening procedure are shown in Table 5.8. It is noted that the NPV of the biodiesel process integrated with hydrogen and fatty alcohol processes (6.33x10^8\$/year) is lower than that of the biodiesel process with fatty alcohol production ($7.88x10^8$\$/year). This indicates that the use of glycerol for hydrogen production is uneconomical for the design conditions considered. A more detailed study is necessary, however, to establish the conditions under which this may become economically feasible.

Table 5.8 Screening alternative for biodiesel production integrated with hydrogen and fatty alcohol productions

	Criteria	Method	Remaining process	Reduced step		
				Biodiesel production	Fatty alcohol production	Hydrogen production
1	-	Review literature	5.39×10^{8}	54 cat → 6 → 11 → 4 R → S1 → S2 → S3 14,256 processes	2 → 6 → 2 R → S1 → S2 24 processes	25 → 7 → 9 R → S1 → S2 1,575 processes
2	Palm oil is considered as raw material	Interesting raw material	1.8×10^{8}	19 cat → 6 → 11 → 4 R → S1 → S2 → S3 5,016 processes	2 → 6 → 2 R → S1 → S2 24 processes	25 → 7 → 9 R → S1 → S2 1,575 processes
3	Highest productivity	Calculation the kg product/ kg oil	1.4×10^{6}	7 cat → 6 → 11 → 4 R → S1 → S2 → S3 1,848 processes	1 → 4 → 1 R → S1 → S2 4 processes	3 → 7 → 9 R → S1 → S2 189 processes
4	Highest driving force	Calculate the adjacent properties ratios	42	7 cat → 1 → 2 → 1 R → S1 → S2 → S3 14 processes	1 → 1 → 1 R → S1 → S2 1 process	3 → 1 → 1 R → S1 → S2 3 processes
5	Limitation of separation task	LLE diagram	21	7 cat → 1 → 1 → 1 R → S1 → S2 → S3	1 → 1 → 1 R → S1 → S2	3 → 1 → 1 R → S1 → S2
6	Highest NPV	Economic analysis	1	1 cat → 1 → 1 → 1 R → S1 → S2 → S3	1 → 1 → 1 R → S1 → S2	1 → 1 → 1 R → S1 → S2

5.4 Conclusions

The systematic design of processes for multiple main products plus side products has been presented and applied for biodiesel production integrated with fatty alcohol production. Although the methodology has been highlighted in this work for two main products, it is generic, in principle. By increasing the number of renewable sources and main products, the model for an optimal biorefinery can be obtained. The mathematically complex problem has been managed by decomposing it into different hierarchical levels. According to the methodology, a heterogeneous acid catalyzed process for biodiesel production integrated with fatty alcohol production is better than other process alternatives. Process intensification improves the process by reducing heat duties and production costs. When glycerol obtained from biodiesel production is employed to produce hydrogen for use in fatty alcohol production, an alkali catalyzed process for biodiesel production integrated with hydrogen and fatty alcohol productions is the best process alternatives. The results also point out that the use of glycerol for hydrogen production is uneconomical. Note also that if the biodiesel and fatty alcohol process is located as part of a chemical process network where excess hydrogen is likely to be available, then the optimal process will become even more profitable.

CHAPTER VI

APPLICATION OF METHODOLOGY FOR DESIGN REACTIVE DISTILLATION

Application of proposed the methodology for design reactive distillation is presented through a case study, biodiesel production. This chapter is divided into 2 case studies. The first study is involving the production of biodiesel from pure palm oil by using alkali catalyst. Another case study is to the production of biodiesel from waste cooking oil by using heterogeneous acid catalyst.

6.1 Case study 1 : biodiesel production using alkali catalyst

Step 1 : List the components

There are 6 components in the process such as triglycerides, diglycerides, monoglycerides, methanol, glycerol and methyl esters. However, diglycerides and monoglycerides are not considered because of the lack of informations of properties such as boiling point. Therefore, the number of components is reduced to 4 components. Triolein is represented as triglyceride in palm oil. While methyl oleate is represented as biodiesel or methyl ester.

Step 2 : Compute ratio of boiling point

In this step, the boiling point of components is ranked increasing order. Then ratio of boiling point of adjacent component is computed as shown in table 6.1. It presents that ratio of boiling point of methanol and glycerol is the highest value. Thus, only methanol is removed at the top of the column, while other components are obtained at the bottom.

Table 6.1 The ratio of boiling point of adjacent components for case 1

Component	Ratio of boiling point ($^oC/^oC$)
Glycerol/Methanol	4.465
Methyl oleate/Glycerol	1.1
Triolein/Methyl oleate	1.47

Step 3: Define elements and compute element fraction

Regarding the biodiesel production system considered, there are 4 components with 3 elements. Triolein contains element A and element C while methyl oleate contains element A and element B. Element B is pure methanol while element C is pure glycerol. In this work, element A, element B, and element C are defined as:

Element A is $CH_2(CH_2)_{14}CH{=}CHCO$
Element B is CH_3OH
Element C is $CH_2OHCHOHCH_2OH$

Four components can be writen to element representation as shown in table. 2 and element fraction is computed in eq.6.1-6.3. Transesterification of triolein can be writen in term of element equation as shown in eq.6.4

Table 6.2 Formula matrix of transesterification of triolein

component	Element		
	A	B	C
Triolein (x_1)	3	0	1
Methanol(x_2)	0	1	0
Glycerol(x_3)	0	0	1
Methyl oleate(x_4)	1	1	0

$$W_A = \frac{3x_1 + x_4}{4x_1 + x_2 + x_3 + 2x_4} \tag{6.1}$$

$$W_B = \frac{x_2 + x_4}{4x_1 + x_2 + x_3 + 2x_4} \tag{6.2}$$

$$W_C = \frac{x_1 + x_3}{4x_1 + x_2 + x_3 + 2x_4} \tag{6.3}$$

$$\mathrm{A_3C + 3B \leftrightarrow 3AB + C} \tag{6.4}$$

Element fraction in vapor phase is computed by using ICAS-PDS at fixed operating pressure and temperature. In this work, pressure of 1 atm and temperature of 414K are defined. The mole fraction of components in liquid phase and vapor phase is shown in table 6.3. It is found that methanol is only the component that can vaporize.

Table 6.3 Mole fraction in liquid phase and vapor phase of different components

Component	Mole fraction	
	Liquid phase	Vapor phase
Triolein	0.05	0
Methanol	0.66	0.998
Methyl oleate	0.24	0.0019
Glycerol	0.06	0.0016

Step 4: Identify the separation task

From table 6.3, methanol is only the component that can vaporize. Therefore, separation task of this case study is to separate excess methanol from product mixtures. Methyl oleate and glycerol are obtained at the bottom of reactive distillation. Few number of reactive stages is required for biodiesel production.

Step 5 : Process simulation

The production of biodiesel from the tranesterification of palm oil and methanol with sodium hydroxide catalyst is studied in literatures (Narvaéz et al., 2007). In this work, triolein is assumed as triglyceride and methyl oleate is presented as methyl ester. Although rate expressions of reactions of triglyceride, diglyceride and monoglyceride are shown as follows open literature, overall transesterification is used as shown in equation (6.5).

$$\mathrm{TG} + 3\mathrm{CH_3OH} \leftrightarrow \mathrm{GL} + 3\mathrm{RCOOCH_3} \qquad (6.5)$$

where TG, CH_3OH, GL, and $RCOOCH_3$ denote the triglyceride, methanol, glycerol and methyl ester (biodiesel), respectively.

Standard condition

At the standard condition, the feed streams at the flow rates of 46.33 kmol/h. and ratio of methanol to oil at 6 to 1, are separately fed to the reactive distillation column at the first stage. While methyl oleate and glycerol are obtained at the bottom of column. The configuration of reactive distillation is shown in fig. 6.1. The column is operated at pressure of 1 atm with the reflux ratio of 3, feed temperature of 25 ^{o}C and the reboiler duty of 1.2×10^{7} kJ/h. From fig. 6.2, temperature profile is stable. It implies that it is not necessary to increase the number of stage.

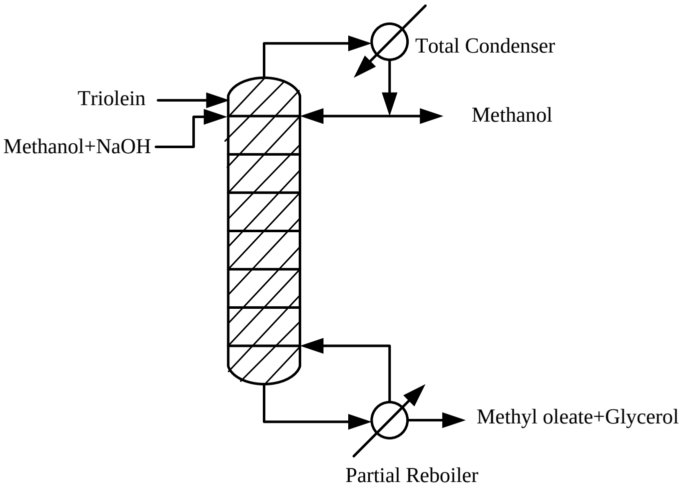


Fig. 6.1 Configuration of reactive distillation

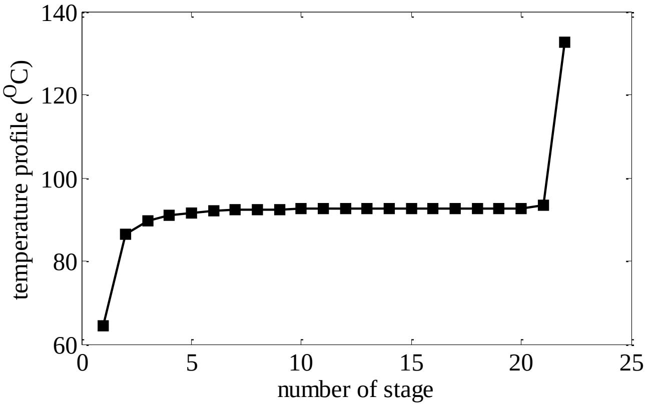


Fig. 6.2 Temperature profile at standard conditions

6.1.5.2 Effect of number of reactive stage on fraction of elements

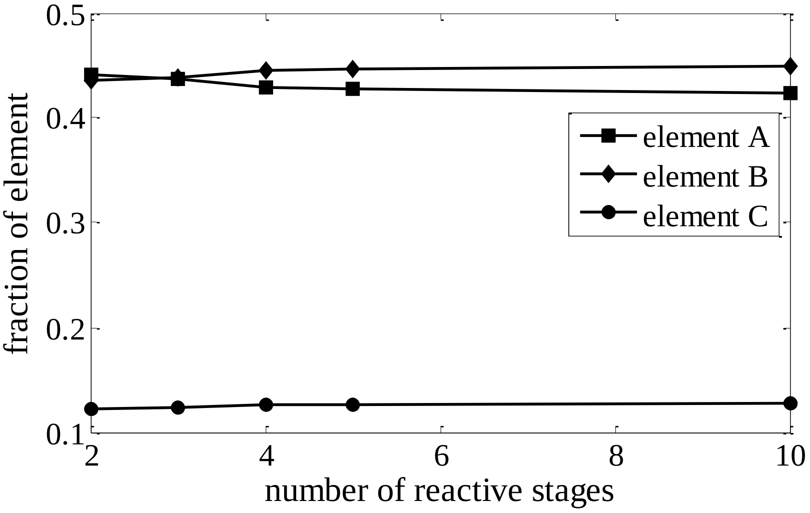


Fig. 6.3 effect of number of reactive stages on fraction of element A, B and C

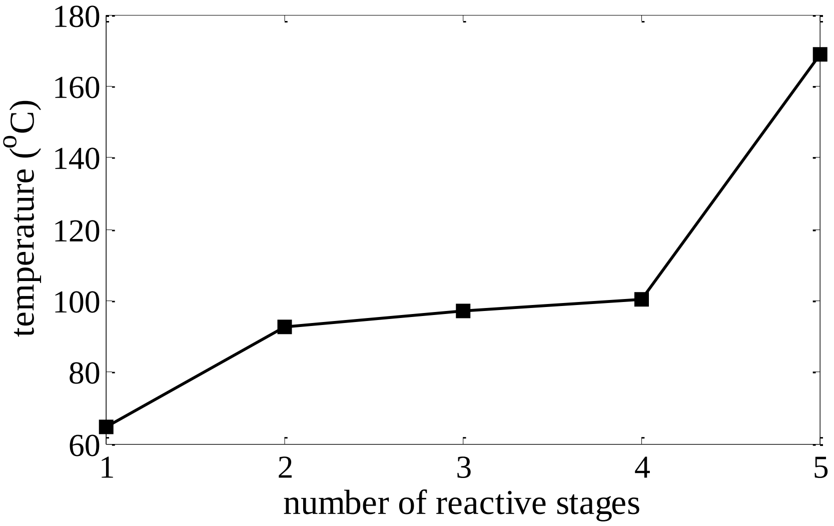


Fig. 6.4 temperature profile when number of reactive stage is 3 stages

Effect of a number of reactive stages is investigated as shown in Fig. 6.3. Although reactive flash operator is recommended to produce biodiesel, reactive distillation is preferred for the production because conversion can be nearly completed. Although at a number of reactive stages of 3 stages, amount of methyl ester occurred at the highest content. The suitable number of reactive stages is 2 stages because capital cost is lower than the number of reactive stage of 3 stages. Fig 6.4 shows that temperature profile is quite stable when the number of reactive stages is 2 stages. It means that the number of reactive stages of 2 stages is enough stages for biodiesel production.

6.1.6 Step 6: Determine suitable parameters

6.1.6.1 Effect of ratio of methanol

Fig 6.5 shows the effect of ratio methanol to oil on fraction of element A, element B and element C, respectively. It presents that increasing ratio of methanol to oil reduce the fraction of element A. While element B has an opposite trend due to the dilution effect of unreacted methanol. The combination of element A and element B leads to convert triglyceride to methyl ester (element AB). The suitable ratio of methanol to oil is 4.3 because fraction of element A and element B is equal at 0.43. At this value, it implies that amount of methyl ester occurred the highest content while amount of excess methanol and unreacted triglyceride have the lowest content. Fig. 6.6 shows ternary phase diagram with different ratio of methanol to oil where No. 1, 2, 3, 4, 5, and 6 are ratio of methanol to oil at 3, 3.5, 4, 4.5, 5 and 6, respectively. It shows that pure methyl ester is obtained at W_A and W_B of 50%. While pure triolein is obtained at WA and WC of 70% and 30%. This is because triolein consists of element A in 3 elements and element C in 1 element as shown in formula matrix. As the W_A and W_B do not equal to 50% in all points. the bottom product is not pure methyl ester; methanol is mixed with the biodiesel product. From the simulation results, the element fraction at the top is element B that is pure methanol. This means that separation task cannot separate one product from the other products; therefore, biodiesel product is mixed with methanol and glycerol. From the ternary phase diagram, reaction is not feasible below 0.5 of elements A and B because element A is distributed in triolein and methyl oleate and there is no compound consisting of pure element A.

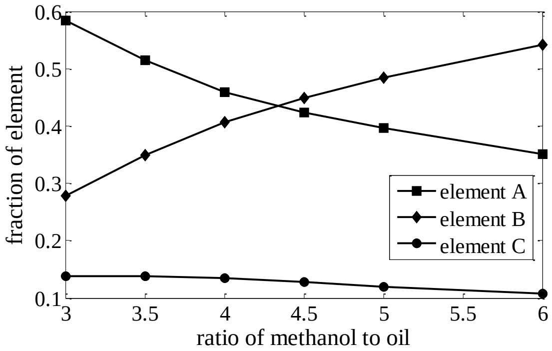


Fig. 6.5 effect of ratio of methanol to oil on fraction of element A, B and C

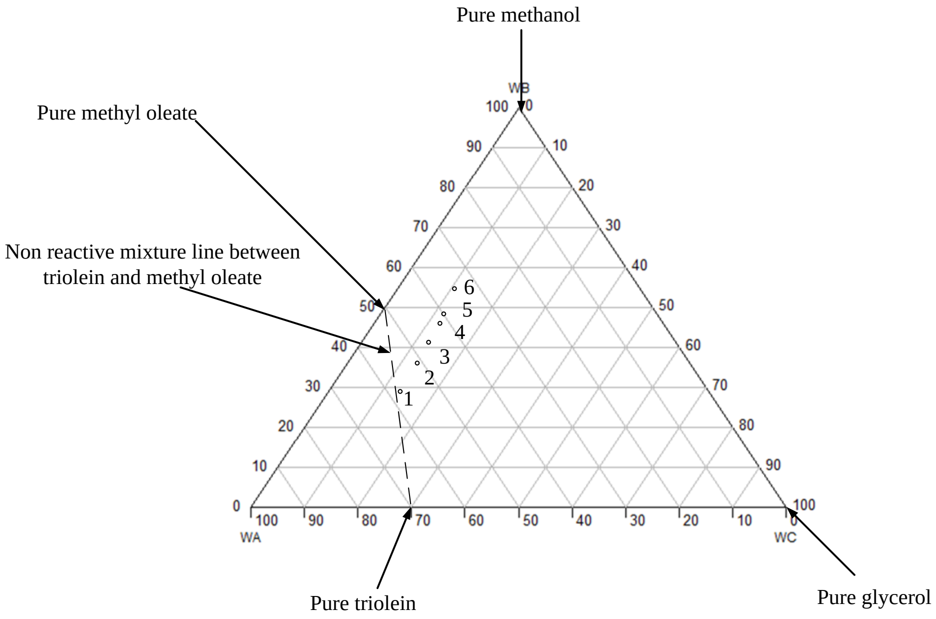


Fig. 6.6 Ternary phase diagram for transesterification of triolein and methanol with different ratio of methanol to triolein

6.1.6.2 Effect of Distillate rate and reflux ratio

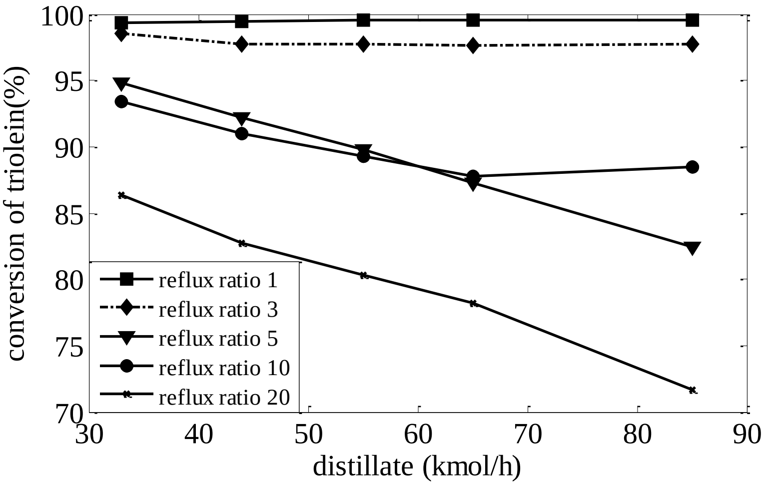


Fig. 6.7 effect of distillate rate on conversion of triolein

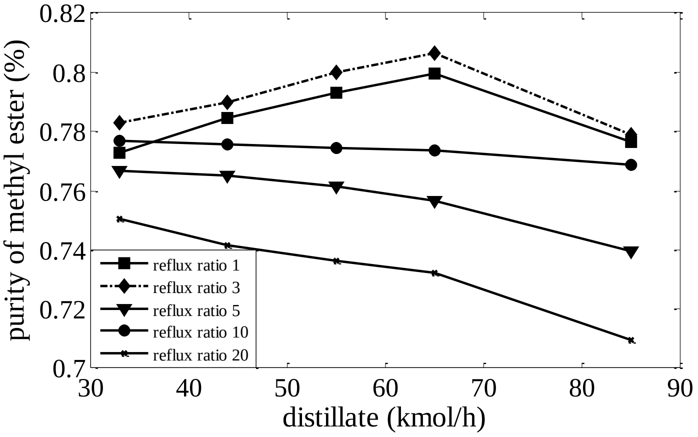


Fig. 6.8 effect of distillate rate on purity of methyl esters

Fig. 6.7 shows the effect of distillate rate on conversion when ratio of methanol to oil is 4.3. At lower reflux ratio, increasing of distillate rate improves the conversion because the reboiler duty and temperature in the reaction section increases. However, the performance of reactive distillation for biodiesel production is degraded at high distillate. This is caused by a large amount of methanol in the distillate stream that is removed from the column. Increasing reflux ratio results in increasing of conversion. This is because higher reflux ratio enhances high methanol that recycle back to the column and leads to lower temperature profile within column. Fig. 6.8 shows effect of distillate rate and reflux ratio on purity of methyl ester. Higher reflux ratio results in lower purity of methyl ester. This is because methanol that recycled back into the column is driven at the bottom of column. The suitable distillate rate and reflux ratio are 65 kmol/h and 3, respectively.

6.2 Case study 2 : biodiesel production using heterogeneous acid catalyst

In general, pure vegetable oils are used as feedstock to synthesize biodiesel; however, their price highly increases a biodiesel production cost. As a result, the use of waste cooking oil as an economical feedstock for biodiesel production seems to be an attractive option. However, a conventional alkali-catalyzed process for biodiesel production is sensitive to the impurity of raw materials, i.e., free fatty acid (FFA), which is produced during cooking processes. To overcome such a difficulty, the esterification of waste cooking oil with alcohol using acid catalyst is used for reducing FFA. Although there are a number of catalysts for biodiesel production from waste cooking oil such as heterogeneous acid catalysts and enzyme catalysts. Heterogeneous process for biodiesel production from waste cooking oil is more attractive options than other processes. In addition, solid acid catalyst can be recycled, easily removed and can simultaneously catalyze esterification and transesterification (Lien et al, 2010 and Peng et al., 2008)

In this case study, the design of reactive distillation for biodiesel production using heterogeneous acid catalyst is performed. Combining separation of water and methanol from reaction step to improve conversion of equilibrium-limited reaction has been considered. According to methodology, the number of reactive stages is determined. Diglycerides and monoglycerides are neglected to consider; therefore, overall transesterification is assumed.

Step 1 : List the components

There are 6 components in the process such as triolein, methanol, glycerol, methyl oleate, oleic acid and water.

Step 2 : Calculate ratio of boiling point

In this step, the boiling point of components is ranked increasing order. Boiling point ratios of adjacent components are computed to determine which component can be separated at the top of column. The binary ratio of boiling point is shown in table 6.4. It presents that ratio of boiling point of water and glycerol is the highest value; therefore, methanol and water are removed to the top of column while other components such as methyl oleate, glycerol, unreacted triolein are remained at the bottom of column. It can be seen that reactive distillation can separate light product from heavy product.

Table 6.4 the ratio of boiling point of adjacent components

Component	Ratio of boiling point ($^{o}C/^{o}C$)
Water/Methanol	1.5625
Glycerol/Water	2.88
Methyl oleate/Glycerol	1.1
Oleic acid/Methyl oleate	1.04
Triolein/Oleic acid	1.39

Step 3: Define elements and compute element fraction

Because biodiesel is produced from waste cooking oil, two reactions such as transesterification of triolein and esterification of oleic acid are involved. In this case, overall transesterification is assumed and writen in element reaction as in eq 6.6 and 6.7, respectively. The element fractions of element A, element B, and element C are defined in eq 6.8 to 6.10.

$$\mathrm{TG} + 3\mathrm{CH_3OH} \rightarrow \mathrm{GL} + \mathrm{ME} \tag{6.6}$$

$$\mathrm{A_3C} + 3\mathrm{B} \leftrightarrow 3\mathrm{AB} + \mathrm{C} \tag{6.7}$$

Where Element A is $CH_2(CH_2)_{14}CH{=}CHCO$

Element B is CH_3OH

Element C is $CH_2OHCHOHCH_2OH$

$$W_A = \frac{3x_1 + x_4}{4x_1 + x_2 + x_3 + 2x_4} \tag{6.8}$$

$$W_B = \frac{x_2 + x_4}{4x_1 + x_2 + x_3 + 2x_4} \tag{6.9}$$

$$W_C = \frac{x_1 + x_3}{4x_1 + x_2 + x_3 + 2x_4} \qquad (6.10)$$

For esterification reaction of oleic acid, the reaction is shown in eq 6.11 and element equation of esterification is shown in eq 6.12. The element fraction of components of esterification are shown in eq 19-21.

$$\mathrm{RCOOH} + \mathrm{CH_3OH} \rightarrow \mathrm{H_2O} + \mathrm{ME} \qquad (6.11)$$

$$\mathrm{AD} + \mathrm{B} \leftrightarrow \mathrm{AB} + \mathrm{D} \qquad (6.12)$$

Where Element A is $CH_2(CH_2)_{14}CH{=}CHCO$

Element B is CH_3OH

Element D is H_2O

$$W_A = \frac{x_5 + x_4}{2x_1 + x_2 + x_6 + 2x_4} \qquad (6.13)$$

$$W_B = \frac{x_2 + x_4}{2x_1 + x_2 + x_6 + 2x_4} \qquad (6.14)$$

$$W_D = \frac{x_1 + x_6}{2x_1 + x_2 + x_6 + 2x_4} \qquad (6.15)$$

Component of esterification reaction of oleic acid can be writen in term of element as shown in table 6.5.

Table 6.5 Formula matrix of esterification of oleic acid

component	Element		
	A	B	D
Oleic acid (x_5)	1	0	1
Methanol(x_2)	0	1	0
Water (x_6)	0	0	1
Methyl oleate(x_4)	1	1	0

To consider element fraction of overall reactions combining transesterification and esterification, element fraction of components is defined in eq 6.16– 6.18. Components of transesterification and esterification can be writen to element representation as shown in table 6.6. It can be seen that there are 4 elements in the system. Triolein consists of element A and element C while methyl oleate consists of element A and element B. Element B is pure methanol while element C is pure glycerol. Oleic acid contains element A and element D; Therefore, element D is pure water.Element A is $CH_2(CH_2)_{14}CH{=}CHCO$, Element B is CH_3OH, Element C is $CH_2OHCHOHCH_2OH$. Element D is H_2O. Element fraction is computed in eq.25-28.

$$W_A = \frac{3x_1 + x_4 + x_5}{4x_1 + x_2 + x_3 + 2x_4 + 2x_5 + x_6} \tag{6.16}$$

$$W_B = \frac{x_2 + x_4}{4x_1 + x_2 + x_3 + 2x_4 + 2x_5 + x_6} \tag{6.17}$$

$$W_C = \frac{x_1 + x_3}{4x_1 + x_2 + x_3 + 2x_4 + 2x_5 + x_6} \tag{6.18}$$

$$W_A = \frac{x_5 + x_6}{4x_1 + x_2 + x_3 + 2x_4 + 2x_5 + x_6} \tag{6.19}$$

Table 6.6 Formula matrix of esterification and transesterification

component	Element			
	A	B	C	D
Triolein	1	0	1	0
Methanol	0	1	0	0
Glycerol	0	0	1	0
Methyl oleate	1	1	0	0
Oleic acid	1	0	0	1
Water	0	0	0	1

For pressure at 5.5 atm and temperature at 414 K, mole fraction are computed in table 6.7. It can be seen that methanol and water can vaporize so element fraction in vapor phase is below 0.99. Therefore, Lewis Methason's method is applied to determine the suitable number of reactive stages.

Table 6.7 Mole fraction in liquid phase and vapor phase of different components for biodiesel production from waste cooking palm oil

Component	Mole fraction	
	Liquid	vapor
Methanol	0.6487	0.9387
Water	0.0452	0.0611
Methyl oleate	0.2312	0
Gycerol	0.0692	0.0002
Oleic acid	0.0012	0
Triolein	0.0044	0

Step 4: Identify the separation task

Separation task of this case study is to separate products. Methanol and water are obtained at the top of column, while methyl oleate and glycerol are obtained at the bottom.

Step 5: Determine the suitable number of reactive stages

In this step, Lewis-Methason method is applied to determine element fraction in liquid phase and vapor phase for each stage. Product specifications such as product compositions, boilup ratio and bottom flow rate are specified to determine the number of reactive stages. The information of product specifications is shown in table 6.8. However, it cannot specify glycerol in product at small value because glycerol cannot be separated from methyl oleate. It is noted that amount of glycerol is occurred 25 % by mole of total product that is element fraction of C is approximately at 0.12. Table 6.8 and table 6.9 show the details of the design of this method. The design is startly from define product specification at the top and bottom product corresponding with boilup ratio and reflux ratio. Element balance around stages and over balance are also considered. Operating pressure is fixed at 5.5 atm and ratio of methanol to oil is 4.5. From table 6.8 and 6.9, it can be seen that 3 reactive stages plus condenser are required to achieve product specification.

Table 6.8 product specification for biodiesel production from waste cooking oil

composition	value
Triolein	0.0174
Methanol	0.12
Glycerol	0.194
Methyl oleate	0.65
Water	0.009
Oleic acid	0.006
Reboil ratio	2.694
Bottom flow rate	138 kmol/h

Table 6.9 Calculation of element fraction for each stage by using Lewis Methason's method

Stage	Element fraction in liquid phase			
	A	B	C	D
Condenser	0	0.8923	0	0.1075
1	0.2269	0.6318	0.0676	0.0737
2	0.2269	0.6537	0.0676	0.052
3	0.161	0.7108	0.084	0.044
Reboiler	0.414	0.452	0.124	0.0094

Table 6.10 Calculation of element fraction for each stage by using Lewis Methason's method

Stage	Element fraction in vapor phase			
	A	B	C	D
1	0	0.8923	0	0.1075
2	0	0.9207	0	0.0792
3	0	0.9461	0	0.0538
Reboiler	0	0.8751	0.0589	0.0584

Step 6 : Process simulation

Fig. 6.9 shows element profile along reactive distillation column. It can be seen that the rigorous simulation results are similar to calculation of element fraction by using Lewis Methason's method. Element fraction of A and B are closely 0.5 at the reboiler. It implies that amount of methyl ester occurred the high content while amount of excess methanol and unreacted triglyceride are low content. In addition, reactive distillation can separate water from methyl oleate because element D is very low content.

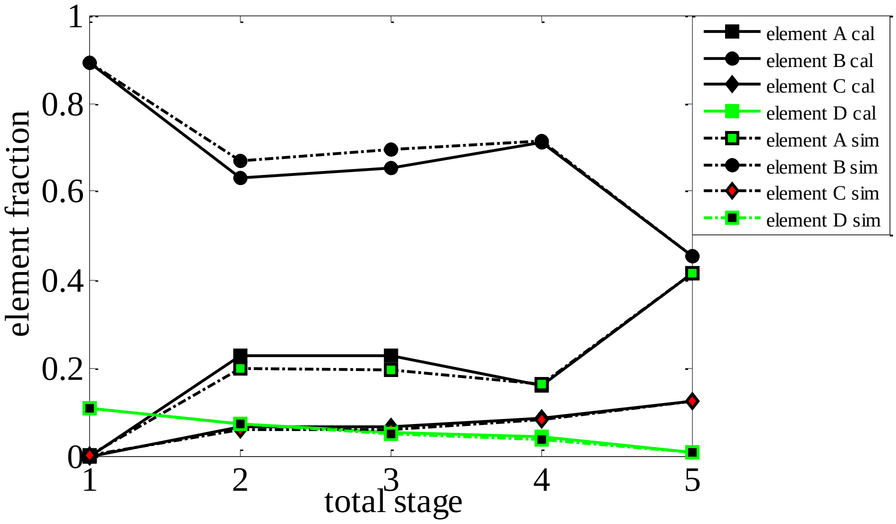


Fig. 6.9 Element profile comparison of calculation and simulation

Step 7: Determine of suitable parameters

Effect of ratio of methanol to oil

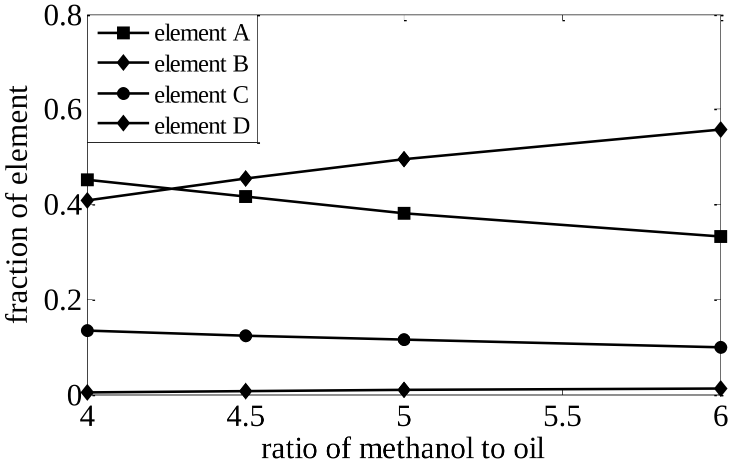


Fig. 6.10 Effect of ratio of methanol to oil on fraction of element A, B and C

Fig. 6.10 shows the effect of ratio of methanol to oil of elements. The suitable ratio of methanol to oil is similar to biodiesel production from palm oil although vegetable oil contains free fatty acid contents. The suitable ratio of methanol to oil is obtained when element fraction of A and B are closely 0.5 that is the lowest triolein contents and methanol contents in methyl oleates.

6.3 Conclusion

A methodology including element based method and heuristic method is proposed for design of reactive distillation. Furthermore, this methodology is flexible in any case of multi-components especially in case of a large different of boiling points of components. The element based method is used to find suitable configuration and operating parameters of the reactive distillation. In this work, the implement of methodology is used to design reactive distillation for biodiesel productions from pure vegetable oil and waste cooking oil. From calculation of element fraction for biodiesel production from pure vegetable oil, it can be concluded that the suitable number of reactive stages is 2 stages. Therefore, biodiesel production is a special case that increasing the number of reactive stages is not necessary to improve the performance. The results show that distillate rate is the most important parameter because it can change reboiler temperature. For biodiesel production from waste cooking oil, triolein is assumed as triglyceride while oleic acid is assumed as free fatty acid in waste cooking oil. In this case, reactive distillation can separate products. The number of reactive stages is 3 stages at product specification.

CHAPTER VII

APPLICATION OF METHODOLOGY FOR DESIGN HEAT INTEGRATION OF REACTIVE DISTILLATION

Application of proposed the methodology for heat integration of reactive distillation is presented through a case study, biodiesel production by using reactive distillation from waste cooking oil. Because high conditions are required to operate biodiesel production from waste cooking oil, heat integration of reactive distillation can reduce the energy consumption.

7.1 Case study : Biodiesel production by using reactive distillation from waste cooking oil

7.1.1 Configuration of conventional process

In this case study, a biodiesel production from waste cooking oil using heterogeneous acid catalyst is studied. Trilinolein is represented as triglyceride while oleic acid is represented as free fatty acid. A reactive distillation is applied to produce the biodiesel product (methyl ester) at high pressure operation. Crude biodiesel consisting of biodiesel, methanol, glycerol and unreacted triglyceride is obtained at the bottom of the reactive distillation column while excess methanol is removed at the top of the column. This process is compared with alkali catalyzed process using a reactive distillation. A conventional reactive distillation for biodiesel production is shown in Figure 7.1.

Reactive distillation process consists of a reactive distillation column and a purification process. The transesterification and esterification reactions are occurred simutaneously in the reaction zone of the reactive distillation. A rigorous simulation is required in order to determine the suitable of parameters such as amount of catalyst, operating pressure, the number of stripping stages, the number of rectifying stages, the number of reactive stages and feed location. UNIQUAC model is used to predict the missing data.

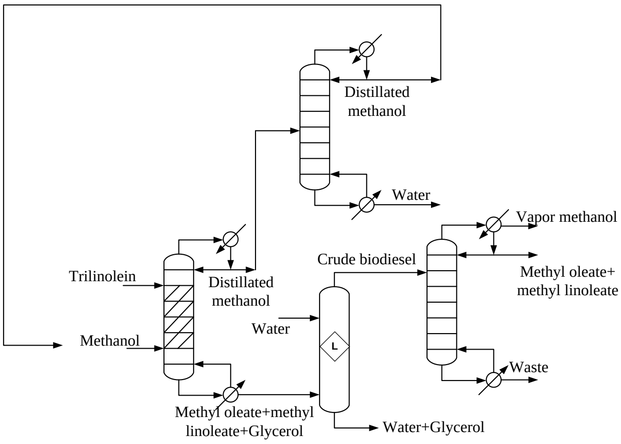


Fig. 7.1 Conventional reactive distillation process for heterogeneous acid catalyzed process.

Effect of catalyst

The effect of catalyst loading on total annual cost with different column pressure is performed in figure 7.2. It shows that total annual cost increases with an increasing of catalyst loading and then decreases at higher than optimum catalyst loading. This is because increasing of catalyst loading per stage decreases the trilinolein concentration at the bottom stream of reactive distillation thus requiring less reflux ratio and reboiler heat duty to achieve the desired product specifications. However, as adding catalyst loading more than optimum value requires more condenser duty that leads to be higher operating cost.

According to the figure 7.2, the column pressure also affects on total annual cost. Increasing column pressure results in an increasing of capital cost due to higher reaction rate and an increasing of column diameter. Because transesterification and esterification are endothermic reactions, the temperature in reactive zone increases with an increasing of column pressure in order to decrease the reactant composition in the bottom stream. Consequently, less reboiler heat duty is required with an increasing of column pressure. Figure 7.3 shows the effect of catalyst loading and operating pressure on vapor boilup. It presents that operating at low pressure increases the requirement of vapor boilup. A lot of vapor boilup leads to higher net vapor rate within the column; therefore, reboiler duty is required to increase reaction rate. In addition, lower column pressure results in low reaction rate thus require large vapor boilup. There is a different optimum catalyst loading per stage with different operating column pressure that minimizes vapor boilup. At lower column pressure, catalyst loading and vapor boilup are required so energy cost is increased. The simulation results show that the optimum catalyst loading per stage and column pressure are 1.1kg and 5.5 bar, respectively with the value of total annual cost 1×10^6 \$/year.

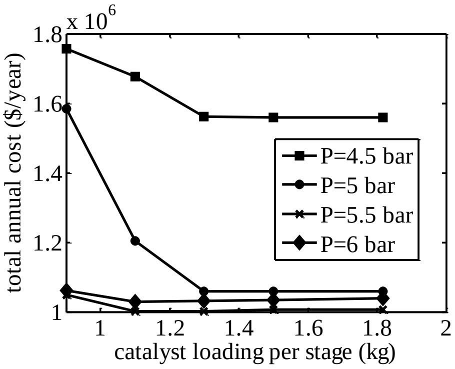


Fig. 7.2 Effect of catalyst loading per stage (kg) on total annual cost with different column pressure

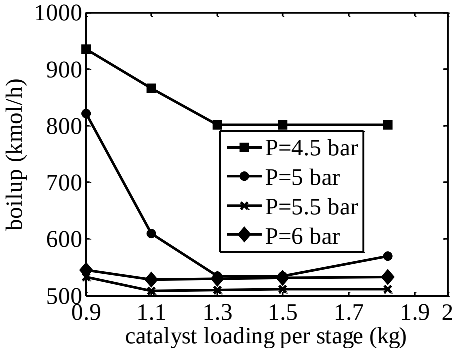


Fig.7.3 Effect of catalyst loading per stage (kg) on boilup (kmol/h) with different column pressure

Effect of reactive stage, rectifying stage and stripping stage

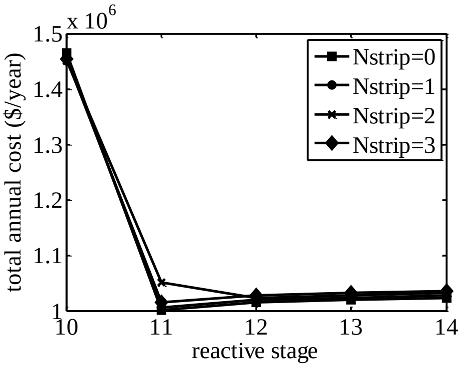


Fig.7.4 Effect of a number of reactive stages of first reactive distillation for heterogeneous catalyzed process on total annual cost of a single column (a) no rectifying stage

The figure 7.4 shows that the total annual cost decreases with an increasing the number of reactive stages and then increases at higher values. This is because reflux ratio increases and the reactive distillation effluent has a higher concentration of unreacted trilinolein as the reactive stage gets lower. Thus, there is a need for more reboiler heat duty to achieve the desired product specification with less reactive stage. In addition, high condenser duty with less reactive stage increases cooling water cost affecting on operating cost. More than 11 reactive stages result in higher capital cost and catalyst cost. From this case, the minimum total annual cost is observed at N_{rxn} = 11. Adding more rectifying stage and stripping leads to high capital cost. The simulation results show that the optimum configuration of the reactive distillation column is Nrxn=11 N_{strip}=0 and N_{rec}=1with the value of total annual cost of the reactive distillation column 1×10^6 \$/year.

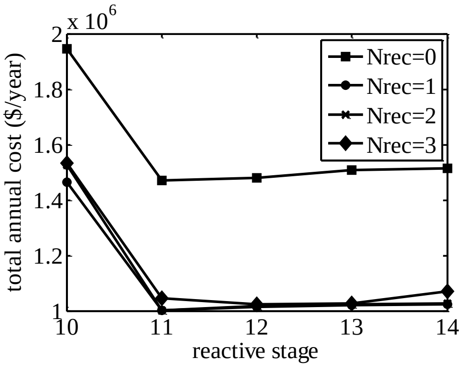


Fig. 7.5 Effect of a number of reactive stages of first reactive distillation for heterogeneous catalyzed process on total annual cost of a single column (b) no stripping stage

From simulation studies as shown in figure 7.5, it is found that the optimum configuration of reactive distillation with molar ratio of 10:1 for biodiesel production from waste cooking oil with 10 wt% of free fatty acid is 11 reactive stages and 1 rectifying stage. Whereas the optimum configuration of second distillation column is 9 total stage including of reboiler and condenser. Finally, figure 7.6 shows the composition (mass fraction) of components for the reactive distillation column. It can be seen that water content is lower than 0.05%V/V which is also followed biodiesel specification. The reboiler temperature is lower than 150 °C which is lower than decomposition temperature of biodiesel.

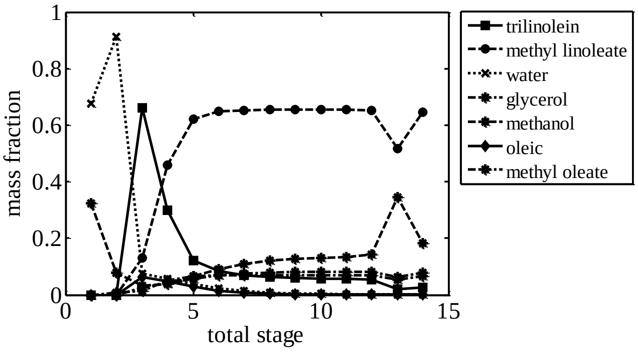


Fig. 7.6 Composition process at optimum configuration reactive distillation of heterogeneous catalyzed process

Separation water from methanol

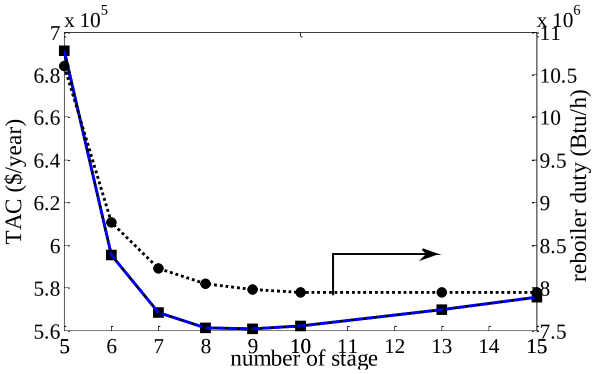


Fig. 7.7 Effect of number of stage of distillation column on total annual cost ($/year) and reboiler heat duty (Btu/h)

Fig. 7.7 shows that although reboiler heat duty is stable value at number of stage more than 9 stages, total annual cost is still increased. A mininum total annual cost at suitable number of stage is shown when composition of methanol and water is fixed at 0.99 and 0.83, respectively because of tradeoff between increasing capital cost and decreasing operating cost. In this work, the suitable number of stage of distillation column using separation of water from methanol is 9 stages. The summation of total annual cost of conventional reactive distillation and separation of methanol is 1.56×10^6 $/year.

7.2 Application of methodology of heat integrated reactive distillation

Step 1 : Define problem for heat integrated reactive distillation

The proposed methodology is applied. The methodology starts with the problem definition (Step 1). Here, the minimization of a total annual cost is considered as the objective function, as given in Equation 7.1.

$$\min TAC = OperatingCost + \frac{CapitalCost}{3} \tag{7.1}$$

subject to process model, the product specification (purity of methyl ester from reactive distillation = 84%), purity of methanol is 99.5% , production rate and binary decision variable (a selection of type of the heat integrated reactive distillation).

Step 2 : Analyze conventional reactive distillation

Step 2.1 : Identify the limitation of conventional reactive distillation

Table 7.1 shows that the performances the conventional reactive distillation using heterogeneous acid catalyzed process are less than the convenational process using alkali catalyzed process. Thus, heat integration of reactive distillation has a potential to improve the performance by reducing the energy consumption.

Table 7.1 The comparison between performance of based case design and conventional process

	Operating pressure (atm)	Performance	
		Conversion	
Conventional reactive distillation (heterogeneous acid catalyzed process)	5	97.1%	Conventional reactive distillation (heterogeneous acid catalyzed process)
Conventional reactive distillation (alkali catalyzed process)	1	98.52%	Conventional reactive distillation (alkali catalyzed process)

Step 2.2 : List components and product specification

Biodiesel production from waste cooking oil using heterogeneous catalyst involve 1 step of transesterification. Therefore, the components in the process are trilinolein, oleic acid, methanol, water, methyl oleate, glycerol, and methyl linoleate. Methyl oleate and methyl linoleate are represented as methyl esters (biodiesel).

Step 2.3 : Rank the boiling point of components

In this step, the boiling points of components (as shown in table 3) are ranked that is important for further step.

Table 7.2 The rank of boiling point of components

Component	boiling point (^oC)
Methanol	64
Water	100
Glycerol	285
Methyl linoleate	343.85
Methyl oleate	344
Oleic acid	358.85
Triolein	454.70

Step 2.4 : Compute the ratio of boiling point of components

The boiling point ratio of adjacent component is computed as shown in Table 7.3.

Table 7.3 The ratio of boiling point of adjacent components

Component	Ratio of boiling point ($^oC/^oC$)
Water/Methanol	1.45
Glycerol/Water	2.85
Methyl oleate/Glycerol	1.1
Oleic acid/Methyl oleate	1.03
Triolein/Oleic acid	1.45

Step 2.5 : Find the component at the top and bottom of column

From table 7.3, it is found that the ratio of boiling point of water and glycerol is the highest value; therefore, methanol and water are removed at the top of the column while other components, such as methyl oleate, glycerol, unreacted triolein, are removed at the bottom. It can be seen that the reactive distillation can separate the light product from the heavy product.

Step 2.6 : If the ratio is equal to 1, solvent selection is needed.

From table 7.3, the all ratio of boiling point of components are higher than 1 so the solvent for separation is not required.

Step 3 : Identify heat integrated reactive distillation

A full set of alternatives for heat integrated reactive distillation is identified (Step 3). They include HiRDC without heat exchanger, HiRDC with heat exchanger, petyuk RD, feed split multi-effect RD, HiRDC with distillation column without heat exchanger, thermally coupled indirect sequence of RD integrated with distillation column, thermally coupled direct sequence of RD integrated with distillation column, multi-effect direct split arrangement of RD, and multi-effect indirect split arrangement of RD integrated with distillation column. Thus, the number of alternatives is 10.

Step 4 : Screen the number of alternatives

Step 4.1 : Fast screen the number of alternatives.

In this step, the purity of water is considered as a criteria because water is the light key components. However, the purity of water is not mentioned that it is a waste stream. Therefore, the number of alternatives are not reduced.

Step 4.2 : Reduce the number of alternatives from ratio of boiling point of key components

The ratio of boiling point is used as criteria. Since the boiling point ratio of the key component is 2.85. the feed split multi-effect RD, HiRDC without heat exchanger, HiRDC with heat exchanger (Divided reactive distillation into two small sections) are eliminated. As a result, the number of alternatives is reduced from 10 to 7. Figure 7.8 shows the configuration of the feed split multi-effect RD. Figure 7.9 shows the configuration of Heat integrated reactive distillation without heat exchanger (divided reactive distillation into 2 sections). Figure 7.10 shows the configuration of

Heat integrated reactive distillation with heat exchanger (divided reactive distillation into 2 sections). Figure 7.12 shows the configuration of Petlyuk reactive distillation.

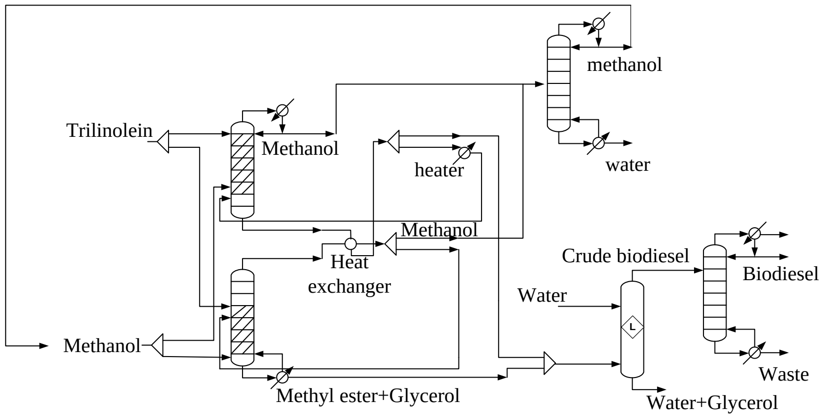


Fig. 7.8 Feed split multi-effect reactive distillation process for biodiesel production

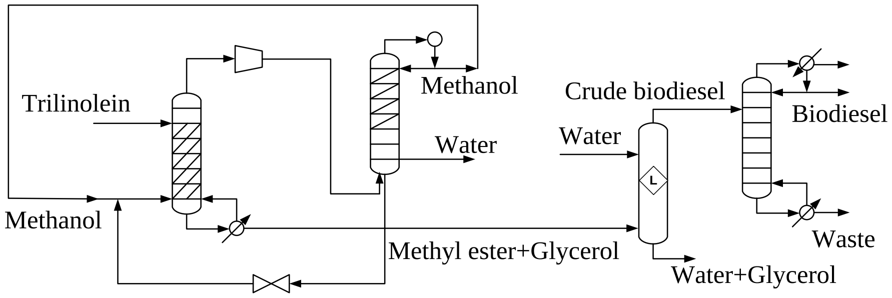


Fig. 7.9 Heat integrated reactive distillation without heat exchanger (divided reactive distillation into 2 sections)

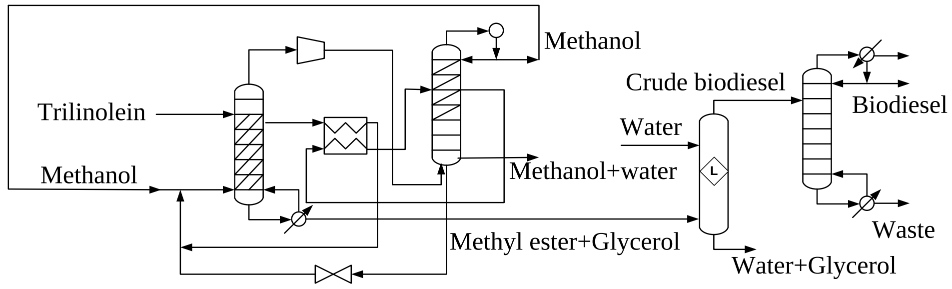


Fig. 7.10 Heat integrated reactive distillation with heat exchanger (divided reactive distillation into 2 sections)

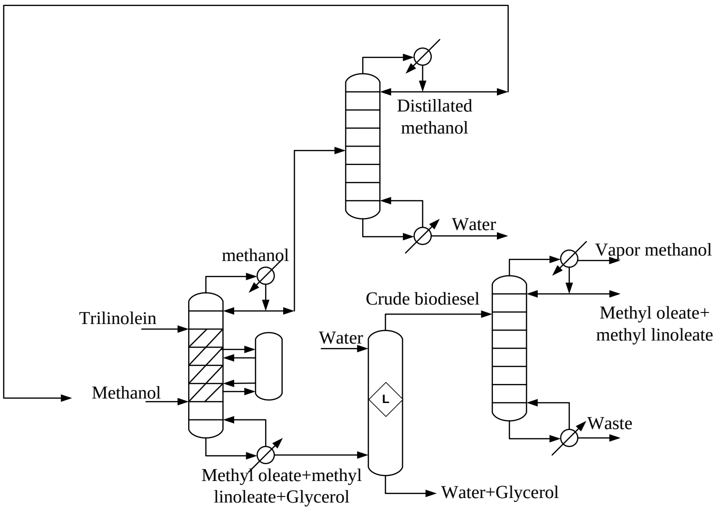


Fig. 7.11 Petyuk reactive distillation

Step 4.3 : Reduce the number of alternatives from key components

Since the key components are the light component (water) and the heavy component (glycerol), the thermally coupled direct sequence of RD integrated with distillation column are multi-effect direct split arrangement of RD are eliminated. The number of alternatives are remained 5.

Step 4.4 : limitations of the separation technique

In this step, petlyuk RD is eliminated because components in the system consist of trilinolein and water. So two liquid phase is occurred when liquid stream is driven from main column to minor column. The number of alternatives is retained 4.

Step 5 : Minimize objective function

Next, a rigorous simulation by using a process simulator is performed and the suitable process parameters, such as operating pressure, the number of reactive stages, the number of stripping stages and the number of rectifying stages are determined based on the minimization of TAC (Step 5). The most suitable configuration of the heat integrated RD is obtained at the end of this step. There are 4 remaining alternatives such as thermally coupled indirect sequence of RD integrated with distillation column, multi-effect indirect split arrangement of reactive distillation, heat integrated reactive distillation with distillation column (with heat exchanger) and heat integrated reactive distillation with distillation column (without heat exchanger). Details of this simulation step will be described in the next section.

Multi-effect indirect split arrangement reactive distillation

Figure. 7.12 shows multi-effect indirect split arrangement of reactive distillation. It is heat integration between reactive distillation and distillation column through heat exchanger which acts as a condenser for the reactive distillation and as a reboiler for the distillation column. Operating pressure of reactive distillation is raised in order to increase the temperature of vapor stream at the top of reactive disitillation column. This vapor can heat the liquid from bottom column of distillation. In this work, reactive distillation consists of reactive zone and stripping zone. Methyl oleate, methyl linoleate, and glycerol are obtained at the bottom of reactive distillation column while water and methanol are removed to the top of reactive distillation as a vapor stream. The algorithm of the design multi-effect indirect split arrangement of reactive distillation in term of minimization of total annual cost is shown in figure. 7.13. The details of effect of parameters are described at next section.

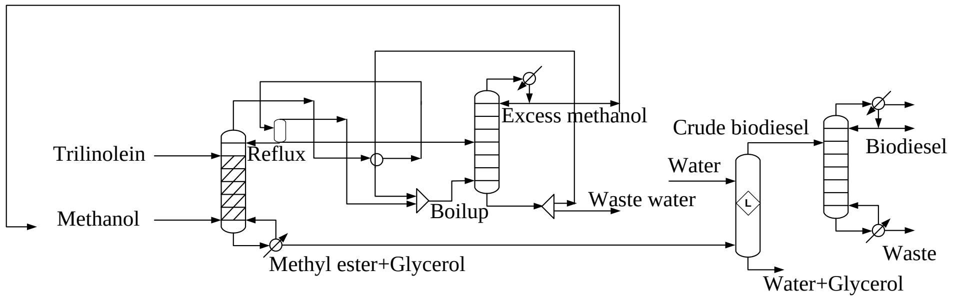


Fig.7.12 Multi-effect indirect split arrangement of reactive distillation

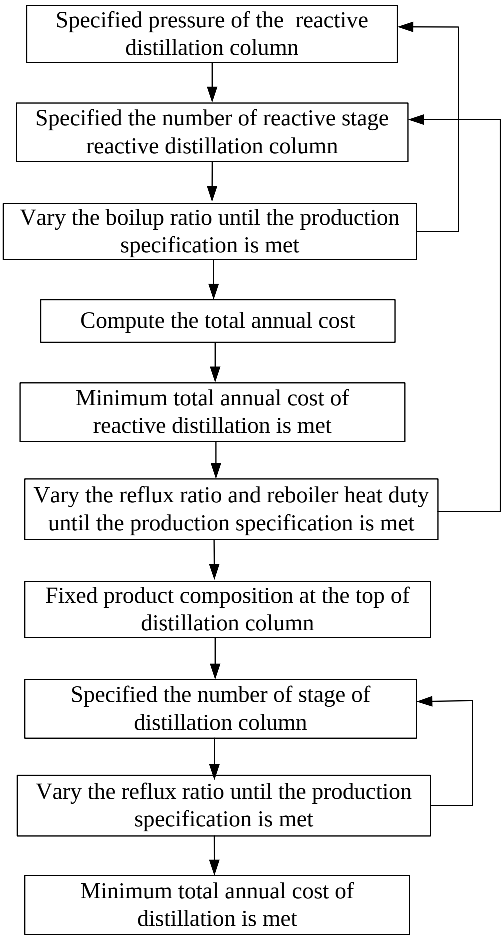


Fig. 7.13 Design procedure of multi-effect indirect split arrangement of reactive distillation for biodiesel production from waste cooking oil.

Effect of pressure

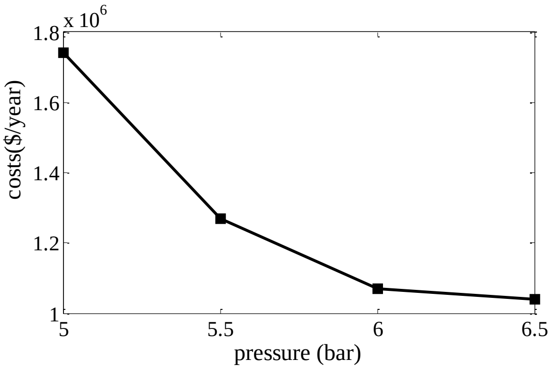


Fig. 7.14 Effect of pressure on total annual cost.

Figure. 7.14 shows that increasing of pressure results in the reduction of total annual cost because reboiler heat duty of reactive distillation decreased with an increasing of pressure. In addition, temperature within reactive distillation that leads to higher reactive rate is increased according to increasing of pressure. Unlike conventional reactive distillation, increasing of operating pressure leads to lower net vapor rate within column. Therefore, reboiler heat duty gets lower because the reduction of amount of excess methanol in distillation column which recycled back to reactive distillation. Thus less reboiler heat duty is required to achieve the desired product specifications.

Effect of reaction stage

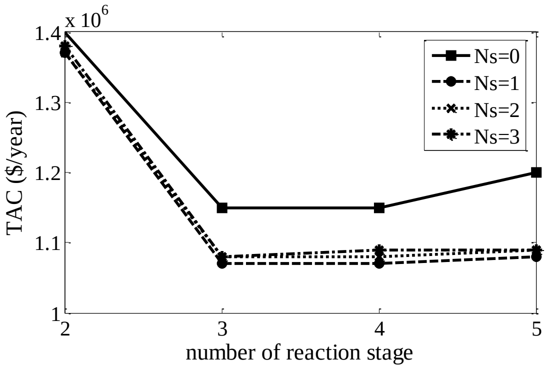


Fig. 7.15 Effect of number of reaction stages and stripping stages on total annual cost ($/year) and reboiler heat duty of reactive distillation (Btu/h)

Figure.7.15 shows that increased the number of reaction stages results in the reduction of total annual cost because there is more contacting area between reactants, thus requiring less reboiler heat duty of reactive distillation and condenser heat duty of distillation column. However, total annual cost is increased with an increasing of number of reaction stages more than 3 stages due to increasing of capital cost. The minimum total annual cost is observed at $N_{rxn} = 3$. According to figure 7.15, stripping stages are required to purify methyl ester and glycerol. Therefore, increased the number of stripping stages reduces reboiler heat duty and condenser heat duty. Adding more stripping stages lead to high capital cost so total annual cost is increased. However, number of rectifying stage has no effect on total annual cost because there is no condenser to reflux methanol and water back to reactive distillation. The simulation results show that the optimum configuration of the reactive distillation column is N_{rxn}=3 N_{strip}=1 and N_{rec}=0 with the value of total annual cost of the reactive distillation column 1.07×10^6 \$/year.

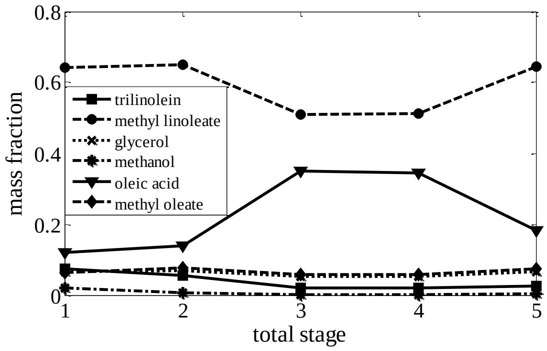


Fig. 7.16 Composition profile of high pressure column in liquid phase of multi-effect indirect split arrangement of reactive distillation

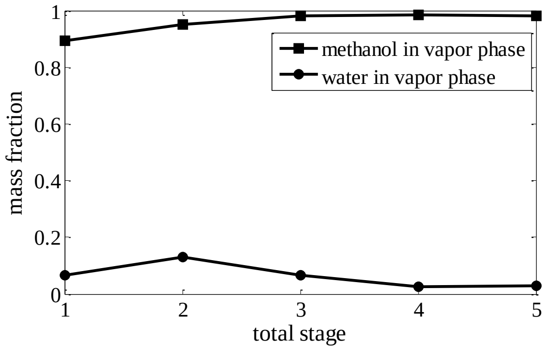


Fig. 7.17 Composition profile of high pressure column in vapor phase of multi-effect indirect split arrangement of reactive distillation

Figure 7.16 show mass fraction of all components of reactive distillation column at the suitable parameters while figure 7.17 shows mass fraction of components in vapor phase of reactive distillation. It presents that there are only two components such as methanol and water in vapor phase of vapor stream from the top of reactive distillation. This stream can transfer the heat through heat exchanger to liquid stream of distillation column because of higher temperature in this stream (162 ^{o}C). The overall heat duty of this configuration is lower than conventional reactive distillation because Vapor stream from the top of reactive distillation column can supply heat to liquid stream of distillation column. According to methodology for selection type of heat integration reactive distillation, multi-effect indirect split arrangement is an alternative of heat integration with respect to criteria.

Thermally coupled indirect sequence of RD integrated with distillation column

The principle of thermally coupled indirect sequence of RD integrated with distillation column is similar to multi-effect indirect split arrangement; however, there is no heat exchanger to transfer the heat (figure 7.19). Thus the number of unit operations is reduced because condenser of reactive distillation is eliminated. Vapor stream from reactive distillation column is sent to distillation column whileas the liquid stream from distillation is sent to reactive distillation column. The details of effect of parameters are described at next section.

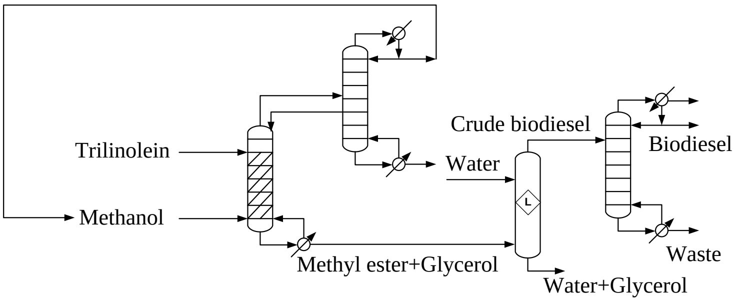


Fig.7.18 Thermally coupled indirect sequence of RD integrated with distillation column

Effect of pressure

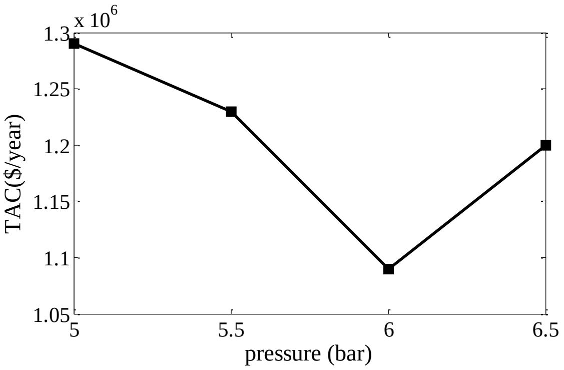


Fig. 7.19 Effect of pressure on total annual cost.

Fig. 7.19 presents the effect of pressure on total annual cost. Increased pressure of reactive distillation enchances decreasing of reboiler duty of both reactive distillation and distillation column. There is a minimum total annual cost at optimum operating pressure because of tradeoff between capital cost and operating cost. Although pump cost is increased with an increasing of pressure, net vapor flow rate is decreased because of low boilup ratio. The suitable operating pressure is 6 bar.

Effect of reaction stages

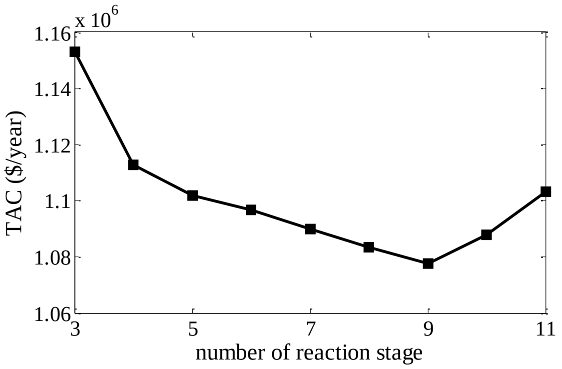


Fig. 7.20 Effect of number of reaction stage on total annual cost

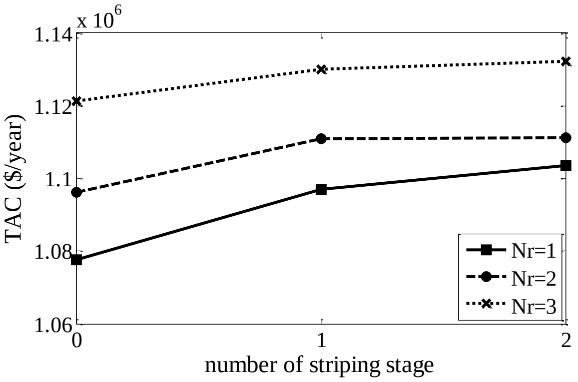


Fig. 7.21 Effect of number of stripping stage on total annual cost

Figure.7.20 shows that increased the number of reactive stages results in the reduction of total annual cost because there is more contacting area between reactants, thus requiring less reboiler heat duty of reactive distillation and condenser heat duty of distillation column. However, total annual cost is increased with an increasing of number of reaction stages due to increasing of capital cost. From this case, the minimum total annual cost is observed at N_{rxn} = 9. Figure 7.21 shows the requiring of stripping stages to purify methyl ester and glycerol. Adding more stripping stages lead to high capital cost so total annual cost is increased. However, number of rectifying stage has no effect on total annual cost because there is no condenser to reflux methanol and water back to reactive distillation. The simulation results show that the optimum configuration of the reactive distillation column is Nrxn=3 N_{strip}=1 and N_{rec}=0 with the value of total annual cost of the reactive distillation column 1.08×10^6 \$/year.

Effect of feed location of vapor stream to distillation column

Feed location of vapor stream and side draw stream of distillation column affects on total annual cost because they affect on temperature profile within column. Fig. 31 shows that TAC is decreased when feed stage of vapor stream moves down to the bottom of column. This is because heat from vapor stream can transfer effectively that the temperature at the bottom of column is increased. However, feed stage of vapor stream at the 5th stage increases the temperature profile within column as shown in fig. 7.22. So the suitable feed stage of vapor stream to distillation column is at 5th stage when the number stage of reactive distillation and distillation column are fixed at 10 and 10 stages, respectively.

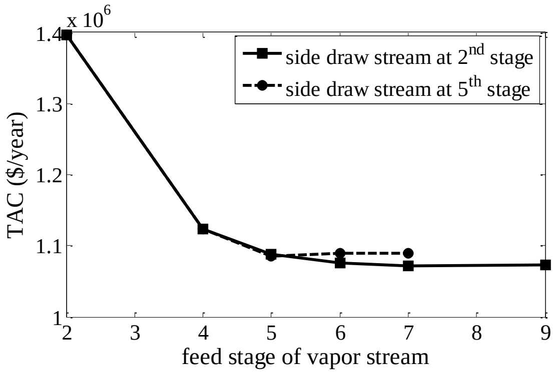


Fig. 7.22 Effect of location of feed stage of vapor stream on total annual cost with different the location of side draw

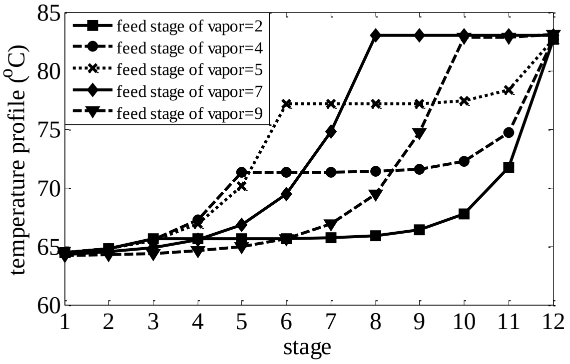


Fig. 7.23 Temperature profile of feed stage of vapor stream when side draw stream of distillation column is at 2^{nd} stage

Heat integrated reactive distillation(HiRDC)

Heat integrated reactive distillation is a process intensification between vapor recompression and heat integration of distillation column (assumed as rectifying section) and reactive distillation (assumed as stripping section). The liquid at the bottom of distillation column that is higher pressure is sent to reactive distillation for supplying the heat. Heat exchanger between reactive distillation and distillation is not installed. In this work, trilinolein and methanol are fed to reactive stripping column to produce methyl ester and glycerol. Excess methanol from reactive stripping section is become vapor and compressed; then sent to rectifying section. Liquid stream containing methanol and water are fed back to stripping section. The purification process is similar to conventional reactive distillation process. The configuration of heat integrated reactive distillation without heat exchanger is shown in fig 7.24.

Heat integrated reactive distillation with heat exchanger

The heat integrated reactive distillation with heat exchanger is shown in fig 7.25. The principle of heat integrated reactive distillation with heat exchanger is similar to heat integrated reactive distillation without heat exchanger; however, there are heat exchangers between rectifying section and stripping section so heat from rectifying section can be transferred to stripping section due to the difference of temperature between two columns. The heat exchanger leads to reflux flow for rectifying section and vapor flow for stripping section. As a result, reboiler duty of reactive distillation can be reduced. In general, heat transfer from rectifying section to stripping section will transferred tray by tray; therefore, a number of heat exchangers need to be installed is equivalent the number of stages (Mali et al., 2009). From fig 7.26 -7.28, there are 3 configurations of heat integrated reactive distillation with heat exchanger depending on the location of heat exchanger. Fig 7.26 shows the configuration of heat integrated reactive distillation that heat exchangers are installed at the top of column, the middle of column and the bottom of column between rectifying column and strippping column. Fig 7.27 shows top-integrated heat integrated reactive distillation that is heat exchangers are installed at the top of column and the middle of column. Fig 7.28 shows bottom-integrated heat reactive distillation that is heat exchangers are installed at the middle of column and the bottom of column. The configuration of heat integrated reactive distillation are determined from the step of design of reactive distillation. The suitable location of heat exchanger is determined by using minimum total annual cost as a criteria.

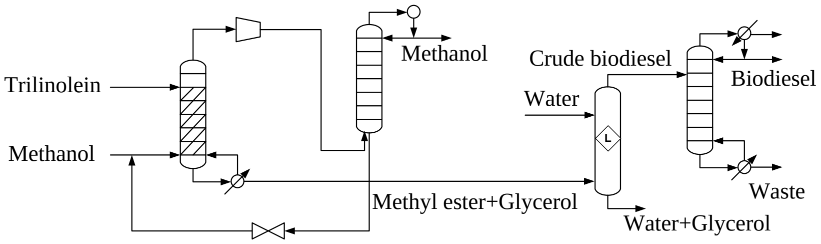


Fig. 7.24 Heat integrated reactive distillation configuration

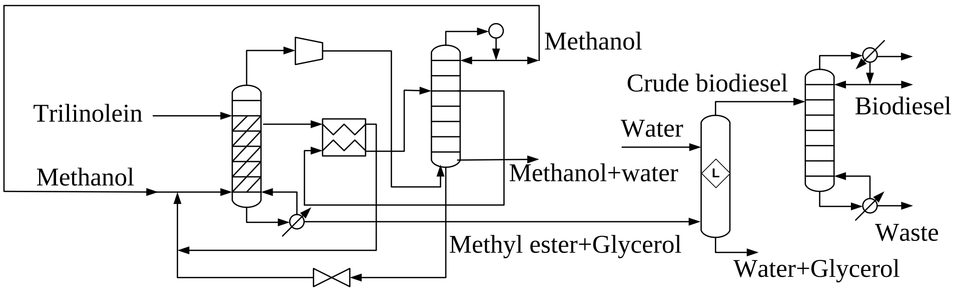


Fig. 7.25 Heat integrated reactive distillation configuration (HiDRC)

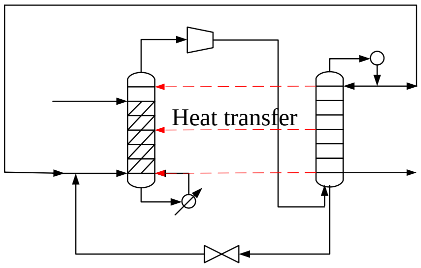


Fig. 7.26 Heat integrated reactive distillation with heat exchanger (HiRDC) configuration

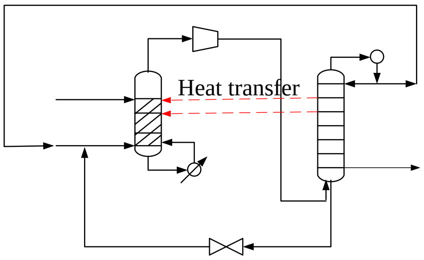


Fig. 7.27 Top-integrated heat integrated reactive distillation with heat exchanger (HiRDC) configuration

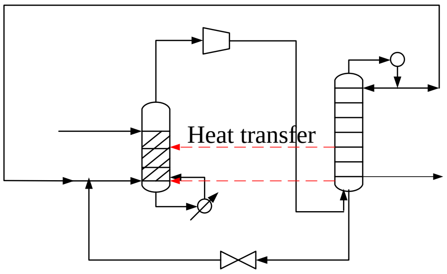


Fig. 7.28 Bottom-integrated heat integrated reactive distillation with heat exchanger (HiRDC) configuration

Effect of pressure

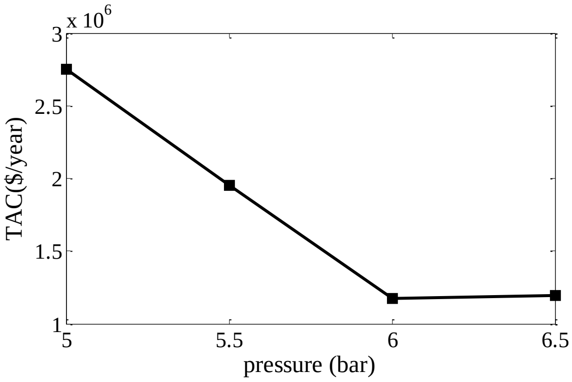


Fig. 7.29 Effect of pressure on total annual cost.

Fig 7.29 presents the tradeoff between pressure and total annual cost. In addition, increased pressure of reactive distillation results in a decreasing of duty of compressor that sent the vapor stream at the top of reactive distillation column to distillation column. However, pressure value above suitable pressure results in an increasing of total annual cost. The suitable operating pressure is 6 bar.

Effect of number of reactive stages

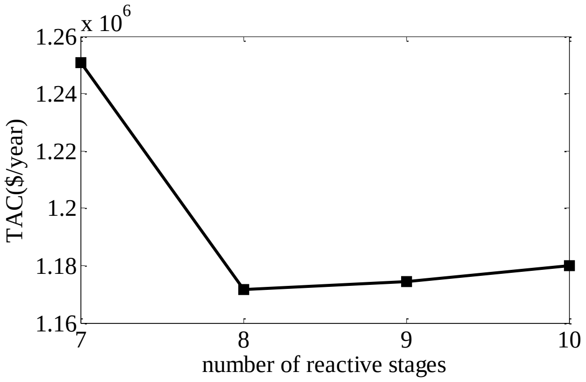


Fig. 7.30 Effect of number of reaction stage on total annual cost

Fig.7.30 shows that increasing the number of reaction stages results in the reduction of total annual cost because there is more contacting area between reactants, thus requiring less reboiler heat duty of reactive distillation and condenser heat duty of distillation column. However, total annual cost is increased with an increasing of number of reaction stages more than 8 stages due to increasing of capital cost. From this case, the minimum total annual cost is observed at N_{rxn} = 8.

Heat integrated reactive distillation with heat exchanger is designed after heat integrated reactive distillation without heat exchanger. The parameters for design this configuration are pressure of distillation column, the location of heat exchanger and number of heat exchanger. The figure 7.31 shows the temperature of reactive distillation and distillation column before the installation of heat exchanger when ΔP between reactive distillation and distillation is 2000 kPa. It is shown that temperature of distillation column is higher than reactive distillation 20 °C. It means that heat from distillation column can supply to reactive distillation. At the bottom column of reactive distillation, it presents that the difference of temperature between reactive distillation and distillation column is higher than other stages. Therefore, heat exchanger should be installed at the bottom of reactive distillation and distillation column.

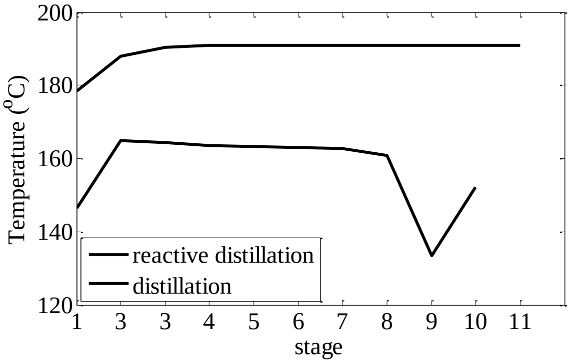


Fig. 7.31 Temperature profile of reactive distillation and distillation when ΔP is 2000 kPa

Number of heat exchanger and location of heat exchanger

The starting point is to install heat exchanger between the bottom column of reactive distillation and distillation column because the largest driving force of temperature between two columns. Figure 7.32 shows the effect of the stage of reactive distillation that install heat exchanger on total annual cost when heat transfer at the bottom of distillation column. It presents that total annual cost is the lowest value when the first heat exchanger is installed at the 9th stage of reactive distillation because the heat exchanger area that affects on the capital cost is lower. The second heat exchanger is installed for further step to decrease condenser duty.

Figure 7.33 shows the effect of the stage that installation of heat exchanger on condenser duty of distillation column. It presents that condenser duty of distillation column is stable because temperature profile in distillation column is not different. Although the second heat exchanger can reduce more heat duty, heat exchanger area is highly affects on total annual cost when it compared with heat duty. Therefore, total annual cost is increased with an increasing of the number of heat exchangers. It means that there is no need to install the second heat exchanger.

Figure 7.34 shows temperature profile of reactive distillation and distillation column with different stages after the installation of heat exchanger. The heat is transferred on 9th stage of reactive distillation to 10th of distillation. It can be seen that temperature profile of distillation column (high pressure column) after the installation of heat exchanger is dropped; therefore, it is necessary to recheck that the temperature difference between the corresponding stages of the reactive distillation and the distillation is set to be greater than 10 °C. Therefore, ΔP between reactive distillation and distillation of 2000 kPa is acceptable value although smaller ΔP give the lower total annual cost.

Figure 7.35 shows that the heat integration between reactive distillation and distillation column reduce the vapor flow that affects on condenser duty because of condensation. However, vapor flow rate after install the 1st and the 2nd heat exchanger is not different value. Therefore, single heat-integrated stage of reactive distillation is suitable configuration for biodiesel production from waste cooking oil as shown in figure 7.36.

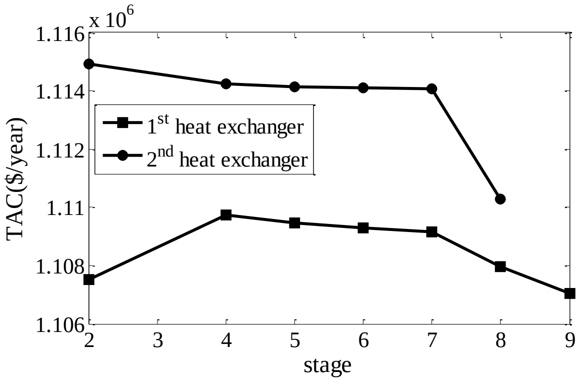


Fig. 7.32 The effect of the stage of reactive distillation that install heat exchanger on total annual cost when ΔP between reactive distillation and distillation is 2000 kPa

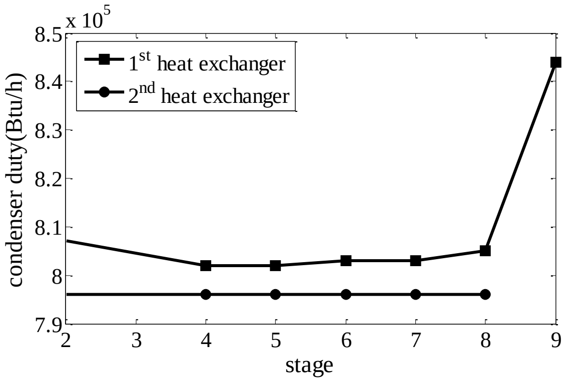


Fig. 7.33 The effect of the stage that install heat exchanger on condenser duty when ΔP between reactive distillation and distillation is 2000 kPa

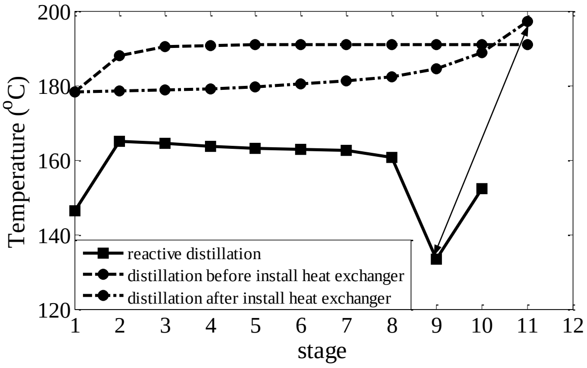


Fig. 7.34 Temperature profile of reactive distillation and distillation when ΔP is 2000 kPa before and after installation of heat exchanger

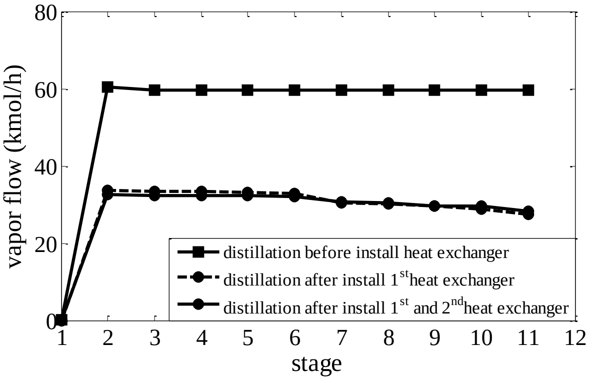


Fig. 7.35 Vapor flows for HIDRC designs with heat exchangers compared with HIDRC designs without heat exchangers

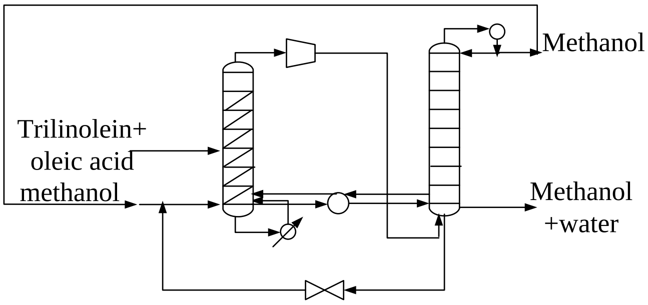


Fig. 7.36 Configuration of single heat-integrated stage of HiRDC

The comparison of heat integrated reactive distillation for biodiesel production from waste cooking palm oil is shown in table 7.5.

Table 7.4 Comparison of type of heat integrated reactive distillation for biodiesel production from waste cooking oil.

	Base case design (Conventional reactive distillation)	multi-effect indirect split arrangement reactive distillation	Thermal reactive distillation	heat integrated reactive distillation without heat exchanger	heat integrated reactive distillation with heat exchanger
Pressure of reactive distillation column(bar)	5.5	6	6	6	6
Pressure of distillation column	1	1	1	23	23
Reaction stage of reactive distillation	11	3	9	8	8
Purity of methyl esters after separation	99%	99%	99%	99%	99%
Rectifying stage of reactive distillation	-	-	1	1	1
Stripping stage of reactive distillation	1	-	-	-	-

Table 7.4 Comparison of type of heat integrated reactive distillation for biodiesel production from waste cooking oil.

	Base case design (Conventional reactive distillation)	multi-effect indirect split arrangement reactive distillation	Thermal reactive distillation	heat integrated reactive distillation without heat exchanger	heat integrated reactive distillation with heat exchanger
Total stage of distillation column for separation water and methanol	9	4	10	10	10
Reboiler duty of reactive distillation ($x10^7$Btu/h)	1.82	1.88	1.88	1.92	1.87
Reboiler duty of distillation for separation methanol from water ($x10^6$Btu/h)	7.98	-	0.00147	-	-
Condenser duty of RD ($x10^5$Btu/h)	7.46	-	-	-	-

Table 7.4 Comparison of type of heat integrated reactive distillation for biodiesel production from waste cooking oil.

	Base case design (Conventional reactive distillation)	multi-effect indirect split arrangement reactive distillation	Thermal reactive distillation	heat integrated reactive distillation without heat exchanger	heat integrated reactive distillation with heat exchanger
Condense duty of distillation for separation methanol from water (x10^6Btu/h)	8.07	1	0.89	1.76	0.844
Capital cost of reactive distillation(x10^5\$/year)	2.23	0.9969	2.11	1.94	1.94
Capital cost of distillation(x10^5\$/year)		1.35			
Capital cost of heat exchanger(x10^3\$/year)	-	4.49	-	-	-
Steam cost of reactive distillation(x10^5\$/year)	6.9	7.23	7.14	7.31	7.12

Table 7.4 Comparison of type of heat integrated reactive distillation for biodiesel production from waste cooking oil.

	Base case design (Conventional reactive distillation)	multi-effect indirect split arrangement reactive distillation	Thermal reactive distillation	heat integrated reactive distillation without heat exchanger	heat integrated reactive distillation with heat exchanger
Stream cost for separation methanol (x10^5\$/year)	3.04	-	-	-	-
Cooling cost of RD(x10^3\$/year)	1.21	1.9	-	-	-
Cooling cost for separation methanol (x10^4\$/year)	1.34	-	0.145	0.286	0.137
TAC of RD (x10^6\$/year)	1	1.05	1.07	1.17	1.107
TAC of distillation (x10^5\$/year)	5.6				
TAC of the processes (x10^6\$/year)	2.255	1.74	1.76	1.865	1.8
Cost saving (%)	-	22.35	21.95	17.3	20.17

The chosen configurations of a heat integrated reactive distillation obtained after performing a screening process are shown in Table 7.4. Operating pressure for all types of the heat integrated reactive distillation is higher than a conventional RD because high operating pressure is needed to increase the reboiler duty of reactive distillation and to achieve the production rate. The results shown in Table 7.4 indicate that the multi-effect indirect split arrangement of RD can reduce the number of unit operations because heat is transferred from the vapor stream (hot stream) of RD to the liquid stream (cold stream) of distillation. Multi-effect indirect split arrangement of RD can achieve the lowest TAC. Although the other types of the heat integrated RD can reduce the TAC, compared to the conventional RD, the multi-effect indirect split arrangement RD is the most feasible one as it is operated at atmospheric pressure. The result for screening procedure is given in Table 7.5. At the end, the best process is found to be the multi-effect indirect split arrangement of reactive distillation.

Table 7.5 Reducing alternative processes from constraint consideration

Step	Criteria	Number of alternatives
4.1	the purity of water from distillation column	10
4.2	ratio of boiling point of key components	7
4.3	Type of key components	5
4.4	Limitation of separation technique	4
5	Minimum total annual cost	1

7.3 Conclusion

In this study, a design methodology for a heat integrated reactive distillation is proposed. A full set of all possible heat integrated reactive distillations is first generated. Component purify, a boiling point ratio of adjacent components, type of key component and limitation of separation technique are considered to screen the process alternatives. The proposed design methodology is demonstrated via a biodiesel production from waste cooking oil, as a case study. According to the methodology, multi-effect indirect split arrangement of reactive distillation is better than other alternatives in term of a minimum total annual cost. However, other separation processes are required in order to achieve biodiesel specification of 99.5 wt%.

CHAPTER VIII

DESIGN THE SEPARATION OF FATTY ALCOHOL

8.1 Introduction

Fatty alcohol is long chained carbon (C12-C20) of aliphatic alcohol. It is among the important chemicals that are used for cosmetic and pharmaceutical industries (Voeste and Buchold, 1984) Fatty alcohol is produced from hydrogenation of methyl esters and hydrogen. Methyl esters are derived from either transesterification or esterification from vegetable oils such as palm oil and palm kernel oil (Lam et al., 2010). Although main reaction of fatty alcohol is hydrogenation, side reactions are occurred due to overhydrogenation and esterification of fatty alcohol and methyl ester (Kreutzer, 1984). Side products are formed such as heavy hydrocarbon, methanol and wax esters. Fatty alcohol separation is a complicated process involving multi-components and products. This requires the design of separation for purification of fatty alcohol. Methanol is easy to remove from multi-components by using flash separator (Pelzer et al, 2004). However, the boiling point of residue methyl ester, fatty alcohols and wax esters are not different that leads to separate difficultly.

The fatty alcohol production process was developed by improving the purification of crude fatty alcohol (Lurgi, 1991). The distillation columns were used for the separation fatty alcohol from unconverted methyl ester. For this process, alkane which was a side product was considered. The first distillation column was used for separation the alkane while the other column was used for purification of fatty alcohol. Willmott et al., 1992 proposed the separation of wax esters from fatty alcohol by using transesterification of wax ester and methanol. Methyl esters are formed by transesterification so they can be recycled for fatty alcohol production. However, this work focused on the esterification of crude fatty alcohol with unconverted methyl ester. Furthermore, wax esters are converted to fatty alcohol and alkali soap by using saponification reaction with NaOH (Josten, 2012) Fatty alcohol is separated from residue wax ester by using gravity separator subsequent the washing step. Namba et al., 2005 improved the purification process by using KOH to mix in the fatty alcohol produced from methyl palmitate before distillate at vacuum pressure. This hot aqueous alkali solution help remove unreacted methyl ester. Although their works claimed that the separation of crude fatty alcohol was difficult, a few details of the purification of crude fatty alcohol such as optimum condition and optimum configuration of purification which obtain production specification did not mention. However, a limited work has concerned on the separation of crude fatty alcohol.

This study presented a new design for purification of crude fatty alcohol. The types of heat integration for purification is concerned to reduce energy consumption. The design of purification process is based on thermodynamic insights algorithm (Jaksland et al., 1995). Therefore, the alternative process for separation of fatty alcohol is obtained not only based on the most economically process but also the lowest energy consumption. The types of heat integration is selected according to the criterias. The heat integrated distillation column is also designed in term of the minimum total annual cost. Thus the suitable parameters of heat integrated distillation can be achieved.

8.2 Phase diagram

The known information of components are based on Rieke et al., 1997. The composition of crude fatty alcohol is shown in table 8.1. Dodecanol is assumed as fatty alcohol while lauryl laurate and dodecane are assumed as wax ester and heavy hydrocarbon, respectively.

Table 8.1 Composition of crude fatty alcohol

component	Composition (%wt)
Dodecanol (lauryl alcohol)	86
Methanol	5.5
Methyl laurate	0.4
Lauryl laurate	6.6
dodecane	1.5

VLE diagrams of methyl laurate with dodecanol and VLE diagram of methyl laurate with lauryl laurate are shown in fig.8.1-8.2. Figure represents that the separation of methyl laurate and dodecanol is difficult because of narrow curve of diagram. While there is no problem for the separation of lauryl laurate from other mixtures.

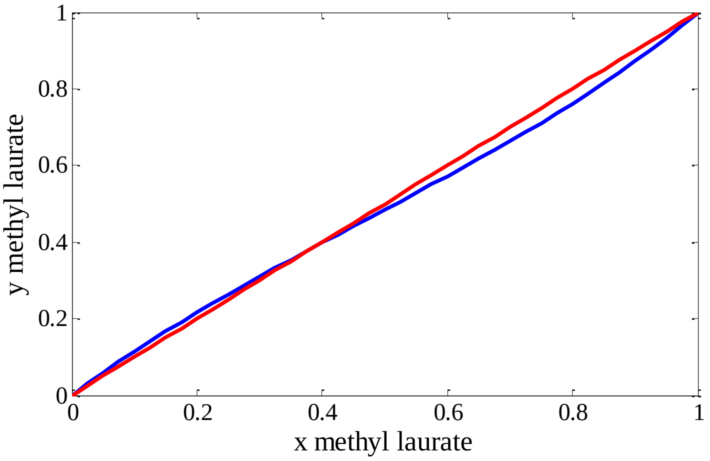


Fig 8.1 VLE diagram of methyl laurate with dodecanol

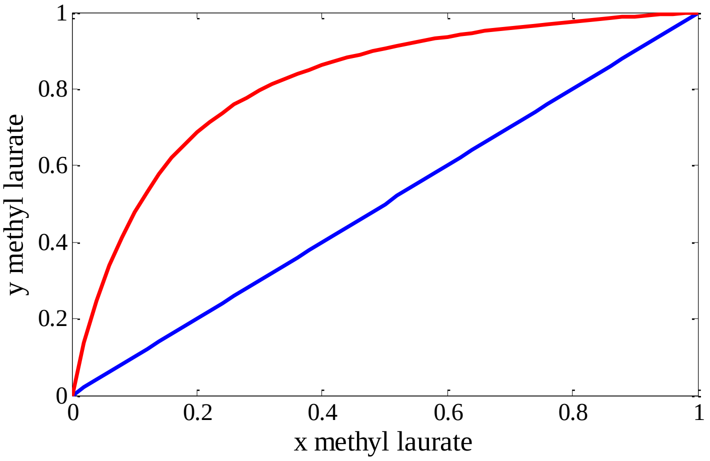


Fig 8.2 VLE diagram of methyl laurate with lauryl laurate

After separation of methanol from product stream, there are 4 components in the system such as methyl laurate, dodecanol, dodecane and lauryl laurate. However, methyl laurate is neglected because it is almost consumed. Residue curve map can explain the behavior of ternary components. The product stream after separation by flash operator contains methanol because persentage of recovery of flash operator is fixed at 90%. In this work, methanol and dodecane are represented as light component. Dodecanol is represented as middle component and lauryl laurate represented as heavy component. Fig 8.3 shows residue curve map of ternary components, such as lauryl laurate, dodecanol and dodecane. Binary azeotrope and ternary azeotrope are not existed in this ternary component. Pure components such as dodecane, dodecanol and lauryl laurate are settled at the corner of diagram. From the ranking of boiling point, dodecane is unstable node while lauryl laurate is stable node and dodecanol is saddle node.

This figure shows the feed composition from flash operator and possible distillate and bottom composition because sending to a single distillation column. If the dodecane, the lightest component, is removed first, the bottom products contains lauryl laurate and dodecanol corresponding to point D. The sequence of distillation columns is arranged direct sequence. However, lauryl laurate, the heaviest component, is first removed at the bottom column (point B). Dodecanol and dodecane are mixed at overhead product. Indirect sequence of distillation columns are arranged. Figure shows that dodecanol is a saddle node; therefore, purified fatty alcohol cannot be obtained in a single distillation column.

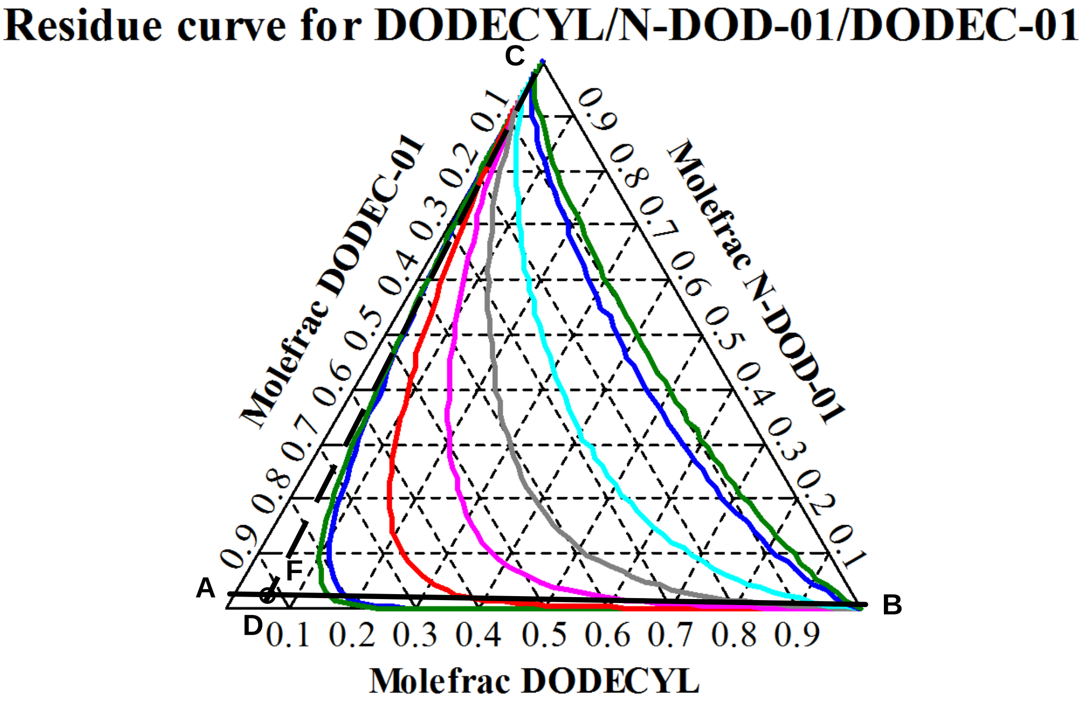


Fig 8.3 Residue curve map for dodecane, dodecanol and lauryl laurate

8.3 Process design

8.3.1 Conventional process

The conventional process is investigated according to Lurgi (1991). In the conventional process, methanol is removed by flash separator. The bottom from flash separator is sent to the first distillation to eliminate dodecane as overhead product. The bottom product of distillation column consisting of dodecanol, methyl laurate and lauryl laurate are sent to distillation column. Dodecanol is separated from higher boiler at the top of column while lauryl laurate are obtained at the bottom of column. The sequence of distillation columns is rearranged like direct sequence. From residue curve map, line CFD connects distillate and bottom product for conventional process. The conventional process is shown in fig 8.4

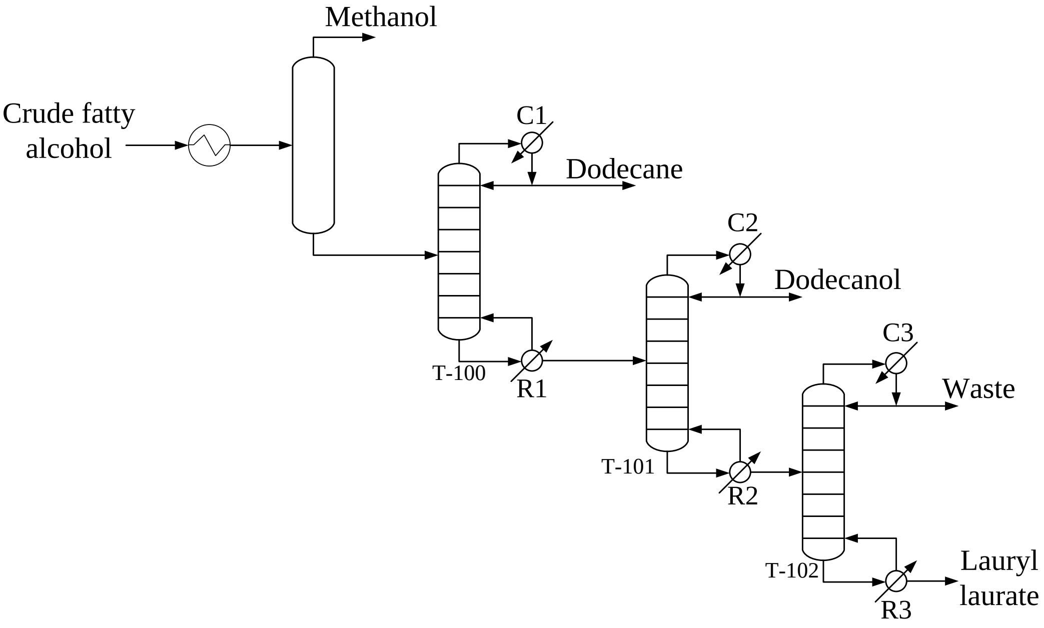


Fig 8.4 Conventional process for purification fatty alcohol

8.3.2 Design process

The proposed process is the heat integration of separation fatty alcohol that designed based on thermodynamic insights algorithm (Jaskland et al, 1995). The sequence of distillation column is rearranged corresponding to the highest driving force. The various properties of components such as vapor pressure, boiling point, melting point, solubility parameters, molecular weight and critical properties are gathered for further the generation of superstructure. All feasible separation techniques are identified and screened with respect to the highest driving force of separation tasks. For binary mixture analysis, binary azeotrope is not existed in all binary pairs. Thus mass separation agent is not required.Finally,a rigorous simulation of a feasible altenative is required in order to determine the suitable parameters such as the number of stages and feed location when the purity of fatty alcohol is fixed at 98.5 wt%. The proposed process before heat integration is shown in fig 8.5. From the highest binary ratio of vapor pressure, methanol and dodecane are the key component, methanol from the reactor effluent is separated by using flash separator that is fixed 90 % of recovery. Calculation of binary ratio is repeated. Then dodecanol and lauryl laurate are key components so bottom stream from separator consisting of mostly dodecane, dodecanol, methyl laurate and lauryl laurate is sent to the distillation column (T-100) in order to eliminate lauryl laurate. However, lauryl laurate that obtained from distillation column is not purified. It is sent to another distillation column (T-102) to obtain 99 wt% of lauryl laurate. So it can be used as emulsifier in chemical industries. Distillated stream from the first distillation column (T-100) is sent to the second distillation column to purify dodecanol. From residue curve map, line AFB connects distillate and bottom product for proposed process. Neither the configuration of conventional process nor proposed process show that purified dodecanol in the first distillation column. The suitable parameters such as the number of stages and feed location are described in next section.

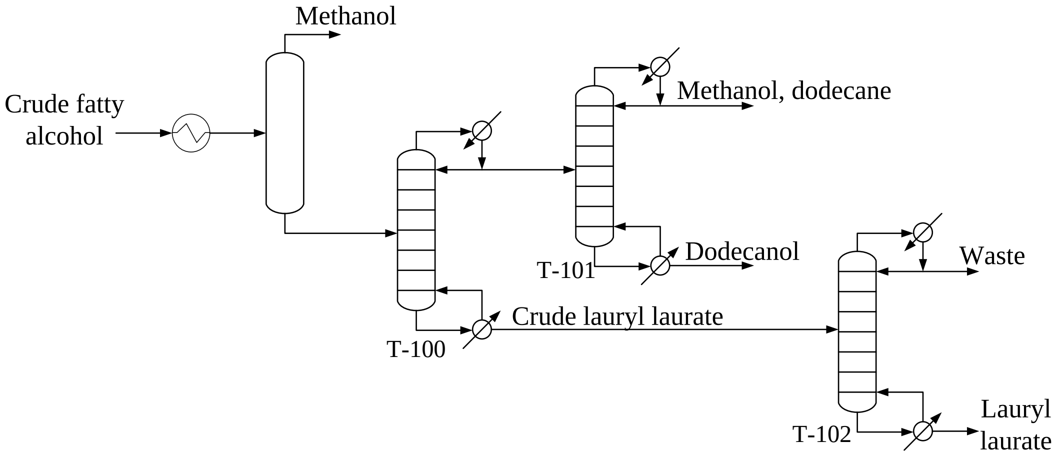


Fig 8.5 Design process for purification of fatty alcohol before heat integration

8.4 Results and discussions

Fig 8.6a and 8.6b show the effect of the number of stages for column T-100, T-101, T-102. As the number of stages increases, total annual cost initially decreases. However, increasing the number of stages above the suitable number of stages results in higher total annual cost. So a minimum total annual cost is obtained at the suitable stages. In this work, the suitable number of stages for column T-100, T-101, T-102 are 11, 7, 5 stages,respectively for conventional process. While the suitable number of stages for column T-100, T-101 and T102 of designed process are 9, 10, 5 stages, respectively. Table 8.2 compares the suitable parameters of conventional process and designed process before heat integration. It shows that the energy consumption and total annual cost of designed process before heat integration are similar to conventional process because of the large amount of desired product (dodecanol).

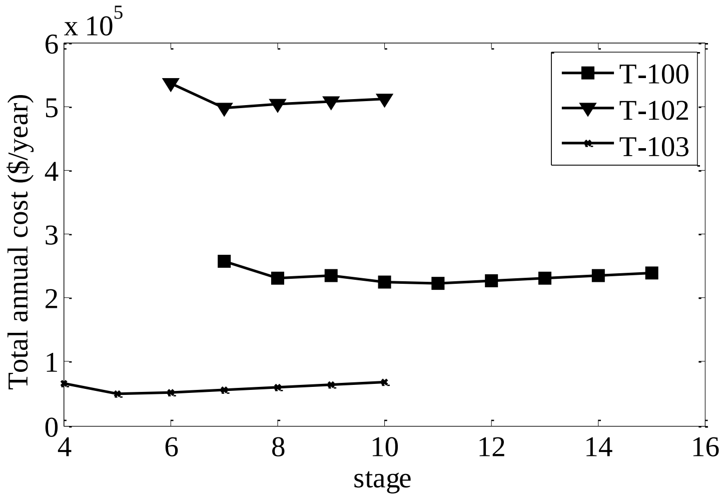


Fig 8.6a the effect of the number stages for column T-100, T-101, T-102 on total annual cost ($/year) of conventional process.

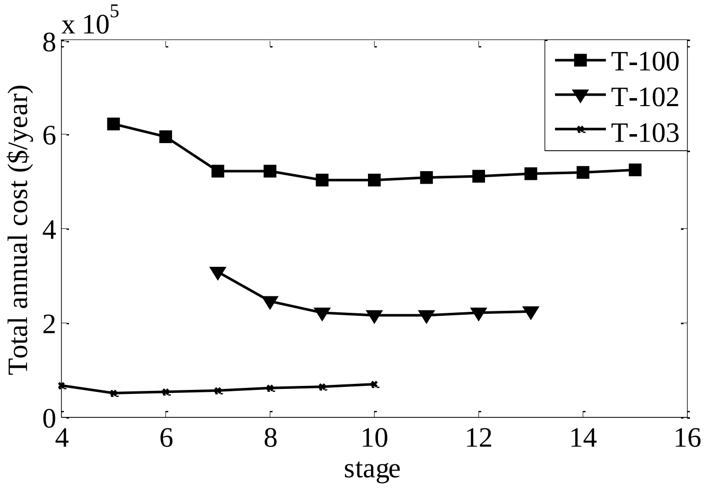


Fig 8.6b The effect of the number stages for column T-100, T-101, T-102 on total annual cost ($/year) before heat integration of designed process

Table 8.2 The suitable parameters with the minimum total annual cost

	Conventional process	Designed process before heat integration
Pressure of distillation column (T-100) (atm)	1	1
Pressure of distillation column (T-101) (atm)	1	1
Pressure of distillation column (T-102) (atm)	1	1
Number of stages of distillation column (T-100)	11	9
Number of stages of distillation column (T-101)	7	10
Number of stages of distillation column (T-102)	5	5
Condenser duty of distillation column (T-100) ($\times 10^5$Btu/h)	6.23	112.9
Condenser duty of distillation column (T-101) ($\times 10^5$Btu/h)	115	6.114
Condenser duty of distillation column (T-102) ($\times 10^5$Btu/h)	2.634	2.634
Reboiler duty of distillation column (T-100) ($\times 10^6$Btu/h)	4.34	11.47

Table 8.2 The suitable parameters with the minimum total annual cost

	Conventional process	Designed process before heat integration
Reboiler duty of distillation column (T-101) ($\times 10^6$Btu/h)	11.57	4.28
Reboiler duty of distillation column (T-102) ($\times 10^5$Btu/h)	5.39	5.39
Total annual cost ($\times 10^5$\$/year)	7.7	7.68
Cost saving (%)	-	0.26

8.5 The heat integration of separation of fatty alcohol

8.5.1 The heat integration of separation of fatty alcohol for conventional process

Table 8.3 Duty and temperature of streams of unit operations of conventional process

	Condenser duty ($\times 10^5$Btu/h)	Reboiler duty ($\times 10^5$Btu/h)	Temperature of to condenser stream (^{o}C)	Temperature of distillate stream (^{o}C)	Temperature of bottom stream (^{o}C)
T-100	6.22	43.48	198.1	75.07	259.6
T-101	114	115.7	258	258	301
T-102	1.8	5.39	265.3	259	374.4

Heat integration between two distillation columns can reduce the energy consumption of condenser duty and reboiler duty. There are many types of heat integration of distillation due to the different pressure and temperature of both columns. The principle to generate heat integration of distillation when the sequence of distillation arrangement is to eliminate the number of heat exchanger (condenser or reboiler) (Doherty and Malone, 2001). When Reboiler R1 is missing, the types of heat integration are thermal coupling between T-100 and T-101, and multi-effect distillation between T-100 and T-101. For thermal coupling between T-100 and T-101, vapor and liquid flows from column T-100 are shared with column T-101. While condenser of column T-101 is acted as reboiler of column T-100 for multi-effect distillation between T-100 and T-101. When reboiler R2 is missing, the types of heat integration are thermal coupling between T-101 and T-102, and multi-effect distillation between T-101 and T-102. However, condenser C1, condenser C2, and condenser C3 are needed for purifying light components.

The criteria for selection type of heat integration are condenser duty, reboiler duty, temperature stream and operating pressure. Higher condenser duty and higher temperature of distillate stream can supply the heat to lower reboiler duty of another distillation column. For thermal coupling between T-100/T-101, condenser duty of T-101 column is higher than reboiler duty of T-100 column. The desired product (fatty alcohol) is obtained at the top of T-101 column; therefore, low vapor side draw rate of T-101 column to share with T-100 column is not adequate to supply heat at bottom of T-100 column. In this work, operating pressure of three distillation columns is fixed at 1 atm. Multi-effect of distillation columns between T-100/T101 and T-101/T-102 are infeasible options when operating pressure is fixed at 1 atm. This is because temperature of distillate stream of T-101 column is lower than temperature of bottom stream of T-100 column. In addition, temperature of distillate stream of T-102 column is lower than temperature of bottom stream of T-101 column. It implies that there is no suitable configuration of heat integration of conventional process.

8.5.2 The heat integration of separation of fatty alcohol for designed process

Table 8.4 Duty and temperature of streams of unit operations of designed process

	Condenser duty ($\times 10^5$Btu/h)	Reboiler duty ($\times 10^5$Btu/h)	Temperature of to condenser stream (^oC)	Temperature of distillate stream (^oC)	Temeperature of bottom stream (^oC)
T-100	112.9	114.7	256.3	178.1	289.2
T-101	6.114	42.8	172	69.23	258.4
T-102	2.634	5.39	262.5	259.1	374.4

In this work, the possible configurations of heat integration for designed process are thermal coupling between T-100/T-101, thermal coupling between T-100/T-102, multi-effect between T-100/T-101, multi-effect between T-100/T-102, internal heat integrated distillation (HiDiC)between T-100/T-101, and internal heat integrated distillation (HiDiC) between T-100/T-102. However, there are limitation in types of heat integration especially pressure and temperature. Therefore, condenser duty, reboiler duty, temperature of each stream are gathered for further analysis. The criteria for screening the feasible types of heat integration are pressure, temperature of stream and temperature profile. Table 8.4 shows the duty and temperature of three distillation columns.

The first criteria for screening the type of heat integration is temperature stream when operating pressure is constant at 1 atm. From table 8.5, it is noted that To condenser stream is vapor phase. The temperature of to condenser stream of distillation (T-100) is lower than temperature of bottom stream in distillation columns (T-101 and T-102) so multi-effect distillation between T-100 and T-101 is eliminated. Multi-effect distillation between T-100 and T-102 is also eliminated. This is because the principle of multi-effect distillation is that vapor stream supplies heat to liquid stream of bottom column; however, the temperature of vapor stream is not adequate to supply the heat. To consider temperature of vapor stream of T-101, vapor stream cannot supply heat to liquid stream of T-100 and T-102 column. Therefore, multi-effect distillation is eliminated.

The second criteria for screening the type of heat integration is duty of condenser and reboiler. Although temperature of vapor stream of T-101 column is higher than liquid stream of T-102 column, multi-effect distillation between both columns is also eliminated because condenser duty of T-101 column is lower than reboiler duty of T-102 column. Thermally coupled distillation column between T-100 and T-102 is eliminated.

The third criteria for screening the type of heat integration is temperature profiles within three columns. Fig 8.7 shows that temperature profile of column T-100 is similar to column T-101; therefore, internal heat integrated distillation (HiDiC)between T-100/T-101 is not feasible alternative configuration. From the criterion, thermally coupled distillation between T-100/T-101 is preferred to be designed process as shown in fig. 8.8 Thermally coupled distillation between T-100/T-101 requires reboiler for the main column (column T-100). Condenser and reboiler of T-101 are required for separation dodecane and dodecanol.

Fig 8.9 shows simple distillation columns consisting of 4 sections. It can be replaced with thermal coupling between two columns as shown in fig. 8.10. The sections of thermal coupling of two distillation columns are similar to simple distillation columns. However, the section of thermal coupling can be rearranged (Rong et al., 2012) . The equivalent configuration of thermal coupling between two distillation columns is distillation with side stripper as shown in fig 8.11.

Table 8.5 Criteria for selecting type of heat integration

	Criteria	Eliminate type of heat integration
1	Temperature of stream	- multi-effect distillation between T-100 and T-101 - multi-effect distillation between T-100 and T-102
2	Condenser duty and reboiler duty	- Thermal coupling distillation column between T-100 and T-102
3	Temperature profile	- HiDiC between T-100/T-101

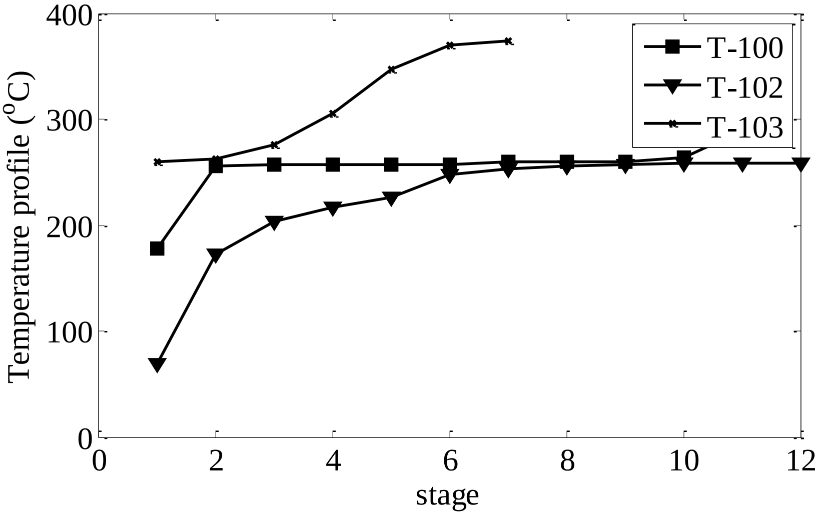


Fig 8.7 Temperature profile of T-100, T-102 and T-103 column.

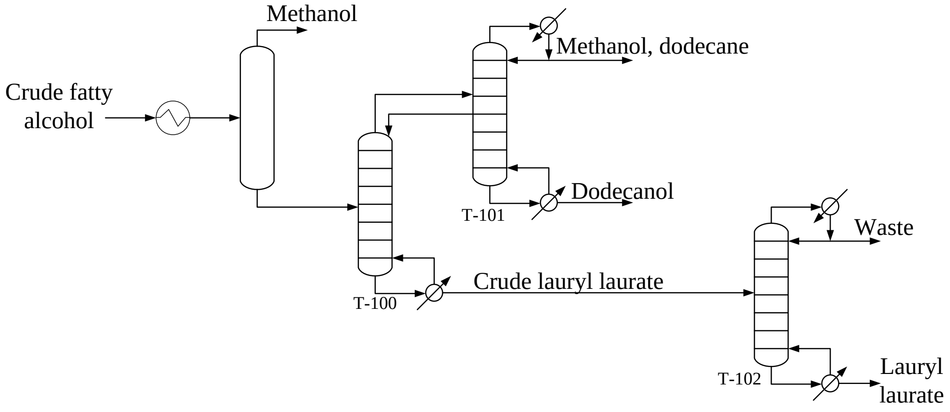


Fig 8.8 Thermal coupling distillation for fatty alcohol separation

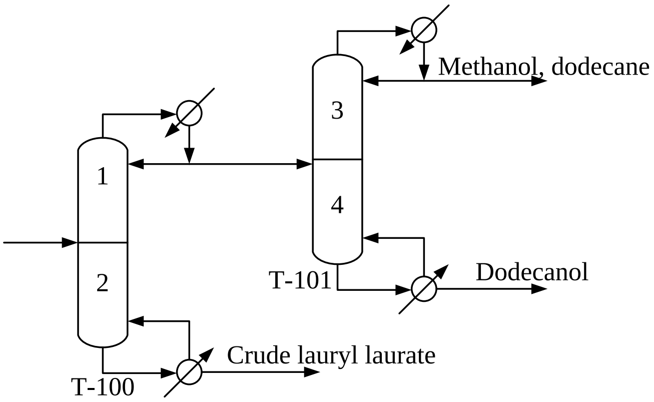


Fig 8.9 Two simple distillation columns.

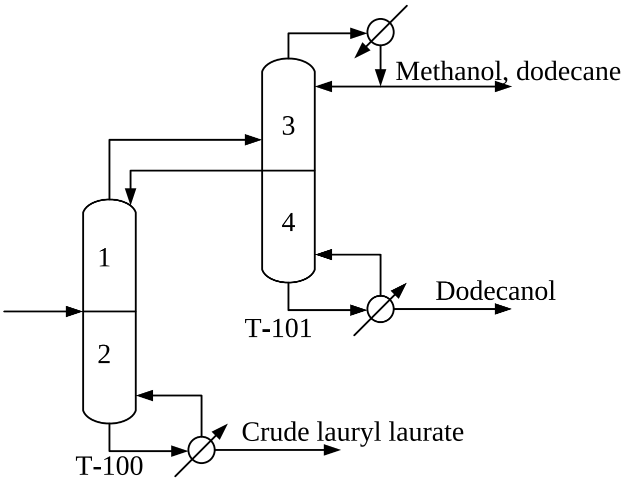


Fig 8.10 Thermal coupling of two simple distillation columns

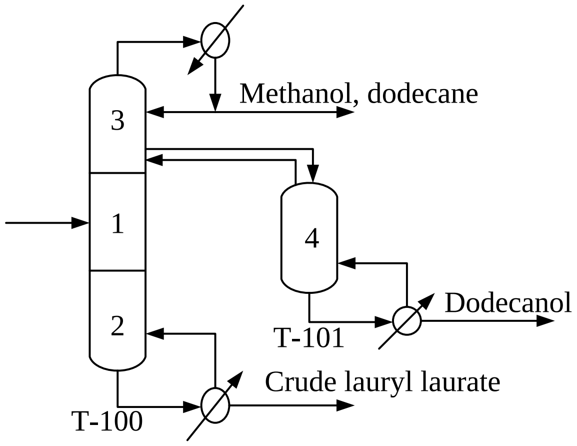


Fig 8.11 Distillation column with side stripper

8.5.3 Thermal coupling of distillation columns

In this work, the number of stages of distillation columns after heat integration is similar to designed process before heat integration. The suitable parameters are side draw rate and side draw location of distillation column (T-101). Fig 8.12 shows that side draw rate has no effect on total annual cost when side draw stream is located at the bottom of column. This is because temperature profiles of T-100 and T-101 column are not different. However, side draw stream located at the bottom stage is better than at the top stage because net vapor flow rate is lower.

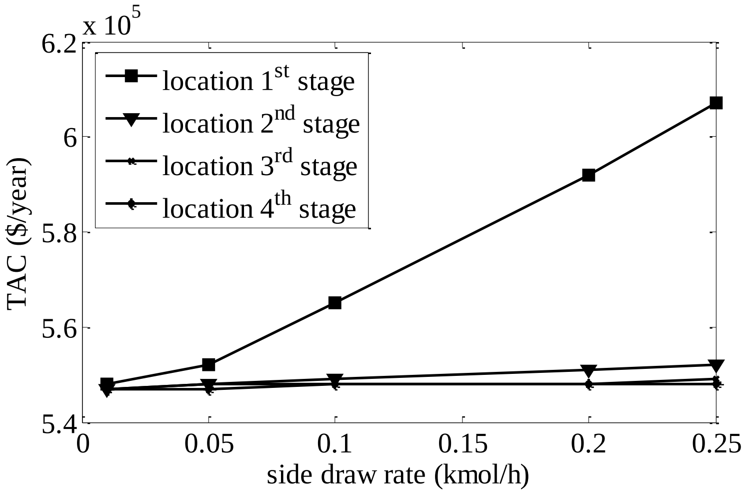


Fig 8.12 Effect of side draw rate on total annual cost ($/year) with different location of side draw stream of thermal coupling distillation columns

8.5.4 Distillation column with side stripper

Fig 8.13a shows the effect of the number of stages for main column when distillation with side stripper is used for the fatty alcohol separation. It can be seen that a minimum total annual cost is achieved at the optimum number of stages of main column. It is tradeoff between capital cost and operating cost. Liquid from main column is driven and sent to the side column at the top of column because main column produces the middle product (fatty alcohol). Fig 8.13 b shows that although increasing number of stages of side column reduces reboiler duty, capital cost has more affect on total annual cost than operating cost. Therefore, the optimum number of stages of main column and side column are 13 and 2 stages, respectively.

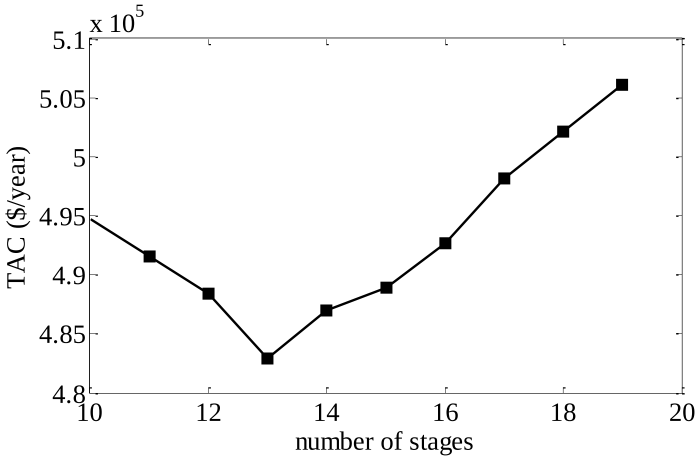


Fig 8.13a Effect of number of stages on TAC ($/year) of main column when distillation with side stripper

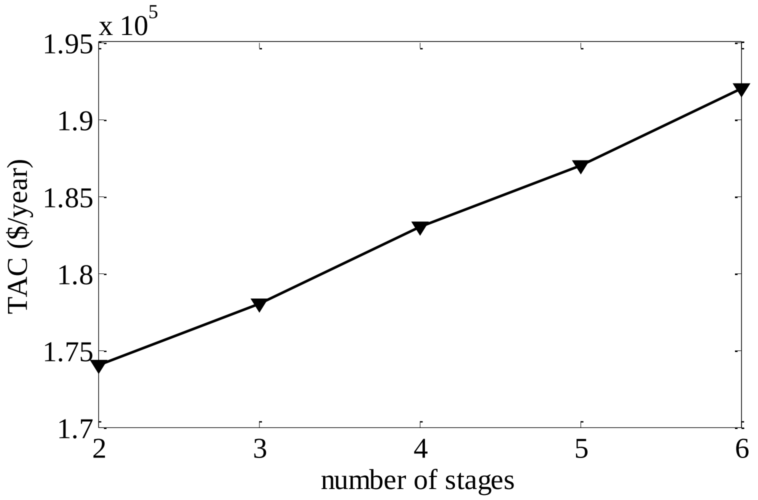


Fig 8.13b Effect of number of stages on TAC ($/year) of side column when distillation with side stripper

The composition within distillation columns for designed process before and after thermal coupling are shown in ternary diagram as shown in fig 8.14 and fig 8.15 respectively. The circles are of liquid composition of column T-100 while the rectangles are of liquid composition of column T-101. F1 locates feed composition of distillation column T-100. F2 locates feed composition of distillation column T-101 and the distillate stream of column T-100. B1 locates bottom composition of distillation T-100 and B2 locates bottom composition of distillation T-101. Circle symbols show the composition profile in column T-100. It presents that mostly dodecanol is obtained at the top stage of column; however, distillate rate cannot handle purified dodecanol. This is because purified dodecanol is a saddle node that leads to remix and dilute with methanol and dodecane. The composition profile in column T-101 for both processes is along the edge of diagram (line B2-D2). Purified dodecanol is obtained at the bottom of T-101 and light components consisting of dodecane and methanol are obtained at the top of column T-101. However, the profile of designed process before heat integration is different from designed process after heat integration.

Fig 8.15 shows the composition profile of the thermal coupling of designed process. Fig 8.15 indicates B1 at the corner of diagram. It means that purified lauryl laurate can be obtained at the bottom of column of distillation column T-100. The column T-100 after heat integration is more efficient than before heat integration because dodecanol is not be retained at the bottom of column. Therefore, distillation column T-102 is eliminated. The suitable configuration (fig. 8.17) is thermal coupling between two distillation columns that reduce energy consumption and the number distillation column. In addition, thermal coupling between column T-100 and T-101 is eliminated condenser of column T-100. Therefore, the minimum number of heat exchanger of 3 is required for distillation column. The minimum number of heat exchanger is equal to the number of components in the feed before sending to distillation columns (Rong et al., 2012).

Fig 8.16 shows the composition profile of distillation with side stripper. It presents that B1 locates bottom composition of main distillation column. D1 locates the top composition of main distillation column. B2 locates composition of the bottom of side column. Circle symbols present the composition profile of main column while rectangle symbols show the composition profile of the side stripper. The figures show that the the composition of the bottom of main column is similar to the composition at the bottom column T-100 of conventional process. Therefore, a distillation column is required to separate lauryl laurate. From Fig 8.16, the composition profile of distillation with side stripper is different from the composition profile of conventional process and thermal coupling of designed process. Light components (methanol and dodecane) are obtained at the top of main column. Purified fatty alcohol is not obtained at the main column because it is a saddle node. The feed composition of the side stripper is the composition of liquid side stream of main column. This composition is the mixtures of dodecanol and dodecane. The purified dodecanol is obtained at the bottom of side stripper.

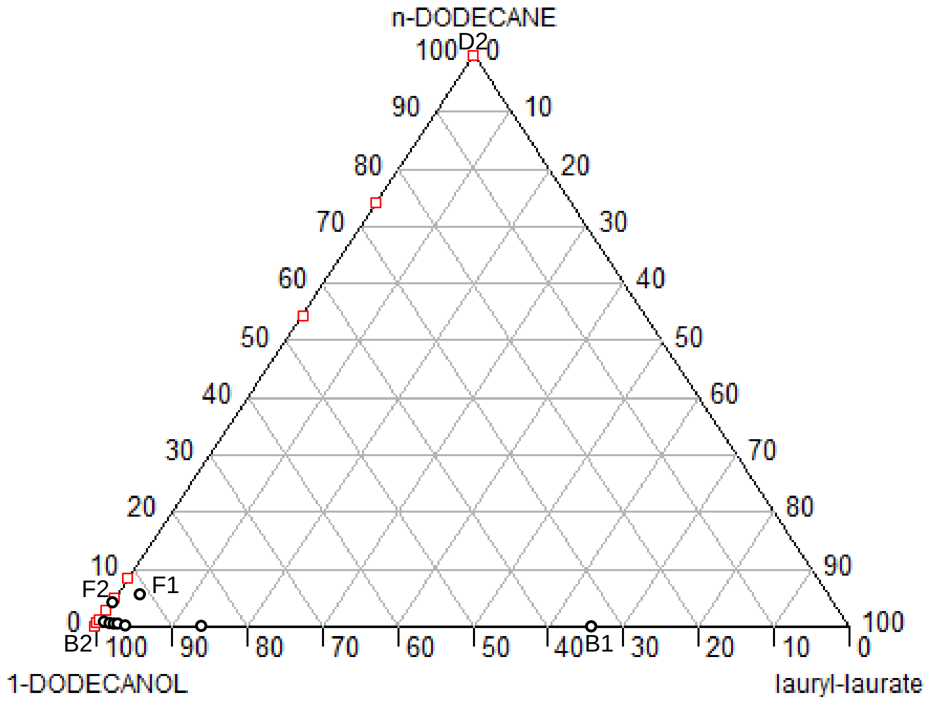


Fig 8.14 Residue curve map before heat integration

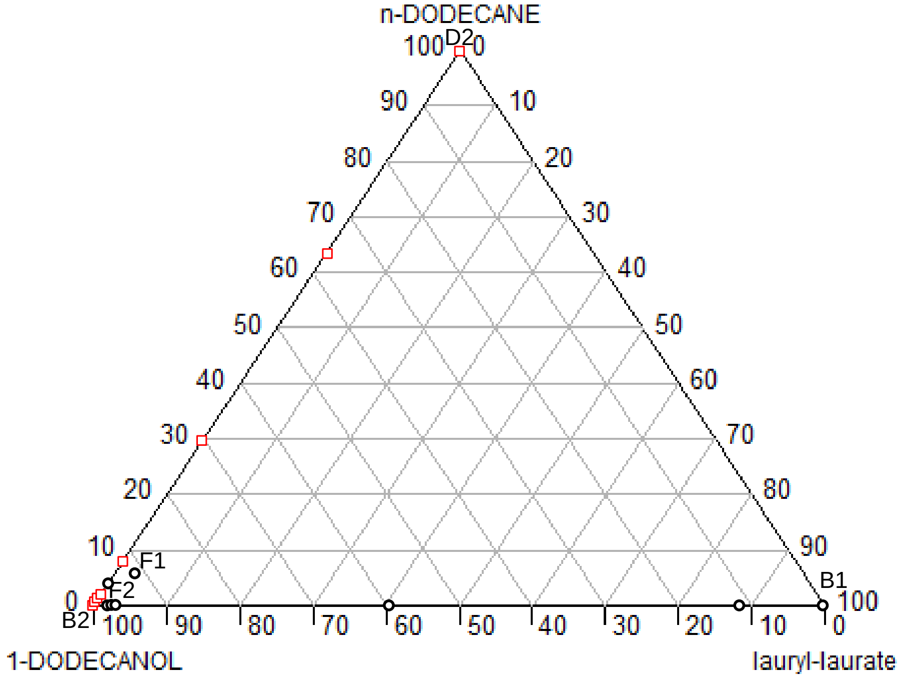


Fig 8.15 Residue curve map of thermal coupling distillation column

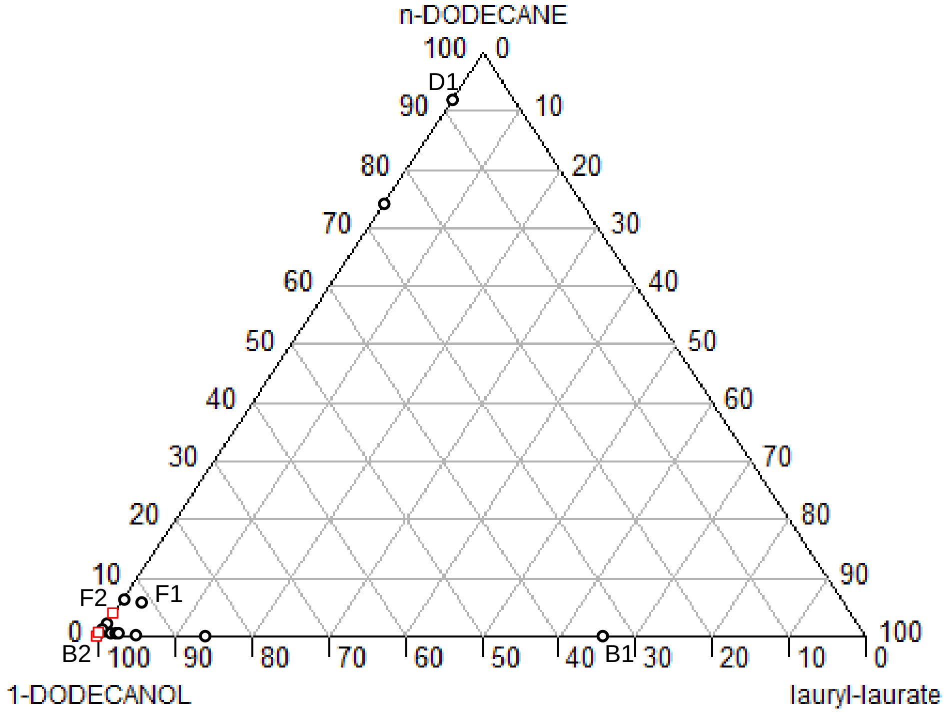


Fig 8.16 Residue curve map of distillation with side stripper

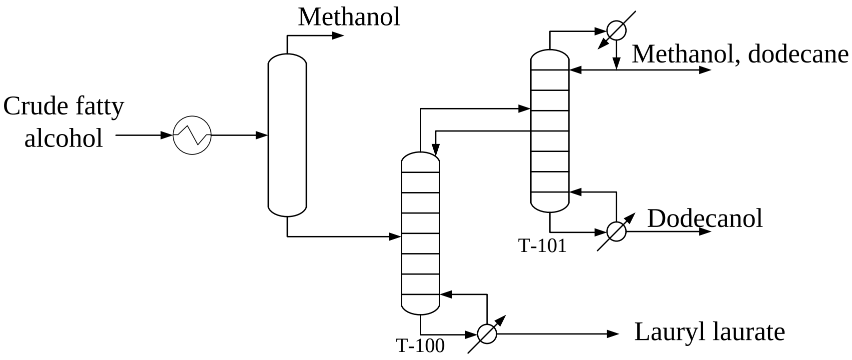


Fig 8.17 The suitable configuration of fatty alcohol separation

Table 8.6 Comparison of TAC and cost saving of conventional process, designed process before heat integration and designed process after heat integration.

	Conventional process	Designed process before heat integration	Thermal coupling of designed process	Distillation with side stripper of designed process
Condenser duty ($\times 10^6$Btu/h)	12.4	12.2	7.54	11.3
Reboiler duty ($\times 10^7$Btu/h)	1.64	1.63	1.14	1.58
TAC ($\times 10^5$\$/year)	7.7	7.68	5.47	7.07
Cost saving (%)	-	0.26	28	8.18

Table 8.7 shows the comparison of total annual cost, heat duty and cost saving of heat integration. It indicates that thermal coupling of designed process and distillation with side stripper can reduce energy consumption of condenser duty and reboiler duty because heat can be transferred from vapor stream to another column. In addition, these configurations can reduce the number of unit operation that reduces capital cost and operating cost. However, distillation with side stripper is less cost saving when it compares with thermal coupling column. This is because distillation with side stripper produces dodecanol in the side stream. In addition, distillation with side stripper is not suitable option when the middle product (dodecanol) is more than 30% of feed (Douglas, 1988). Thermal coupling of designed process reduces total annual cost 28% compared with designed process before thermal coupling of designed process.

8.6 Conclusion

In this study, a separation of fatty alcohol production consisting of multi-components is proposed. Thermodynamic insights technique is applied for selecting separation tasks and sequence of separation tasks although the energy consumption is similar to conventional process. The limitation of heat integration of distillation are analyzed through the criterion. According to screening alternatives, thermal coupling between two distillation columns is preferred than other types of heat integration in terms of total annual cost. It can reduce condenser duty and reboiler duty because vapor flow and liquid flow can be shared within two columns. Moreover, thermal coupling between two distillation columns reduces the number of operations because purity of fatty alcohol and wax ester can be achieved at 99 wt%.

CHAPTER IX

CONCLUSION AND RECOMMENDATION

9.1 Conclusion

The objective of this research is to propose the design biodiesel production integrated with fatty alcohol production process by using proposed methodology. Glycerol obtained from biodiesel production process is considered as byproduct and raw material to produce fatty alcohol. The best process is obtained through the economic criteria. At the final step, reactive distillation combining between reaction task and separation task replace reactor and distillation. Reactive distillation is designed based on element based method to determine the number of reactive stages, ratio of methanol to oil, distillate rate and reflux ratio. From the results, heterogeneous acid catalyzed process is the most economically process. This process required energy consumption due to high operating pressure. Heat integrated reactive distillation can improves the performance of this process by reducing energy consumption. Heat integrated reactive distillation is also designed according to methodology. For the last part of this research, the separation of fatty alcohol including heat integration is designed to reduce energy consumption and total annual cost.

9.1.1 Biodiesel production integrated with fatty alcohol production

In this study, biodiesel production integrated with fatty alcohol production from waste cooking oil is designed through methodology. The number of full sets of alternatives including all possible reaction tasks and separation tasks for biodiesel production integrated with fatty alcohol production when glycerol is considered as byproduct are. The number of alternatives is decomposed to 14 processes at the end of separation task. While the number of alternatives is reduced to 1 process from using economic criteria. According to the methodology, a heterogeneous acid catalyzed process for biodiesel production integrated with fatty alcohol production is better than other process alternatives because of the highest net present value. The suitable fraction of biodiesel to produce fatty alcohol is 1. That is, most of biodiesel should be diverted to fatty alcohol because the price of fatty alcohol is higher than biodiesel. However, when considering the fraction of biodiesel to produce fatty alcohol, it is found that the suitable fraction can be changed when the biodiesel price increases higher than 20%. For second case study, glycerol from biodiesel production is used to produce hydrogen for fatty alcohol production. The number of alternatives for hydrogen production is also reduced through criteria. The fraction of biodiesel to produce fatty alcohol is assumed to be 0.4 because of the availability of glycerol to produce hydrogen. Although glycerol is produced hydrogen that supply for fatty alcohol production, the use of glycerol for hydrogen production is uneconomical for the design conditions considered when it compared with the first case study because net present value of the second study is negative value.

9.1.2 Reactive distillation for biodiesel production

The design of reactive distillation for biodiesel production is divided into 2 case studies. The first case study is biodiesel profuction from pure vegetable oil. Triolein is considered as triglyceride. From methodology, biodiesel production from pure vegetable oil is considered as 1st branch of separation tasks. It means that separation task of reactive distillation is to separate only excess reactants that is a special case. Therefore, increasing the number of reactive stages is not necessary. Reactive flash separation can be handled in this study; however, the number of reactive stages is 3 stages. Ratio of methanol to oil is determined by ternary phase diagram. The suitable ratio of methanol to oil is determined when the element fraction of A and B is equal. The suitable ratio of methanol to oil is 4.3 when distillate rate is 45 kmol/h and reflux ratio is 5. For the second case study, waste cooking oil is considered as raw material. Thus, triolein is considered as triglyceride while oleic acid is presented as free fatty acid in triglyceride. In this case, separation task of reactive distillation is to separate light products from heavy product. It implies that reactive distillation can separate water that obtained from esterification of free fatty acid from product mixtures. However, reactive distillation cannot separate glycerol from methyl oleate due to a large difference of boiling point in transeseterification. The suitable number of reactive stages for the second case study is determined from element based method by fixed product specification at the bottom of column.

9.1.3 Heat integrated reactive distillation for biodiesel production

From the previous study, heterogeneous acid catalyzed process is an alternative option for biodiesel production. However, high conditions such as temperature and pressure are operated that leads to require high energy consumption of heat duty at the reboiler. Heat integrated reactive distillation is designed by the optimization of total annual cost according to methodology. The starting point to select type of heat integrated reactive distillation is to define product specification. The number of alternatives is reduced through the criteria such as ratio of boiling point. At the last step, the feasible type of heat integrated reactive distillation is obtained from the minimization of total annual cost. The design parameters such as the number of reactive stages, operating pressure feed location are also obtained. The results show that multi-effect indirect split arrangement reactive distillation is an alternative option for biodiesel production from waste cooking oil. Heat exchanger of multi-effect indirect split arrangement reactive distillation is used as reboiler for low pressure column so heat of between hot stream and cold stream in multi-effect indirect split arrangement reactive distillation can be transferred. In addition, Multi-effect indirect split arrangement reactive distillation can save energy, and reboiler duty, respectively when it compared with conventional reactive distillation column.

9.1.4 Separation process of fatty alcohol production

Separation of fatty alcohol production is important because it involves multi-components. When raw material (methyl ester) is mostly consumed, the separation is not difficult. Although energy consumption of designed process separation is similar to conventional process, the sequence of separation tasks based on thermodynamic insights technique is rearranged so that energy consumption can be improved by using heat integration. Thermal coupling between two distillation columns is preferred to separate fatty alcohol. This configuration is minimized total annual cost. In addition, the purity of fatty alcohol can obtained 99 wt%.

9.2 Recommendations

In this work, a design methodology of a process producing two main products, such as biodiesel and fatty alcohol, is proposed; however, only waste cooking oil is considered the raw material. In addition, a fixed conversion reactor is applied to the production of biodiesel and fatty alcohol. In the future work, the effect of changing raw materials and demand of products and by-product should be investigated. Process synthesis of biodiesel and fatty alcohol production should take into account their reaction kinetics.

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APPENDICES

APPENDIX A

DETAILS OF APPLICATION OF METHODOLOGY FOR CASE STUDY1

In this sections, the details of application of methodology for biodiesel production integrated with fatty alcohol production are shown in each step.

Step 2: Search literatures/database

In this step, literature reviews of biodiesel production and fatty alcohol production including conditions, catalysts and raw materials are shown.

Table A.1 Biodiesel production using homogeneous base as a catalyst

Literature	Raw material	alcohol	catalyst	ratio	Temperature	pressure	Resident time	kinetic	Conversion
Norredini and Zhu (1997)	Soybean oil	methanol	NaOH 0.2wt%	6:1	50 ^oC	1 atm	1 h	available	80%
Darnoko (2000)	Palm oil	methanol	KOH 1wt%	6:1	60 ^oC	1 atm	1 h	available	82.5%
Narvaez (2007)	Palm oil	methanol	NaOH 0.2wt%	6:1	60 ^oC	1 atm	80 min	available	94.3%
Zhang et al. (2003)	Canola oil	methanol	NaOH 0.2wt%	6:1	60 ^oC	400 kPa	1 h	-	95%
		methanol	CH_3ONa 0.5mol%	6:1	60 ^oC	1 atm	1 h		Yield=98%

Table A.2 Biodiesel production using acid as a catalyst

Literature	Raw material	alcohol	catalyst	ratio	Temperature	pressure	Resident time	kinetic	Conversion
Zhang et al. (2003)	Canola oil	methanol	H_2SO_4	50:1	80 ^oC	400 kPa	4 h	-	97%
Wang et al. (2009)	Waste cooking oil	methanol	H_2SO_4 4wt%	20:1		1atm	10 h	-	90%

Table A.3 Biodiesel production using heterogeneous base as a catalyst

Literature	Raw material	alcohol	catalyst	ratio	Temperature	pressure	Resident time	kinetic	Conversion
Liu et al. (2007)	Soybean oil	methanol	$Ca(OCH_2CH_3)_2$ 3wt%	12:1	65 ^oC	1 atm	1.5h	available	Yield 93.5%
Huaping et al. (2006)	Jatropha oil	methanol	CaO 1.5wt%	9:1	70 ^oC	1 atm	3.5h	-	93%
Boz and Kara (2009)	oil	methanol	KF/ Al_2O_3	15:1	60 ^oC	1 atm	8 h	-	99%
Noiroj et al. (2009)	Palm oil	methanol	$KOH/Al_2O_3$3 wt%	15:1	70 ^oC	1 atm	3 h	-	Yield=91.7%
Xie et al. (2006)	Palm oil	methanol	hydrotalcite	30:1	100 ^oC	1atm	6h	-	71.9%
Arzamendi, et al. (2007)	Sunflower oil	methanol	NaOH/alumina	6-48:1	50 ^oC	1atm	10h	-	99%
Albuquerque et al. (2008)	Sunflower oil	methanol	CaO-SBA14	12:1	160 ^oC	1atm	5h	-	95%
Liu et al. (2008)	Soybean oil	methanol	CaO	12:1	65 ^oC	1atm	3h	-	95%
Furuta et al.	Soybean	methanol	WO_3/ZrO_2	40:1	300 ^oC	1atm	20h	-	90%

Table A.4 Biodiesel production using heterogeneous acid as a catalyst

Literature	Raw material	alcohol	catalyst	ratio	Temperature	pressure	Resident time	kinetic	Conversion
Abreu (2005)	Canola	methanol	SnO	4.5:1	60 ^{o}C	1 atm	3h	-	94%
Peng et al. (2008)	Contonseed oil	methanol	SO_4^{2-}/TiO_2 3wt%	9:1	200 ^{o}C	1 atm	3h	-	Yield 90%
Reis et al. (2005)	Coconut oil	methanol	Amberlyst -15	100:1	60 ^{o}C	1 atm	8h	-	80%
Lou et al. (2008)	Waste cooking oil	methanol	Carbon based catalyst 10wt%	30:1	80 ^{o}C	1 atm	8h	-	Yield = 92%
Cao et al. (2008)	Waste cooking oil	methanol	$H_3PW_{12}O_{40}\cdot 6H_2O$ (PW12) (HPA catalyst)	70:1	65 ^{o}C	1 atm	14h	-	Yield = 87%
Zhang et al. (2009)		methanol	Sulfated silica zirconia 2.1wt%	20:1	65 ^{o}C	1 atm	8h	-	Yield = 98%
Melero et al. (2010)	Palm oil	methanol	sulfonic acid-modified mesostructured 6wt%	20:1	140 ^{o}C	-	2h		Yield = 95%

Table A.4 Biodiesel production using heterogeneous acid as a catalyst

Literature	Raw material	alcohol	catalyst	ratio	Temperature	pressure	Resident time	kinetic	Conversion
Ratanawilai	Palm oil	methanol	40% V_2O5/TiO_2	-	100 ^oC	1 atm	10h		80%
Kansedo et al. (2008)	Palm oil	methanol	montmorillonite KSF catalyst	10:1	155 ^oC	1 atm	120 min	-	78.7%
Bokade et al. (2009)	Palm oil	methanol	20% w/w DTPA/Clay, 5%	15:1	170 ^oC	17 atm	6h	available	94%
Bokade et al. (2009)	Sunflower oil	methanol	20% w/w DTPA/Clay, 5%	15:1	170 ^oC	17 atm	6h	available	92%
Bokade et al. (2009)	Soybean oil	methanol	20% w/w DTPA/Clay, 5%	15:1	170 ^oC	17 atm	6h	available	95%
Bokade et al. (2009)	Jatropha oil	methanol	20% w/w DTPA/Clay, 5%	15:1	170 ^oC	17 atm	6h	available	93%
Lien et al. (2010)	Soybean oil	methanol	Carbon based catalyst 3wt%	30:1	150 ^oC	1.7MPa	3h	available	Yield=97%
Shu et al. (2010)	Contonseed oil	methanol	Carbon based catalyst	21:1	140	1 atm	120 min	-	80

Table A.5 Biodiesel production using enzymed as a catalyst

Literature	Raw material	alcohol	catalyst	ratio	Temperature	pressure	Resident time	kinetic	Conversion
Watanabe et al. (2006)	rapeseed oil	methanol	immobilized *Candida antarctica* lipase	1st step 5:1 2nd step3:1	30 °C	1 atm	24 h	-	98%
Shah and Gupta (2007)	Jatropha oil	Ethanol	*Pseudomonas cepacia* Immobilized lipase	4:1	50 °C	1 atm	4h	-	98%
Kaieda et al. (2001)	Soybean oil	methanol	Pseudomonas fluorescensa	3:1 in three steps	35 °C	1 atm	90h	-	Yield=90%
Lee et al. (2006)	Soybean oil	methanol	Rhizopus oryzae mixed with Candida rugosal	4.5:1 in ten steps	45 °C	1 atm	21h		Yield=99%

Table A.5 Biodiesel production using enzymed as a catalyst

Literature	Raw material	alcohol	catalyst	ratio	Temperature	pressure	Resident time	kinetic	Conversion
Lee et al. (2002)	Tallow oil	methanol	Candida antarcticaj	3:1 in three steps	35 ^oC	1 atm	72h		Yield=74%
Soumanou and Bornscheuer	Sunflower oil	methanol	Pseudomonas fluorescensa	4.5:1	40 ^oC	1 atm	24 h		Yield=95%
Noureddini et al. (2005)	Soybean oil	methanol	Pseudomonas cepacia lipase	7.5:1	35 ^oC	1 atm	1h		Yield=67%
Nelson *et al*. (1996)	Rapeseed oil	ethanol and solvent hexane	lipase *Mucor miehei*	3:1	45	1 atm	4h		Yield=98%
Shah *et al*. (2004)	Jatropha oil	Ethanol	lipase *Chromobacterium viscosum*	4:1	40	1 atm	8 h,		Yield 92%
Jegannathan et al. (2009)	Palm oil	methanol	κ-carrageenan 52.5wt%	7:1	30	1 atm	72h	-	Conversion 99%

Table A.6 Biodiesel production by using supercritical methanol

Literature	Raw material	alcohol	catalyst	ratio	Temperature	pressure	Resident time	kinetic	Conversion
Song et al. (2007)	Palm oil	methanol	-	45:1	350 ^{o}C	40 MPa	5 min	available	Concentration methyl ester 95%
West (2008)	Canola oil	methanol	-	42:1	350 ^{o}C	20e3 kPa	0.333h	-	98%

Table A.7 Biodiesel production using hydrolysis of triglyceride

Literature	Raw material	catalyst	ratio	Temperature	pressure	Resident time	kinetic	Conversion
Yow et al. (1999)	Palm oil	Ion exchange resin		155 ^{o}C	1 atm	8h	available	75%
Anozie et al. (2006)	Palm oil	Benzene sulfonate 0.5%wt	3:1	100 ^{o}C	1 atm	8h		82.5%
Anozie et al. (2006)	Palm kernel oil	Benzene sulfonate 0.5%wt	3:1	100 ^{o}C	1 atm	8h		84%
Serri et al. (2009)	Palm cooking oil	*rugosa* Lipase	Don’t know	45 ^{o}C		90 min		95%
Serri et al. (2009)	Soybean oil	H_2SO_4	20:1	463K		8h	-	98%
Serri et al. (2009)	Soybean oil	ZnO	20:1	463K		8h		99%

Table A.7 Biodiesel production using hydrolysis of triglyceride

Literature	Raw material	catalyst	ratio	Temperature	pressure	Resident time	kinetic	Conversion
Serri et al. (2009)	Soybean oil	Sulfated zirconia	20:1	463K		8h		47.8
Serri et al. (2009)	Soybean oil	Amberlyst	20:1	463K		8h		38.5
Serri et al. (2009)	Soybean oil	Co-Zn DMC	20:1	463K		8h		96.7%
Serri et al. (2009)	Soybean oil	Fe-Zn DMC	20:1	463K		8h		93.9
Chew et al. (2008)	palm olein	immobilized lipase	3.3%v/v	55 ^{o}C	1 atm	6h		28%
Chew et al. (2008)	Palm oil	*Candida rugosa* lipase in calcium alginate				3h		74%
Alenezi et al. (2009)	Sunflower oil		50/50 v/v	350 ◦C	20MPa.	10 min	available	98%

Table A.8 Biodiesel production from esterification reaction

Literature	Raw material	alcohol	catalyst	ratio	Temperature	pressure	Resident time	kinetic	Conversion
Donato et al. (2008)	Free fatty acid in palm oil	methanol	H_2SO_4 0.1wt%	3:1	130 ^oC	1 atm	1h	available	90%
Donato et al. (2008)	Free fatty acid in palm oil	methanol	Methanesulfonic acid	3:1	130 ^oC	1 atm	1h	available	90%
Berrios et al. (2007)	Free fatty acid in sunflower oil	methanol	H_2SO_4 5wt%	60:1	60 ^oC	1 atm	120 min	available	Acid value lower than 1%
Rattanaphra et al. (2011)	Myristic acid	methanol	Sulfate zirconia 3wt%	20:1	443K	22 bar	20 min	available	93%
Tesser et al. (2008)	Oleic acid	methanol	Relite CFS	8.6:1	85 ^oC		120 min	available	80%

Table A.8 Biodiesel production from esterification reaction

Literature	Raw material	alcohol	catalyst	ratio	Temperature	pressure	Resident time	kinetic	Conversion
Pasias et al. (2006)	FFA in waste oil	methanol	Polystyrensulphonic acid 2 wt%	6.6:1	393.15 K	650 kPa		available	67%
Lien et al. (2010)	Palmitic in soybean	methanol	Carbon based catalyst 3wt%	30:1	150 ^{o}C	1.7MPa	3h	have	100%

Table A.9 Literature reviews for fatty alcohol production

Literature	Raw material	catalyst	ratio	Temperature	pressure	Resident time	products	Conversion/Yield (%)
Pouilloux et al. (1998)	Methyl oleate	Co1.9Sn3.9±Al_2O_3.	2:1	270 ^oC	8MPa	22h	Oleyl alcohol, wax ester, methanol, sat. alcohol	Oleyl alcohol 42%
Pouilloux et al. (1996)	Methyl oleate	CoSn sol–gel) catalystsa	2:1	270 ^oC	8MPa	24h	Oleyl alcohol, wax ester, methanol, sat. alcohol, hydrocarbon	12.5%
Fleckenstein et al. (1992)	Mixed ester C12-C18	CuCr	100:1	250 ^oC	30 bar	-	Fatty alcohol 85.6%, hydrocarbon 0.12%, methanol 14%	

Table A.9 Literature reviews for fatty alcohol production (cont)

Literature	Raw material	catalyst	ratio	Temperature	pressure	Resident time	products	Conversion/ Yield (%)
Fleckenstein et al. (1991)	Methyl ester derived from coconut oil (C8-C18)	38% of Cu, 29% of Cr, 2.5% of Mn, 1.9% of Ba, 1% of Si and graphite	10:1-500:1	200 °C	250 bar		Product composition 0.1% of FAME, 85% of fatty alcohol, 0.05% of hydrocarbon, 13.9% of methanol	
Fleckenstein et al. (1991)	Methyl ester from coconut	38% of Cu, 29% of Cr, 2.5% of Mn, 1.9% of Ba, 1% of Si and graphite					11.7% of FAME, 70% of fatty alcohol, 0.02% of hydrocarbon, 17.6% of methanol	

Table A.9 Literature reviews for fatty alcohol production (cont)

Literature	Raw material	catalyst	ratio	Temperature	pressure	Resident time	products	Conversion/ Yield (%)
Singleton et al. (1995)	Methyl ester (C6-C22)		125:1	200-220 ^{o}C	600 psig		75% of fatty alcohol, 0.4% of hydrocarbon, 23.8% of wax ester	97-99%
Fleckenstein et al. (1991)	Mixed ester C16-C18	CuCr	50:1	250 ^{o}C	30 bar	-	Fatty alcohol 87%, hydrocarbon 0.03%, methanol 11.95%	

step 3.3: Find azeotrope of binary mixture by using VLE diagram

VLE diagram of binary mixtures are needed to determine azeotrope. The VLE diagram of binary mixtures are shown in fig.A.1-fig. A.5.

Methanol/water

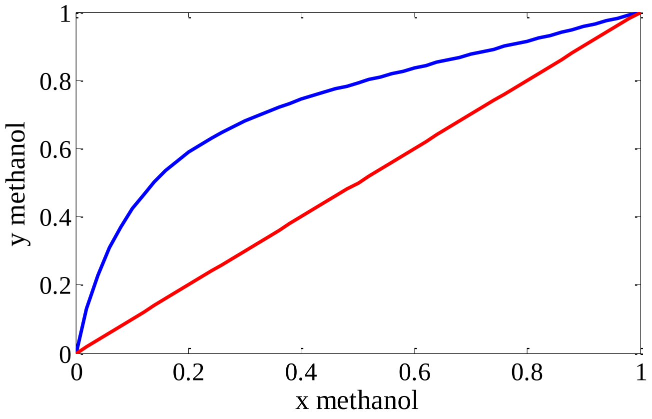

Fig. A.1 VLE diagram between methanol and water.

Methyl oleate/palmitic acid

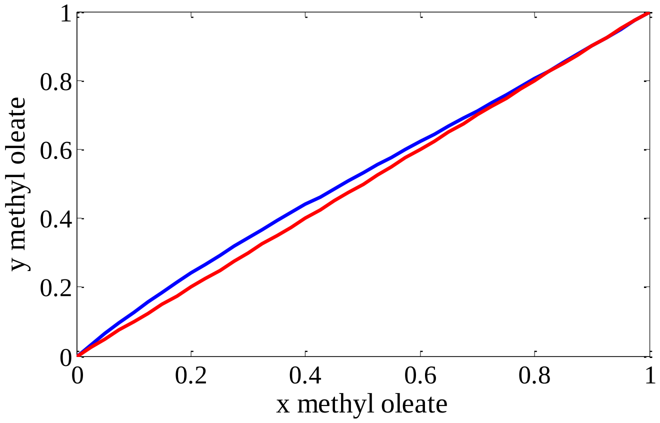

Fig. A.2 VLE diagram between methyl oleate and palmitic acid

Methanol/myristyl alcohol

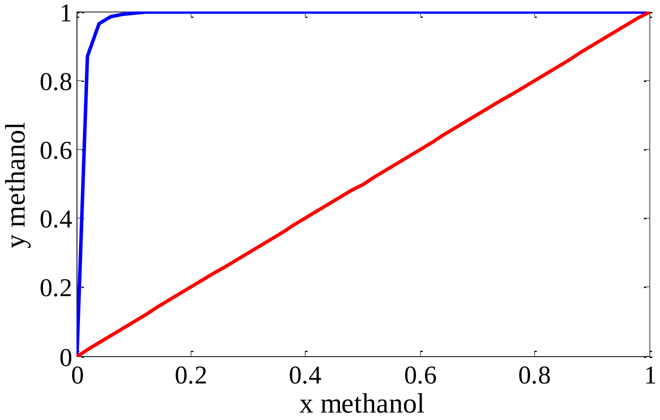

Fig. A.3 VLE diagram between methanol/myristyl alcohol

Methanol/cetyl alcohol

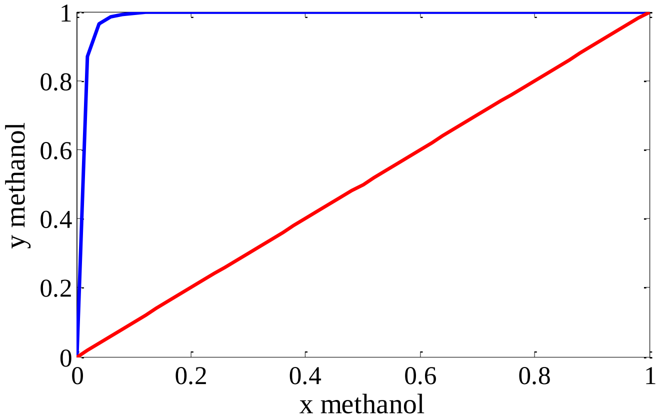

Fig. A.4 VLE diagram between methanol/cetyl alcohol

Myristyl alcohol/cetyl alcohol

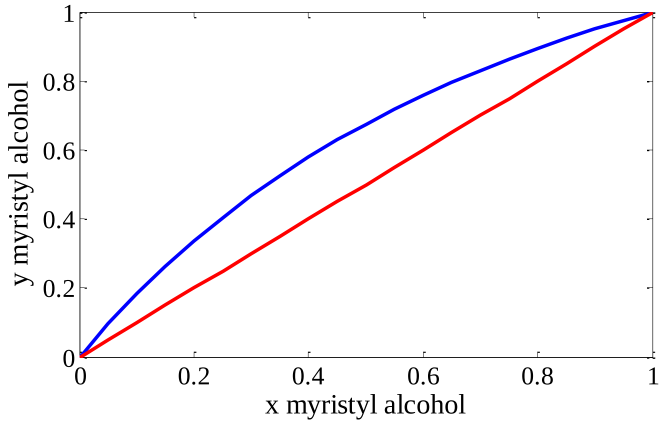

Fig. A.5 VLE diagram between myristyl alcohol/cetyl alcohol

Methyl laurate/ lauryl alcohol

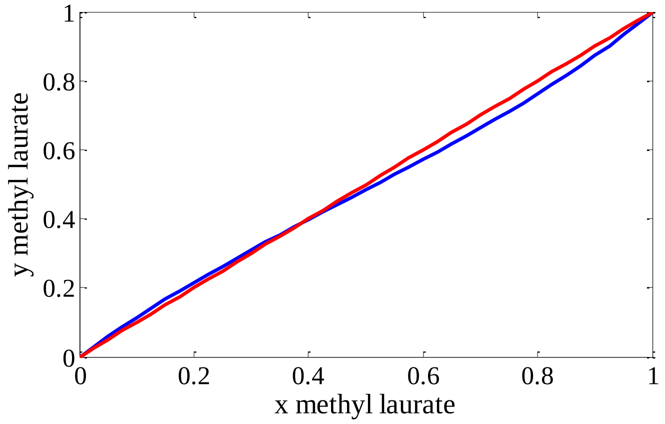

Fig. A.6 VLE diagram between methyl laurate/lauryl alcohol

Methyl palmitate/stearyl alcohol

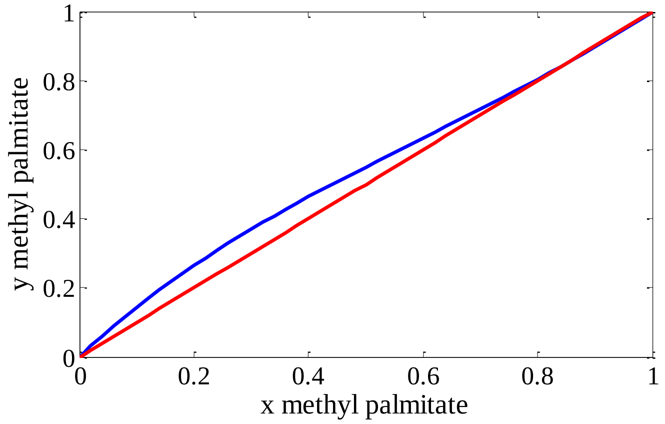

Fig. A.7 VLE diagram between methyl palmitate/stearyl alcohol

Step 3.4: Calculate binary ratio of properties

For the identified chemicals present in the system, binary ratios of properties, such as vapor pressure, melting point, boiling point, solubility and molecular weight, for all components are computed. Binary ratio of all properties for biodiesel and fatty alcohol production are shown in table A.9.

Table A.10 Binary ratio of component properties for biodiesel production

Component/ properties	Molecular weight	Acentric factor	Tc	Pc	Normal boiling point	Dipole moment	Rad of gyration	Melting point	Triple P temp	Molar volume	solubility	Van der waal volume	Vapor pressure
Water/glycerol	5.11	3	1.12	10.4	2.85	2.27	72	1.07	1.07	4.06	1.4		1.4x10^{5}
Water/methyl esters	16.46	3.04	1.18	17.23	1.65	50	16.99	1.07	1.07	18.86	2.82	16.39	5.2 x10^{5}
Water/methanol	1.78	1.64	1.26	2.72	1.45	50	11.15	1.02	1.02	11.61	2.56	11.71	5794
Glycerol/methyl esters	3.22	1.02	1.06	1.66	1.1	50	2.97	1.01	1.01	4.64	2.01	3.95	26.11
Glycerol/methanol	2.87	1.83	1.41	3.82	1.66	2.47	2.27	1.66	1.66	1.81	1.15	2.37	2.8 x10^{6}
Methyl esters/methanol	9.25	1.86	1.49	6.33	1.83	50	6.73	1.67	1.67	8.4	1.75	9.34	2.8 x10^{6}
Water/ffa	15.68	3.43	1.21	15.87	1.7	1.29	13.88	1.05	1.05	17.69	2.6	15.63	5.2 x10^{5}
Glycerol/ffa	3.07	1.14	1.08	1.53	1.13	2.92	2.43	1.02	1.02	4.36	1.85	3.76	242.14
Methyl ester/ffa	1.05	1.13	1.02	1.02	1.03	50	1.22	1.02	1.02	1.07	1.09	1.05	9.27
Methanol/ffa	8.82	2.1	1.52	1.52	1.87	1.18	5.5	1.63	1.63	7.88	1.61	8.91	2.8 x10^{6}

Table A.11 Binary ratio of component properties for fatty alcohol production

Component/ properties	Molecular weight	Acentric factor	Tc	Pc	Normal boiling point	Dipole moment	Rad of gyration	Melting point	Triple P temp	Molar volume	solubility	Van der waal volume	Vapore pressure
Methanol/methyl esters	9.25	1.86	1.49	6.33	1.83	50.00	6.73	1.67	1.67	8.40	1.75	9.34	2.8 x10^{6}
Methanol/ lauryl alcohol	5.82	1.18	1.40	4.06	**1.59**	**1.01**	**3.94**	**1.69**	1.69	**5.53**	**1.46**	6.18	2.5 x10^{4}
Methanol/ lauryl alcohol	6.69	1.32	1.46	4.47	1.68	1.10	4.34	1.77	1.77	6.42	1.52	7.13	
Methanol/ myristyl alcohol	7.57	1.45	1.50	5.03	1.77	1.02	4.71	1.84	1.84	7.30	1.57	8.07	1.2 x10^{6}
Methanol/ oleyl alcohol	8.44	1.58	1.54	5.62	1.85	1.02	5.11	1.89	1.89	8.21	1.62	9.01	1.2 x10^{6}
Methyl ester/dodecanol	1.59	1.57	1.06	1.56	1.15	1.6	1.71	1.01	1.01	1.52	1.20	1.51	141.06

Table A.11 Binary ratio of component properties for fatty alcohol production (Cont)

Component/ properties	Molecular weight	Acentric factor	Tc	Pc	Normal boiling point	Dipole moment	Rad of gyration	Melting point	Triple P temp	Molar volume	solubility	Van der waal volume	Vapor pressure
Methyl ester/myristyl alcohol	1.38	1.41	1.02	1.41	1.08	1.68	1.55	1.06	1.06	1.31	1.15	1.31	107.61
Methyl ester/palmityl alcohol	1.22	1.29	1.01	1.26	1.03	1.69	1.43	1.10	1.10	1.15	1.11	1.16	164.94
Methyl ester/oleyl alcohol	1.10	1.18	1.03	1.12	1.01	1.6	1.32	1.13	1.13	1.02	1.08	1.04	134.05
Lauryl alcohol/myristyl alcohol	1.15	1.12	1.04	1.10	1.06	1.09	1.10	1.05	1.05	1.16	1.04	1.15	1.31
Lauryl alcohol/palmityl alcohol	1.30	1.22	1.07	1.24	1.11	1.01	1.19	1.09	1.09	1.32	1.07	1.30	1.17

Table A.11 Binary ratio of component properties for fatty alcohol production (Cont)

Component/ properties	Molecular weight	Acentric factor	Tc	Pc	Normal boiling point	Dipole moment	Rad of gyration	Melting point	Triple P temp	Molar volume	solubility	Van der waal volume	Vapor pressure
Lauryl alcohol/oleyl alcohol	1.45	1.33	1.10	1.38	1.16	1.02	1.30	1.11	1.11	1.48	1.11	1.46	1.05
Myristyl alcohol/palmityl alcohol	1.13	1.10	1.03	1.12	1.05	1.08	1.09	1.04	1.04	1.14	1.03	1.13	1.53
Myristyl alcohol/oleyl alcohol	1.26	1.20	1.06	1.26	1.10	1.07	1.18	1.07	1.07	1.28	1.07	1.26	1.25
Palmityl alcohol/oleyl alcohol	1.12	1.09	1.03	1.12	1.04	1.01	1.09	1.03	1.03	1.12	1.03	1.12	1.23

Step 4.5: Screen and reduce the number of synthesis routes based on productivity for each catalyst

Table A.12 Productivity for each catalyst for biodiesel production

Type of process	catalyst	Productivity (kg product/kg oil)
Alkali catalyzed process	NaOH	0.94
	KOH	0.83
Acid catalyzed process	H_2SO_4	0.9538
Heterogeneous base catalyzed process	KOH/Al_2O_3	0.924
	hydrotalcite	0.745
Heterogeneous acid catalyzed process	clay	0.95
	KSF	0.36
	Sulfonic acid	0.36
	V_2O_5	0.36
Enzyme catalyzed process	Immobilized κ-carrageenan	0.995
Supercritical methanol	-	0.999
Hydrolysis/esterification	Bezene sulfonate/ H_2SO_4	0.808
	Enzyme/ H_2SO_4	0.9156
	Ionic resin/ H_2SO_4	0.7438
	Lipase/ H_2SO_4	0.7352
	Bezene sulfonate/ Methanesulfonic acid	0.80
	Enzyme/ Methanesulfonic acid	0.91

Table A.12 Productivity for each catalyst for biodiesel production

Type of process	catalyst	Productivity (kg product/kg oil)
	Ionic resin/ Methanesulfonic acid	0.7
	Lipase/ Methanesulfonic acid	0.73

Table A.13 Productivity of biodiesel production using different catalysts and fatty alcohol production

Biodiesel production	Productivity of biodiesel	Productivity of fatty alcohol (approach1)	Productivity of fatty alcohol (approach 2)
(1) NaOH (base cat.)	0.95	0.83	0.893
(2) H_2SO_4 (acid cat.)	0.95	0.83	0.893
(3) KOH/Al_2O_3 (solid base cat.)	0.92	0.83	0.893
(4) DTPA/Clay (solid acid cat.)	0.955	0.84	0.896
(5) κ-Carrageenan (enzyme process)	0.99	0.83	0.894
(6) Supercritical methanol	0.94	0.83	0.894
(7) Lipase (hydrolysis process)	0.91	0.83	0.894

APPENDIX B

DETAILS OF APPLICATION OF METHODOLOGY FOR CASE STUDY2

In this sections, the details of application of methodology for biodiesel production integrated with fatty alcohol production when glycerol is used to produce hydrogen that supply for fatty alcohol production are shown in each step.

Step 2: Search literatures/database

In this step, literature reviews of biodiesel production and fatty alcohol production including conditions, catalysts and raw materials are shown.

Table B.1 hydrogen production from glycerol reforming

literature	Raw material		catalyst	ratio	Temperature	pressure	Resident time	Conversion
Guo et al. (2012)	glycerol	steam	0.1% NaOH	4:1	526 °C	30MPa		10wt% of glycerol Yield 88%
Chen et al. (2011)	glycerol	steam	Ni	9:1	600 °C	1 atm	4 h	91.4%
Ulianelli et al 2010	glycerol	steam	0.5 wt% Ru/Al_2O_3 (Pd-Ag membrane reactor)	6:1	400 °C	5 bar	WHSV = $0.1h^{-1}$	57%
Sa´nchez et al.	glycerol	steam	Ni/Al_2O_3	16:1	700 °C	1 atm		100%
Araque	glycerol	steam	Ce_2Zr1.5Co0.5O_8–	9:1	650 °C	1 atm	24h	95%
Zhang et al, (2007)	glycerol	steam	Ir/CeO_2	9:1	400 °C	1 atm	3h	100%
Adhikari et al,(2008)	glycerol	steam	Ni/MgO	9:1	650 °C	1atm		100%
Adhikari et al,(2008)	glycerol	steam	Ni/CeO_2	9:1	650 °C	1atm		93
Adhikari et al,(2008)	glycerol	steam	Ni/TiO_2	9:1	650 °C	1atm	1h	98

Table B.1 hydrogen production from glycerol reforming

literature	Raw material		catalyst	ratio	Temperature	pressure	Resident time	Conversion
Adhikari et al, (2007)	glycerol	steam	$Rh/CeO_2/Al_2O_3$	9:1	900 °C	1atm	1h	88%
Adhikari et al, (2007)	glycerol	steam	$Pt/CeO_2/Al2O_3$	9:1	900 °C	1atm	1h	72%
Adhikari et al, (2007)	glycerol	steam	Rh/Al_2O_3	9:1	900 °C	1atm	1h	68%
Adhikari et al, (2007)	glycerol	steam	Ru/Al_2O_3	9:1	900 °C	1atm	1h	58%
Adhikari et al, (2007)	glycerol	steam	Pd/Al_2O_3	9:1	900 °C	1atm	1h	70%
Adhikari et al, (2007)	glycerol	steam	CeO_2/Al_2O_3	9:1	900 °C	1atm	1h	67%
Adhikari et al, (2007)	glycerol	steam	Pt/Al_2O_3	9:1	900 °C	1atm	1h	65%
Adhikari et al, (2007)	glycerol	steam	$Pd/CeO_2/Al_2O_3$	9:1	900 °C	1atm	1h	71%
Adhikari et al, (2007)	glycerol	steam	$Ru/CeO_2/Al_2O_3$	9:1	900 °C	1atm	1h	80%
Adhikari et al, (2007)	glycerol	steam	Ir/Al_2O_3	9:1	900 °C	1atm	1h	80%

Table B.1 hydrogen production from glycerol reforming

literature	Raw material		catalyst	ratio	Temperature	pressure	Resident time	Conversion
Hirai, et al, (2005)	glycerol	steam	Ru/Y_2O_3		600 ^{o}C			
Nichele et al, (2011)	glycerol	steam	Ni/ZrO_2		650 ^{o}C			72%
Buffoni et al,(2009)	glycerol	steam	NiCea	6:1	600 ^{o}C	1atm	11h	90
Pompeo et al, (2009)			PtSiO2		350 ^{o}C		1h	99%
Dave et al., (2011)	glycerol	steam	NieZrO_2/CeO_2		700 ^{o}C	1atm		100%

step 3.1: Identify all components of reactants and products from reactions

Components for biodiesel and fatty alcohol production are similar to the first study. For hydrogen production, components are glycerol, hydrogen, steam, CO_2, CO, CH_4

Step 3.4: Calculate binary ratio of properties

For the identified chemicals present in the system, binary ratios of properties, such as vapor pressure, melting point, boiling point, solubility and molecular weight, for all components are computed. Binary ratio of all properties for biodiesel and fatty alcohol production are shown in table B.2.

Table B.2 Binary ratio of component properties for hydrogen production

Component/ properties	Molecular weight	Acentric factor	Tc	Pc	Normal boiling point	Dipole moment	Rad of gyration	Melting point	Triple P temp	Molar volume	solubility	Van der waal volume	Vapor pressure
Glycerol/ water	5.11	3.00	1.12	10.40	1.50	2.27	5.72	1.07	1.07	4.06	1.40	4.15	1.48×10^5
Glycerol/ hydrogen	45.68	4.78	21.78	1.61	27.51	50.00	9.49	20.88	20.88	2.57	5.13	8.13	∞
Glycerol/ CO	3.29	21.44	5.44	1.65	6.87	37.44	6.31	4.27	4.27	2.07	5.33	3.17	∞
Glycerol/ CO_2	2.09	4.62	2.38	3.48	50.00	50.00	3.38	1.35	1.35	1.97	2.34	2.61	∞
Glycerol/ methane	5.74	89.87	3.79	2.17	5.02	50.00	3.15	3.21	3.21	1.93	2.94	3.01	∞
Water/hydrogen	8.94	-1.60	19.50	16.80	18.30	50.00	1.66	19.58	19.58	1.58	7.19	1.96	12434.91
Water/Co	1.55	7.16	4.87	6.30	4.57	16.50	1.10	4.01	4.01	1.96	7.47	1.31	8539.65

Table B.2 Binary ratio of component properties for hydrogen production

Component/ properties	Molecular weight	Acentric factor	Tc	Pc	Normal boiling point	Dipole moment	Rad of gyration	Melting point	Triple P temp	Molar volume	solubility	Van der waal volume	Vapor pressure
Water/CO2	2.44	1.54	2.13	2.99	**50.00**	50.00	1.69	1.26	1.26	2.06	3.28	1.59	**2035.28**
Water/methane	1.12	29.99	3.40	4.80	3.34	50.00	1.82	3.01	3.01	2.10	4.12	1.38	5906.16
Hydrogen /CO	13.89	-4.48	4.00	2.66	4.01	50.00	1.50	4.89	4.89	1.24	1.04	2.56	1.46

Step 3.5: List the feasible separation techniques of all components

TableB.3 Separation techniques

task	Separation technique
H_2/, CO, CO_2, CH_4,water, glycerol	Filtration, supercritical extraction,flash **pervaporation, membrane**
H_2, CO, CH_4, CO_2/water,glycerol	**Flash**, distillation
H_2, CO/water, glycerol CH_4, CO_2	Stripping, membrane
H_2, CO, CO_2, CH_4,water/ glycerol	membrane

Step 4: Screen of alternatives

From literature reviews, there are 4 types for hydrogen productions such as steam reforming, partial oxidation, autothermal and aqueous reforming; however, steam reforming is only concern because it gives the highest amount of hydrogen. There are several metal catalyst for steam reforming such as Ni, Ir, Pd, Ph, Pt, Ru. I collected 25 literature reviews.

Step 4.5: Screen and reduce the number of synthesis routes based on productivity for each catalyst

Table B.4 Productivity for each catalyst

catalyst	Ratio of steam/glycerol	temperature	pressure	productivity
Ir/CeO_2	9:1	400 ^oC	1 atm	100%
Ni/MgO	9:1	650 ^oC	1 atm	100%
NieZrO_2/CeO_2	-	700 ^oC	1atm	100%

Step 4.7: Reduce the alternatives with respect to the highest driving force of separation process

From table C.2, it shows that binary adjacent ratio of vapor pressure between water and CO_2 is the highest; therefore, flash operation is selected for the first separation. Then membrane separated pure hydrogen from other gases. The important information for membrane separator is

- In this work, dense Pd-Ag membrane is selected.
- Hydrogen flux permeating is in equation B.1

$$J_{H_2} = \frac{Pe}{\delta}\left(P^{n}_{H2,retentate} - P^{n}_{H2,permeate}\right) \quad \text{(B.1)}$$

$$Pe = Pe_0 \exp\left(\frac{-Ea}{RT}\right) \quad \text{(B.2)}$$

Step 4.8: Screen the alternatives in terms of limitations of the separation technique

There is no limitation of separation techniques.

Step 5: Process simulation

Rigorous steady state process simulations of all remaining feasible process alternatives are performed before their corresponding performance criteria are computed in Step 6 for economic analysis and final selection. The UNIQUAC model is used for the phase equilibrium calculations. Distillation columns for separation product mixtures such as methyl esters, methanol,water are designed base on driving force technique. The configuration of distillation columns are similar to the first case study. Amount of glycerol is divided into 2 streams. The first stream is used to produce hydrogen as raw material for fatty alcohol production. The second stream is byproduct of biodiesel production that can be sold to industry. The fraction of amount of glycerol to produce hydrogen is shown in table B.5

Table B.5 Amount of required hydrogen for fatty alcohol production when glycerol is produced to hydrogen at different fraction

	Amount of required hydrogen for fatty alcohol (m^3/year) before hydrogen production					Amount of required hydrogen for fatty alcohol (m^3/year) after hydrogen production					Excess hydrogen (m^3/year)				
	Fraction of biodiesel to produce fatty alcohol					Fraction of biodiesel to produce fatty alcohol					Fraction of biodiesel to produce fatty alcohol				
process	0.2	0.4	0.5	0.8	1	0.2	0.4	0.5	0.8	1	0.2	0.4	0.5	0.8	1
alkali	1.37×10^{4}	2.61×10^{4}	3.17×10^{4}	5.04×10^{4}	6.53×10^{4}	0	0	5.10×10^{3}	2.38×10^{4}	3.87×10^{4}	1.29×10^{4}	5.04×10^{2}	0	0	0
acid	1.36×10^{4}	2.56×10^{4}	3.17×10^{4}	5.00×10^{4}	6.20×10^{4}	0	0	5.10×10^{3}	2.34×10^{4}	3.54×10^{4}	1.30×10^{4}	1.00×10^{3}	0	0	0
solid base	1.34×10^{4}	2.57×10^{4}	3.17×10^{4}	4.97×10^{4}	6.21×10^{4}	0	0	5.10×10^{3}	2.31×10^{4}	3.55×10^{4}	1.32×10^{4}	9.04×10^{2}	0	0	0
solid acid	1.34×10^{4}	2.66×10^{4}	3.25×10^{4}	5.18×10^{4}	6.45×10^{4}	0	0	5.90×10^{3}	2.52×10^{4}	3.79×10^{4}	1.32×10^{4}	4.04	0	0	0
enzyme	1.45×10^{4}	2.89×10^{4}	3.41×10^{4}	5.67×10^{4}	7.01×10^{4}	0	2.30×10^{3}	7.50×10^{3}	3.01×10^{4}	4.35×10^{4}	1.21×10^{4}	5.04×10^{2}	0	0	0
supertical	1.39×10^{4}	3.38×10^{4}	3.31×10^{4}	5.25×10^{4}	6.52×10^{4}	0	7.20×10^{3}	6.50×10^{3}	2.59×10^{4}	3.86×10^{4}	1.27×10^{4}	5.04×10^{2}	0	0	0
hydrolysis	1.27×10^{4}	2.43×10^{4}	4.81×10^{4}	4.71×10^{4}	5.81×10^{4}	0	0	2.15×10^{4}	2.05×10^{4}	3.15×10^{4}	1.39×10^{4}	$2.\ 3\times10^{3}$	0	0	0

Step 6: Perform economic analysis

In this step, economic for hydrogen production from glycerol refoming is analyzed by using net present value. It is noted that glyceride price is related to crude glycerol (purity 75%). Crude glycerol is derived from biodiesel production with different processes such as alkali catalyzed process, acid catalyzed process, heterogeneous base catalyzed process, hterogeneous acid catalyzed process, enzyme catalyzed process, supercritical methanol process and hydrolysis of triglyceride. From the results, there is no profit for all processes although the price of glycerol is not included. The NPV is negative so hydrogen production from all process is not suitable. The results are shown in table B.6.

Table B.6 Economic analysis for hydrogen production

process	fixed capital investment	working capital investment	total capital investment	revenue	operating cost	NPV($/year)
alkali	2.90×10^{6}	4.35×10^{5}	-3.33×10^{6}	1.55×10^{5}	-4.12×10^{6}	-2.96×10^{7}
acid	2.74×10^{6}	4.10×10^{5}	-3.15×10^{6}	1.55×10^{5}	-4.34×10^{6}	-3.07×10^{7}
solid base	3.01×10^{6}	4.52×10^{5}	-3.47×10^{6}	1.55×10^{5}	-4.72×10^{6}	-3.35×10^{7}
solid acid	3.19×10^{6}	4.78×10^{5}	-3.67×10^{6}	1.55×10^{5}	-5.18×10^{6}	-3.67×10^{7}
enzyme	3.53×10^{6}	5.30×10^{5}	-4.06×10^{6}	1.55×10^{5}	-5.26×10^{6}	-3.77×10^{7}
Supertical	2.89×10^{6}	4.33×10^{5}	-3.32×10^{6}	1.55×10^{5}	-5.52×10^{6}	-3.84×10^{7}
hydrolysis	3.22×10^{6}	4.84×10^{5}	-3.71×10^{6}	1.55×10^{5}	-4.66×10^{6}	-3.35×10^{7}

However, when hydrogen production is combined with biodiesel integrated with fatty alcohol production. NPV values are positive in all processes except acid catalyzed process for biodiesel production. It can be concluded that the best economical process is alkali catalyzed process and hydrogen production should be integrated with the first case study. From table B.7, the best economical process in case of the second study is different from the best process in case of the first case study. This is because fixed capital cost for heterogeneous acid catalyzed process is higher than alkali catalyzed process when capital cost of hydrogen production is also considered. Furthermore, amount of hydrogen which derived from all processes is the same. At the end of this step, the remaining process is reduced to 1.

Table B.7 Economic analysis of biodiesel production integrated with fatty alcohol rpoduction when glycerol is used to produce hydrogen (for the case study2)

process	fixed capital investment	working capital investment	total capital investment	revenue	operating cost	NPV($/year)
alkali	2.08×10^{7}	3.11×10^{6}	-2.39×10^{7}	4.05×10^{8}	-2.99×10^{8}	6.32×10^{8}
acid	2.44×10^{7}	3.65×10^{6}	-2.80×10^{7}	3.96×10^{8}	-4.17×10^{8}	-1.64×10^{8}
solid base	2.57×10^{7}	3.85×10^{6}	-2.95×10^{7}	3.97×10^{8}	-2.98×10^{8}	5.76×10^{8}
solid acid	2.82×10^{7}	4.24×10^{6}	-3.25×10^{7}	4.13×10^{8}	-3.05×10^{8}	6.28×10^{8}
enzyme	2.59×10^{7}	3.89×10^{6}	-2.98×10^{7}	4.50×10^{8}	-3.81×10^{8}	3.97×10^{8}
supertical	3.37×10^{7}	5.05×10^{6}	-3.87×10^{7}	4.17×10^{8}	-3.21×10^{8}	5.49×10^{8}
hydrolysis	2.32×10^{7}	3.48×10^{6}	-2.67×10^{7}	3.92×10^{8}	-3.51×10^{8}	2.27×10^{8}

APPENDIX C

COMPARISON OF PROPOSED BIODIESEL PRODUCTION WITH BASE CASE

The main reaction for biodiesel production consists of the three-step transesterification of triglyceride, diglyceride and monoglyceride with methanol. In this study, a waste cooking palm oil containing 10 wt.% of free fatty acids at the flow rate of 46.33 kmol/h is used as feedstock for biodiesel production. The design target is to obtain the biodiesel product with the purity of 99.5 wt.%. Seven process alternatives for biodiesel production based on alkali catalyst, acid catalyst, solid base catalyst, solid acid catalyst, enzyme catalyst, supercritical methanol and two-step process of hydrolysis and esterification are considered.

C.1 Process design

Fig. C.1 shows the superstructure of the proposed biodiesel production process from waste cooking palm oil with different types of catalyst. In the figure, the variable Y_i is varied, depending on the available streams; when the value Y_i is equal to one, such a stream has to be considered. This means that when Y_1 and Y_4 are available streams, the alkali catalyzed process is a preferable option, whereas the acid catalyzed process, heterogeneous catalyzed process, enzyme catalyzed process and supercritical methanol process are involved if Y_2 and Y_5 exist. A pretreatment reactor is used to reduce free fatty acids when alkali catalyst is used as catalyst in the main reactor.

In a conventional biodiesel process, an excess methanol is recovered by using a distillation column and a by-product glycerol is separated from biodiesel by a decanter. The product biodiesel is first purified by using a distillation with partial condenser and then a neutralization reactor is employed to remove the remaining homogenous catalyst. Based on the thermodynamic insight analysis of all components in the biodiesel production process, a new designed process is proposed. To recover the excess methanol in crude biodiesel product, a flash column is chosen; water and methyl laurate are the light and heavy key components. The light key product is sent to a distillation column in order to separate methanol and water and then the recovered methanol from the column is recycled to the biodiesel production process. The heavy key product from the flash separation consists of mostly biodiesel, glycerol and unreacted mixed triglyceride. Two liquid phase region is observed, which implies that the mixed methyl ester can dissolve in glycerol. Therefore, the heavy product of the flash column is sent to a decanter to separate a light phase component (e.g., mixed methyl ester and methanol) from a heavy phase component (e.g., water, glycerol and methanol). The second and third distillation columns are used for further purification of mixed methyl esters from methanol and mixed triglycerides, respectively.

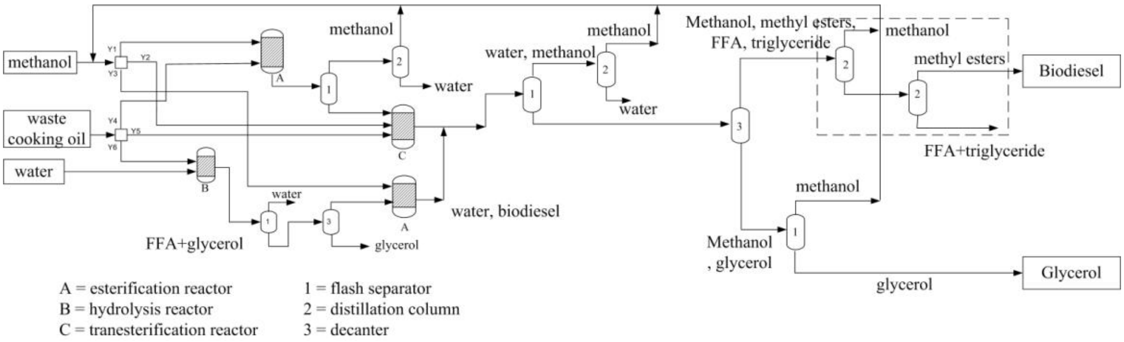

Fig C.1 Superstructure of the proposed biodiesel process

C.2Economic analysis

In this section, steady-state simulations of the proposed biodiesel processes are performed for process economic analysis in terms of a total investment cost, total production cost and profitability in order to determine the best economically feasible process. The prices of raw materials used for the economic evaluation are listed in appendix D. Table C.1 shows the total investment cost of the new design processes, compared with conventional ones, for the production of biodiesel using different catalysts. The results show that the fixed capital cost of distillation columns for methanol recovery and biodiesel purification in the solid acid catalyzed process and supercritical process show the highest value because a large amount of methanol is required for the transesterification reactor. In addition, size of the reactors and distillations are larger than other processes, causing the highest total investment cost. In contrast, the alkali catalyzed process has the lowest total investment cost due to the requirement of a lower feed ratio of methanol to oil. Due to a high pressure operation, the equipment cost (i.e., reactor, pump and distillation) for the heterogeneous acid catalyzed and supercritical methanol processes are very high. The total production cost and economic factors (i.e., net profit and net present values) of the conventional and proposed new design biodiesel proposes are compared in Table C.7. It indicates the dependence of the production cost on the prices of raw material and catalyst as well as the utility cost. Although the enzyme catalyzed process has the highest productivity, a high cost of enzyme results in less profit, compared with other processes. When considering the return on investment regardless a project life year, the alkali catalyzed process shows the best alternative. A net present value (NPV) is another key indicator that should be considered to find an economically feasible process. It is found that among the alternative processes, the heterogeneous acid catalyzed process shows the highest NPV as its net profit is the highest. Fig. C.2 compares costs of the total investment, raw material, revenue, NPV and utility (i.e., steam and cooling) between the conventional and new proposed biodiesel process based on a heterogeneous acid catalyst. With the proposed design methodology, the new developed biodiesel process requires a lower energy consumption (41.7% energy saving), leading to a lower operating cost and thus NPV. The cash flow analysis shown in Fig. C.3 indicates that all the proposed biodiesel processes are economically feasible.

Table C.1 Capital costs of biodiesel production (new design (A) and conventional (B) processes)

	Alkali process		Acid process		Solid base process		Solid acid process		Enzyme process		Supercritical process		Hydrolysis process	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B
Pretreatment reactor (x10^6)	3.95	3.9	-	-	3.94	3.9	-	-	-	-	-	-	-	-
Main reactor (x10^6)	0.605	0.605	3.9	3.9	1.47	1.47	2.86	2.86	2.93	2.93	1.45	1.45	0.605	0.605
Neutralization reactor	3.83	3.83	3.83	3.83	3.83	3.83	-	-	-	-	-	-	-	-
Heater (x10^5)	1.2	2.84	0.6	2.12	1.83	2.84	0.753	2.11	0.72	2.13	0.17	1.78	0.625	2.67
Cooler (x10^5)	0.478	7.14	0.4	-	0.402	7.14	0.983	3.44	0.484	3.29	1.58	4.61	0.586	-
Pump (x10^6)	-	-	-	-	-	-	0.108	0.108	-	-	1.2	1.2	-	-
Decanter (x10^6)	0.73	1.43	1.5	1	1.69	1.43	2.49	1.43	2.02	0.571	3.59	2.12	2.02	0.62

	Alkali process		Acid process		Solid base process		Solid acid process		Enzyme process		Supercritical process		Hydrolysis process	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B
Flash (x10^{6})	0.45	-	0.3	-	1.56	-	0.605	-	0.3	-	1.75	-	0.39	-
Distillation for methanol recovery (x10^{6})	0.324	1.41	-	-	0.4	1.35	1.51	-	1.15	-	4.14	-	1	-
Distillation for methanol recovery (x10^{6})	0.4	1.18	0.3	1.76	0.153	2.71	0.425	2	0.3	1.07	0.41	1.76	-	1.40
Distillation for glycerol sepion (x10^{6})	-	1.46	-	1.20	-	0.607	-	0.628	-	0.636	-	0.666	-	0.847

	Alkali process		Acid process		Solid base process		Solid acid process		Enzyme process		Supercritical process		Hydrolysis process	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B
Distillation for separation methanol from biodiesel ($x10^6$)	1	-	1	-	0.955	-	1.33	-	0.93	-	1.4	-	1.22	-
Distillation for purification biodiesel ($x10^6$)	2.3	3.53	3	3.97	3.02	4.19	2.41	4.50	2.57	4.21	2.55	5.24	3.17	5.23

	Alkali process		Acid process		Solid base process		Solid acid process		Enzyme process		Supercritical process		Hydrolysis process	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B
Total bare module cost($\times 10^7$)	0.856	1.17	1.1	1.2	1.2	1.42	1.35	1.37	1.14	1.1	1.73	1.16	0.969	0.99
Contingency fee ($\times 10^6$)	1.55	2.1	2.0	2.16	2.15	2.56	2.44	2.46	2.05	1.98	3.11	2.1	1.74	1.78
Auxillary cost ($\times 10^6$)	2.58	3.5	3.4	3.6	3.59	4.27	4.06	4.1	3.42	3.31	5.18	3.49	2.91	2.97
Fixed capital cost ($\times 10^7$)	1.27	1.72	1.6	1.77	1.77	2.11	2.00	2.02	1.64	1.63	2.55	1.72	1.43	1.47
Working capital cost ($\times 10^6$)	1.91	2.59	2.5	2.66	2.65	3.16	3.01	3.03	2.53	2.45	3.83	2.59	2.16	2.2
Cost ($\times 10^7$)	1.46	1.98	1.9	2.04	2.04	2.42	2.31	2.33	1.94	1.88	2.94	1.98	1.65	1.69

Table C.2 Total production cost and economic indicators of biodiesel production (new design (A) and conventional (B) processes)

	Alkali process		Acid process		Solid base process		Solid acid process		Enzyme process		Supercritical process		Hydrolysis process	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B
Oil feedstock (x10^8)	2.67	2.67	2.67	2.67	2.67	2.67	2.67	2.67	2.67	2.67	2.67	2.67	2.67	2.67
Methanol (x10^8)	0.239	0.381	1.3	1.43	0.23	0.185	0.202	0.25	0.376	0.252	0.39	0.39	0.205	0.436
Steam (x10^6)	3.03	4.07	3.53	4.98	5.06	6.53	3.48	5.99	2.81	4.16	9.43	9.23	3.09	4.7
Cooling water (x10^7)	5.57	9.54	6.92	6.57	6.92	13.6	12.5	14.7	7.53	7.15	34.4	16.8	9.86	9.63
Labor (x10^6)	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91
Supervisory (x10^5)	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91

	Alkali process		Acid process		Solid base process		Solid acid process		Enzyme process		Supercritical process		Hydrolysis process	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B
Catalyst and solvent ($x10^6$)	4.72	4.72	9.47	9.47	0.028	0.028	0.59	0.59	66.6	66.6	0	0	53.3	53.3
Maintainance ($x10^6$)	0.679	0.907	1.21	1.26	1.01	1.16	1.27	1.21	1.22	1.15	1.23	0.971	0.779	0.771
Laboratory ($x10^5$)	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91
Local tax ($x10^5$)	1.36	1.81	2.42	2.49	2.03	2.34	2.55	2.43	2.44	2.38	2.45	1.94	1.56	1.54
Insurance ($x10^6$)	0.679	0.907	1.21	1.26	1.01	1.16	1.27	1.21	1.22	1.15	1.23	0.971	0.779	0.771

	Alkali process		Acid process	Solid base process	Solid acid process	Enzyme process	Supercritical process	Hydrolysis process	Alkali process	Acid process	Solid base process	Solid acid process	Enzyme process	Supercritical process
	A	B	A	B	A	B	A	B	A	B	A	B	A	B
Total production cost (x10^8)	3.07	4.18	4.2	5.05	3.05	4.38	3.01	4.55	3.84	4.44	3.26	4.92	3.53	4.74
Depreciation (x10^6)	0.78	1.04	1.39	1.43	1.16	1.33	1.47	1.4	1.4	1.38	1.41	1.02	0.89	0.885
Revenue (x10^8)	6.13	7.02	6.36	6.41	6.37	6.83	6.75	7.25	7.05	7.56	6.62	7.5	6.93	7.29
Net profit (x10^8)	3.05	2.82	2.16	1.36	3.3	2.35	3.71	3.04	3.2	3.29	3.34	0.47	3.39	2.54
ROI	21.79	14.2	11.73	6.64	16.78	9.7	16.61	13.074	17	17.53	11.7	2.4	21.45	15.05
NPV (x10^9)	1.9	1.75	1.31	0.883	2.05	1.45	2.3	1.89	1.99	2.04	2.07	0.284	2.11	1.58

C.3 Sensitivity analysis

In this section, the sensitivity analysis of the proposed biodiesel processes is studied to determine the effect of key parameters such as oil feed price, biodiesel price and glycerol price on NPV. The price is varied 10%, 20%, 30%, 40% from its original value. The project life of 20 years is assumed. Figs. C.6.4-C6.6 show that the NPV of the biodiesel process is linearly related to the prices of oil feed, biodiesel and glycerol. The NPV decreases with increasing the oil feed price that affects the total production cost, whereas it increases with increasing the biodiesel and glycerol prices due to an increasing in the revenue. Biodiesel production based on the enzyme process is more sensitive to the biodiesel price than other processes. Due to its highest of net profit, the solid acid catalyzed biodiesel process show the maximum NPV.

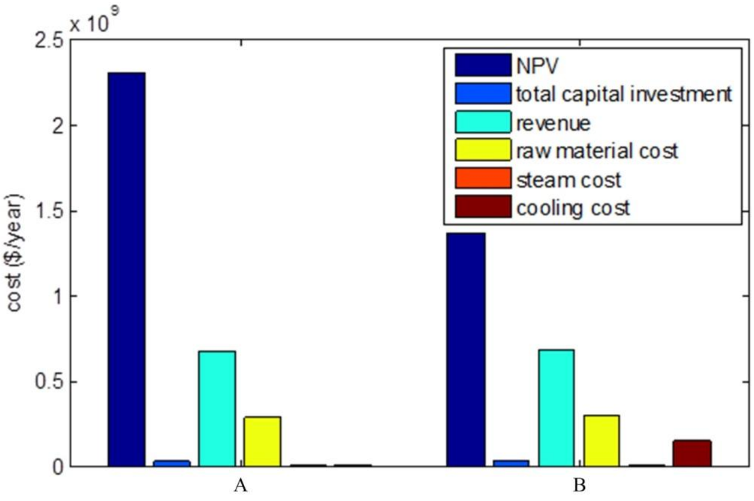

Fig. C.2. Cost comparison of the new design (A) and conventional (B) processes for biodiesel production using solid acid catalyst

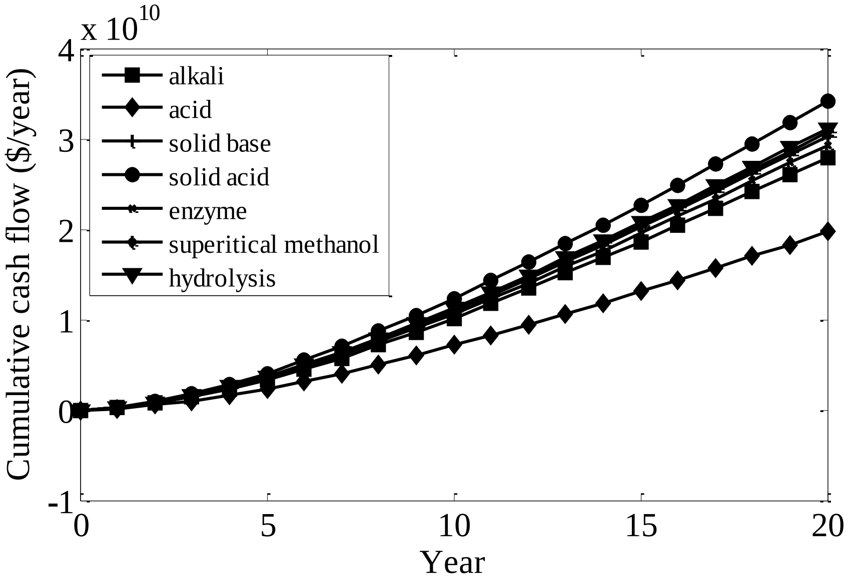

Fig. C.3 Cash flow of biodiesel production processes using the proposed design methodology

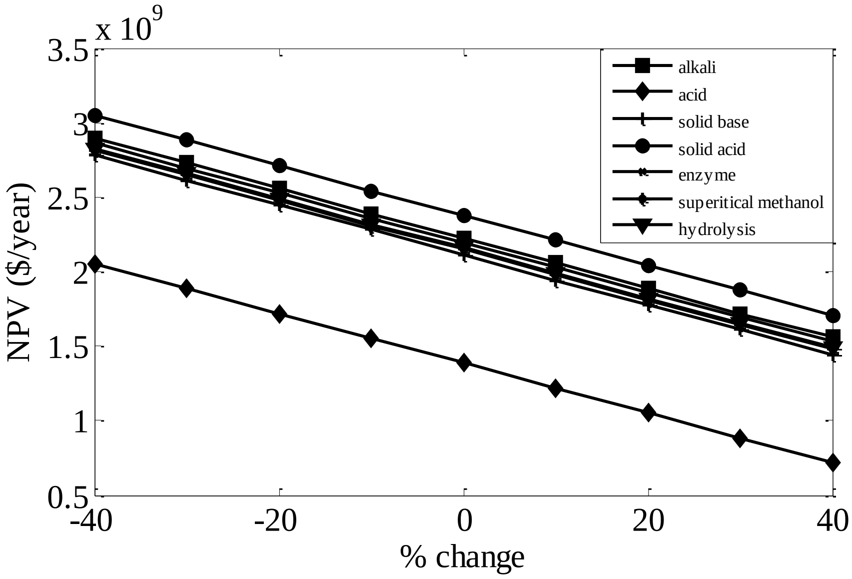

Fig. C.4 Effect of oil feed price on the NPV of biodiesel processes

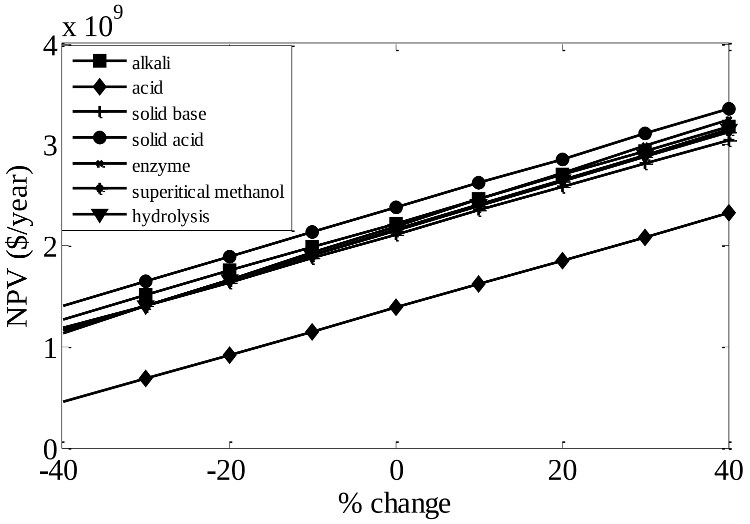

Fig. C.5 Effect of biodiesel price on the NPV of biodiesel processes

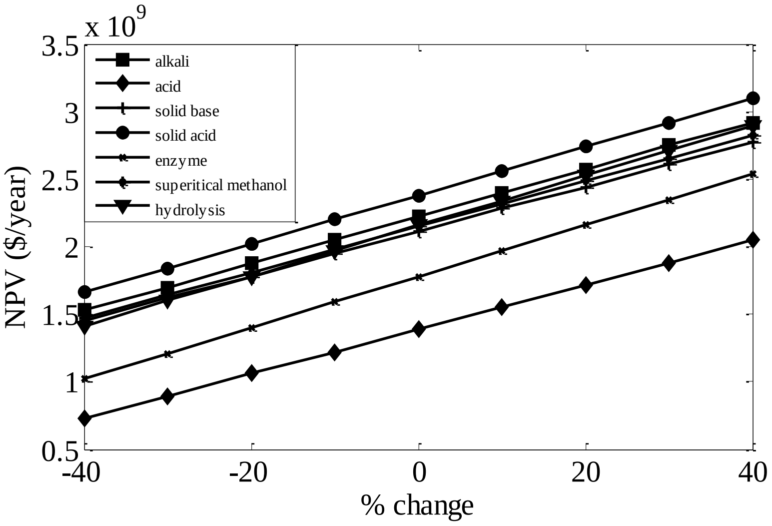

Fig. C.6 Effect of glycerol price on the NPV of biodiesel processes

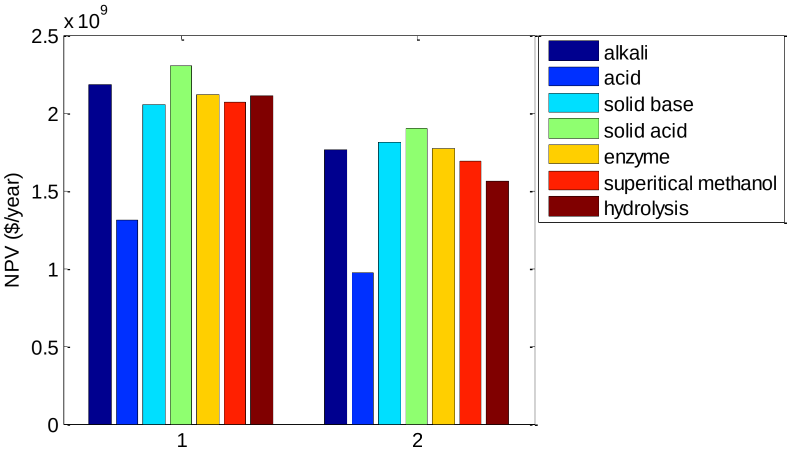

Fig. C.7 Effect of glycerol price on the NPV of biodiesel processes

Since the fraction of free fatty acid in palm oil affects the raw material cost and thus the production cost, its effect on the NPV of biodiesel process is investigated. Fig. C.7 compares the NPV of biodiesel process when crude and waste cooking palm oils with different contents of free fatty acid, 5 wt.% and 10 wt.%, are used. When the crude palm oil is used as feedstock, the productivity and the methanol requirement is decreased. Although the energy consumption of biodiesel production using crude palm oil decreases, the NPV of biodiesel production using crude palm oil is still lower than that using waste cooking palm oil. This is because the price of crude palm oil is high while the revenue is low. For both cases, the heterogeneous acid catalyzed process is the best process. It is noted that when the content of free fatty acids in palm oil increases, the size of distillation columns for separating methanol from water is larger because more water is generated from the esterification of free fatty acid. However, the size of equipments does not significantly affect the NPV because the capital cost is lower than the production cost.

APPENDIX D

SIZING OF EQUIPMENT AND COST ESTIMATION

Correlations used for capital costs of unit operations such as distillation column, heat exchangers, pumps and compressors are shown in Table D.1-D.11. Guthrie's modular method is applied to compute capital costs.

For process vessel

$$BC = C_0 \left(\frac{L}{L_0} \right)^a \left(\frac{D}{D_0} \right)^b$$

For process equipment

$$BC = C_0 \left(\frac{S}{S_0} \right)^a$$

Table D.1 Parameter values for process vessel

equipment type	C_0($)	L_0(ft)	D_0(ft)	a	b	MF2/MF4/MF6/MF8/MF10
Vertical fabrication	1000	4	3	0.81	1.05	4.23/4.12/4.07/4.06/4.02
Horizontal fabrication	690	4	3	0.78	0.98	3.18/3.06/3.01/2.99/2.96
Tray	180	10	2	0.97	1.45	1/1/1/1/1

Table D.2 Parameter values for process equipment

equipment type	C_0($) 10^3	S_0	range (S)	a	MF2/MF4/MF6/MF8/MF10
Heat exchanger Shell and tube, S=area(ft^2)	5	400	100-10000	0.65	3.29/3.18/3.14/3.12/3.09
Heat exchanger Shell and tube, S=area(ft^2)	0.3	5.5	2-100	0.024	1.83/1.83/1.83/1.83/1.83
centrifugal pump	0.39	10	10-2×10^3	0.17	3.38/3.28/3.24/3.23/3.2
compressor	23	100	30-1×10^4	0.77	3.11/3.01/2.97/2.96/2.93

Distillation column

$$MPF = F_m + F_s + F_t$$

Table D.3 Parameter of tray types of distillation column

tray type	F_t
sieve	0
valve	0.4
bubble cap	1.8

Table D.4 Parameter of tray sizing of distillation column

tray sizing (inch)	F_s
24	1
18	1.4
12	2.2

Table D.5 Parameter of material type of distillation column

tray material	F_m
Carbon steel	0
Stainless steel	1.7
Monel	8.9

Heat exchanger

$$MPF = F_m \left(F_p + F_d \right)$$

Table D.6 Parameter of design type of heat exchanger

design type	F_d
kettle reboiler	1.35
floating head	1
u tube	0.85
fixed tube sheet	0.8

Table D.7 Parameter of pressure of heat exchanger

Pressure (psig)	F_p
150	0
300	0.1
400	0.25
800	0.52
1000	0.55

Table D.8 Parameter of materials of heat exchanger

surface area (ft^2) shell/tube materials, F_m	CS/CS	CS/Brass	CS/SS	SS/SS	CS/monel	monel/ monel	CS/Ti	Ti/Ti
up to 100	1	1.05	1.54	2.5	2	3.2	4.1	10.2
100 to 500	1	1.1	1.78	3.1	2.3	3.5	5.2	10.6
500 to 1000	1	1.15	2.25	3.26	2.5	3.65	6.15	10.8
1000 to 5000	1	1.3	2.81	3.75	3.1	4.25	8.95	13.1

Decanter

$$BC = 28100 F_{in}^{0.574}$$

Bare module cost of all equipments

$$BMC = BC(MPF + MF - 1)$$

Table D.9 Chemical price

Chemical	Price
Waste palm oil	0.75 $/kg
Methanol	0.56 $/kg
NaOH	0.6 $/kg
H_2SO_4	0.6 $/kg
KOH/Al_2O_3	19.8 $/kg
DTPA/Clay	0.6 $/kg
κ-carrageenan	10 $/kg
Hydrolysis enzyme	1.5 $/kg
CuCr	10 $/kg
Steam cost	4$/1000lb
Cooling cost	0.05$
Biodiesel price	1.07$/L
Glycerol price	0.75$/kg
Hydrogen price	3.33 $/m^3
C12-C14 Fatty alcohol	3.33 $/kg
C16-C18 fatty alcohol	1.544 $/kg

BIOGRAPHY

Miss Lida Simasatitkul was born on May 25, 1985 in Bangkok, Thailand. She finished high school from Chulalongkorn University Demonstration School. She received the Bachelor’s Degree of Engineering in Chemical Engineering from the Department of Chemical Engineering, Faculty of Engineering, King Mongkut Institute Technology of Ladgrabang, Bangkok, Thailand in 2007 and Master’s degree of Engineering in Chemical Engineering from the Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, Thailand in 2009.