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DESIGN OF REACTIVE DISTILLATION WITH THERMAL COUPLING AND
HEAT INTEGRATION FOR BIODIESEL PRODUCTION

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A Thesis Submitted in Partial Fulfillment of the Requirements
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ไบโอดีเซลผลิตได้จากทรัพยากรหมุนเวียนเป็นพลังงานทดแทนที่มีความสำคัญ แต่มีอุปสรรคคือต้นทุนในการผลิตไบโอดีเซลสูงในทางการค้า ทำให้ต้องการการออกแบบกระบวนการผลิตไบโอดีเซลด้วยวิธีที่มีประสิทธิภาพ วัตถุประสงค์ของงานนี้คือเพื่อออกแบบการกลั่นแบบมีปฏิกิริยาโดยใช้แนวคิดของการคู่ควบความร้อนและการรวมความร้อนสำหรับการผลิตไบโอดีเซล กระบวนการที่ออกแบบคือ การกลั่นแบบมีปฏิกิริยาแบบดั้งเดิม (CRD) การกลั่นแบบมีปฏิกิริยาที่มีการคู่ควบความร้อนแบบสตริปเปอร์ (s-TCRD) การกลั่นแบบมีปฏิกิริยาที่มีการคู่ควบความร้อนแบบเรคติไฟเยอร์ (r-TCRD) และการกลั่นแบบมีปฏิกิริยาที่มีการรวมความร้อน (HIRD) สมรรถนะของกระบวนการเหล่านี้ถูกวิเคราะห์ในเทอมของคอนเวอร์ชันของกรดโอเลอิกและความบริสุทธิ์ของเมทิลโอเลเอท (ผลิตภัณฑ์ไบโอดีเซล) โดยใช้การจำลองกระบวนการ ที่มีพารามิเตอร์ที่สำคัญ ได้แก่ ความดันของหอ อุณหภูมิของสารป้อน อัตราการไหลก้นหอ ขั้นตอนที่ใช้ในการเกิดปฏิกิริยา และตำแหน่งของการป้อนสาร ทุกกระบวนการที่ออกแบบได้ความบริสุทธิ์ของผลิตภัณฑ์ไบโอดีเซลและเมทานอลที่ถูกรีไซเคิลมากกว่า 99% และได้คอนเวอร์ชันของกรดโอเลอิกมากกว่า 99% การใช้พลังงานทั้งหมดของทุกกระบวนการได้ถูกนำมาเปรียบเทียบกัน พบว่ากระบวนการ s-TCRD, r-TDRD และ HIRD สามารถลดการใช้พลังงานได้เท่ากับ 31%, 36.5% และ 40% ตามลำดับ เมื่อเปรียบเทียบกับกระบวนการ CRD

ภาควิชา : วิศวกรรมเคมี .... ลายมือชื่อนิสิต..

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PORNTIDA CHATSIRISOOK : DESIGN OF REACTIVE DISTILLATION WITH THERMAL COUPLING AND HEAT INTEGRATION FOR BIODIESEL PRODUCTION. ADVISOR : ASST. PROF. AMORNCHAI APORNWICHANOP, D. ENG., 120 pp.

Biodiesel produced from agricultural resources becomes an important alternative diesel fuel. However, a major obstacle in biodiesel commercialization is its high production cost. To increase competitive ability of biodiesel, design of a biodiesel process in an effective way is required. The aim of this work is to design a reactive distillation based on the concepts of thermal coupling and heat integration for biodiesel production form esterification of fatty acid. The designed processes are the conventional reactive distillation (CRD), the stripper-thermally coupled reactive distillation (s-TCRD), the rectifier-thermally coupling reactive distillation (r-TCRD) and the heat integrated reactive distillation (HIRD). The performance of such processes in terms of the conversion of oleic acid and purity of methyl oleate (biodiesel product) is analyzed, using a process simulator, with respect to key parameters such as column pressure, feed temperature, reboiler heat duty, reaction stage and feed location. The designed processes can achieve the purities of biodiesel product and recycled methanol at 99 % and the conversion of oleic acid of 99 %. The total energy consumption of all the biodiesel processes is compared. It is found that the s-TCRD, r-TCRD and HIRD processes can reduce the energy consumption by 31%, 36.5% and 40%, respectively, compared with the CRD process.

Department   : Chemical Engineering   Student's Signature ....

Field of Study : Chemical Engineering   Advisor's Signature ....

Academic Year : 2011 ....

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LIST OF ABBREVIATIONS

RD	Reactive distillation
TC	Thermal coupling
HI	Heat integration
CRD	Conventional reactive distillation
s-TCRD	Stripper-Thermally coupled reactive distillation
r-TCRD	Rectifier- Thermally coupled reactive distillation
HIRD	Heat integrated reactive distillation
OLAC	Oleic acid
DOAC	Dodecanoic acid
MEOH	Methanol
MEOL	Methyl oleate
MEDO	Methyl dodecanoate
WAT	Water
MD	Methanol distillation
SEP	Separation
N&D	Nguyen and Demirel model

CHAPTER I

INTRODUCTION

1.1 Introduction

Biodiesel is an important alternative energy source for diesel engine. Presently, it has been received much attention due to the depletion of a conventional petroleum diesel. Biodiesel can be directly used to replace petroleum diesel without modifying an engine as they has similar properties, i.e. cetane number, specific gravity, viscosity, flash point and carbon and hydrogen percentages. In general, biodiesel is known as alkyl ester that can be derived from a catalyzed reaction of vegetable oils or animal fats with an alcohol. These renewable primary feedstock commonly contain triglyceride and free fatty acid which can undergo, respectively, transesterification and esterification reactions to produce the alkyl ester (Garpen, 2005; Gómez-Castro et al., 2010). In Thailand, the main raw material for biodiesel production is palm oil; however, there are few biodiesel plants using waste cooking oil as feedstock. Alternatively, Jatropha oil is considered a potential feedstock for biodiesel production in Thailand.

In a conventional process of biodiesel production, the reaction and separation section are major processes to generate alkyl ester and purify a biodiesel product, respectively. These cause expensive capital and operating costs for biodiesel production. To increase the competitive potential of biodiesel, a number of studies have been focused on design and improve a biodiesel production process with regard to efficient energy usage and production cost. A reactive distillation (RD) is an attractive alternative to improve the production of biodiesel. It is considered a process intensification technology, which combines reaction and separation tasks in a single unit, leading to efficient energy usage (Qiu et al., 2010). In general, RD is suitable for equilibrium-limited reactions since the reaction products are separated during reaction

proceeding, so that the reaction equilibrium is shift to the product side. To date, many efforts have been devoted to study RD for production of various products, e.g., esters and oxygenate a compound, which relies on both experiment and simulation. One interesting issues is about the improvement in the energy efficiency of the RD and various designs of RD have been proposed. Thermally coupled reactive distillation is possibly an alternative as it allows interconnecting the vapor and liquid flows between the two columns to eliminate a reboiler or a condenser (Barroso-Muñoz et al., 2007). Furthermore, operating and capital costs can be minimized by decreasing waste energy with a heat integration among the processes; heat transfer between hot stream and cold stream within the process reduces external heat requirement.

This study is focused on the design of a reactive distillation for biodiesel production. The esterification reaction of oleic acid and methanol in the presence of acid ion-exchange polymeric resin, as a solid catalyst, is chosen as a case study (Tesser, 2005). Simulation studies on the reactive distillation with thermal coupling and heat integration are performed using a process simulator to investigate effects of key parameters such as feed temperature of fatty acid and methanol, reboiler duty, reaction stage and methanol feed location. This leads to an optimal design of the reactive distillation for biodiesel production.

1.2 Objectives

The aim of this work is to design a reactive distillation with thermal coupling and heat integration for biodiesel production with efficient energy usage.

1.3 Scopes of research

1.3.1 To study a biodiesel production from the esterification reaction of fatty acid and methanol in a reactive distillation. The kinetic rate of such a reaction proposed by Tesser et al. (2005) is used and simulations are performed by using HYSYS simulator.

1.3.2 To investigate effects of various key operating parameters such as feed temperature, reboiler duty, reaction stage and feed location of methanol, on reactive

distillation performance in terms of the conversion of fatty acid and the yield and purity of biodiesel.

1.3.3 To investigate a design feasibility of thermal coupling and heat integration in the reactive distillation for the production of biodiesel. Performance of the designed reactive distillation is compared with a conventional process proposed by Nguyen and Demirel (2011).

1.4 Expected benefit

1.4.1 A biodiesel production process from a wide range of feedstock with high free fatty acid contents can be achieved.

1.4.2 A suitable operating conditions and configuration of a reactive distillation for biodiesel production can be determined.

1.4.3 Design of a reactive distillation based on a thermal coupling and a heat integration concept results in an improvement in the energy efficiency of the reactive distillation.

CHAPTER II

LITERATURE REVIEWS

This chapter presents literature reviews on the synthesis of biodiesel. Conventional processes for biodiesel production involves the use of catalyst, which implies high energy consumptions for the separation of both the catalyst and the by-products of the reaction, including those of the undesirable reaction of saponification. To solve this difficulty, the vegetable oil is esterified with alcohol to alkyl ester, which has potential benefits. The studies in the use of a reactive distillation to improve the performance of biodiesel production process are also presented and reviewed in this chapter.

2.1 Biodiesel process

The continuously conventional catalytic processes for biodiesel production have been reported by West et al. (2008). The first two processes employed traditional homogeneous alkali and acid catalysts, the third and fourth processes used a heterogeneous acid catalyst and a supercritical method to convert a waste vegetable oil feedstock into biodiesel, while all four processes were capable of producing biodiesel at high purity. They reported in term of total capital investment, total manufacturing cost and after tax rate-of-return. Those are found the heterogeneous acid catalyst process had the lowest total capital investment and manufacturing costs, and had the only positive after tax rate-of-return.

Bobcock et al. (2008) have shown the conventional base-catalyzed method of biodiesel production to be inappropriate for conversion of high free fatty acid-containing feedstocks such as tall oil, due to undesired saponification reaction that takes place. Likewise, the acid-catalyzed method of biodiesel production has been shown to be inappropriate for the conversion of triglyceride-containing feedstocks,

such as chicken fat, due to the long reaction times and large excess of methanol required. Therefore, an alternate reaction pathway was investigated for these two very different feedstocks. Supercritical methanol treatment, which requires no separate catalyst, was the method chosen. However, supercritical method is obstacle on operational equipment and safety.

Process intensification technologies are reviewed by Qiu et al. (2010) for continuous biodiesel production. These include novel reactors (reactors of static mixer, micro-channel, oscillatory flow, cavitation, rotating/spinning tube, and microwave) and reaction/separation coupled technologies (membrane reactor, reactive distillation, and centrifugal reactor), which were compared in terms of energy efficiency, operating and capital cost and temperature control. In addition, the current status of each technology is presented. They have summarized that reactive distillation (RD) is the best in energy efficiency, coupled technologies is lower operating and capital cost and those can be control temperature easily, but it is current status of pilot plant.

2.2 Applications of reactive distillation

RD has been successfully used and investigated in the past for several reactions such as etherification, esterification, hydrogenation, hydrodesulfurisation and polymerization. Examples of reactive distillation applications are the synthesis of C4-C5 acetate and methyl/ethyl acetate, the esterification of fatty acid, the production of butyl acetate, the hydrolysis of methyl acetate, the hydrolysis and alcoholysis of alkyl halides, the manufacture of glycine from glycinonitrile, the production of MTBE, ETBE and TAME, etc (Hiwale et al, 2004).

Singh et al. (2004) have developed a novel reactor system using reactive distillation (RD) technique in a lab scale sieve-tray RD reactor system. Preliminary results showed that process parameters of methanol-to-oil ratio of 4:1 (molar) and a column temperature of 65°C produced a biodiesel that met the ASTM standards for total glycerol and viscosity.

Omota et al. (2003) have applied reactive distillation to present conceptual design as a systematic methodology based on thermodynamic analysis combined with computer simulation, as well as set targets for limited experimental work based on chemical equilibrium. Method of the esterification of lauric acid with 2-ethylhexanol and methanol is illastated. Both reactions can be accommodated in the same hardware, but with different operation procedures. The alternative with alcohol reflux is suitable for heavy alcohols that form heterogeneous azeotropes with water. Another alternative with acid reflux can accommodate both light and heavy alcohols, and may be seen as a generic process for fatty acid esterification.

Mueanmas et al. (2010) have studied on a feasibility study of using reactive distillation (RD) for biodiesel production from palm oil. The hypothesis of using RD is to reduce the amount of excess alcohol in the feed stream bringing its stoichiometric ratio close to that of oil. That causes less energy to be required for the methanol recovery process. Aspen Plus 2006 has been used to simulate this process. The kinetic constants of the conventional process need to be modified for the RD process. The preliminary results show a 4:1 molar ratio of methanol to oil, and the reboiler temperature at 150∘C produces a 97.36 %(wt) methyl ester in 5.6 minutes. It can be concluded that using the RD process is more efficient and more feasible than using the conventional process to produce biodiesel from palm oil.

Kiss (2010) has proposed a novel energy-efficient integrated production of biodiesel from hydrous bioethanol. The key to success is a novel setup that combines the advantages of using solid catalysts with the integration of reaction and separation. This integrated process eliminates all typical catalyst-related operations, and efficiently uses the raw materials and the reactor volume in a separative reactor that allows significant savings in the capital and operating costs. Sensitivity analysis was used to determine the optimal range of the operating parameters. The main results are given for a plant producing 10 ktpy biodiesel (>99.9%wt) from hydrous bioethanol (96%wt) and waste vegetable oil with high free fatty acids content (~100%), using solid acids as green catalysts.

Santander et al. (2010) have studies the surface response methodology using Aspen Plus software for simulating the castor oil biodiesel production by reactive distillation with the aim of obtaining a deep understanding about the process, finding the best conditions for producing the largest amount of fatty acid esters and assess its viability. They concluded the ethanol:oil molar ratio was 31.6% lower compared with the conventional process. Additionally, the reaction time apparently could be diminished since the simulations were made for a 1 minute residence time at the pre-reactor whereas the conventional process around 30 minutes.

2.3 Reactive distillation with thermal coupling and heat integration for biodiesel production

Distillation systems with simultaneous thermal coupling and heat integration can significantly reduce both energy and capital costs compared with systems employing either thermal coupling or heat integration alone. Thermally coupled reactive distillation is possibly alternative as it allows interconnecting the vapor and liquid flow between the two columns to eliminate the reboiler or condenser or both. There are three well-known configurations of thermal coupling as thermally coupled side-stripper, side rectifier, and fully thermal coupling (Petlyuk column) being analyzed by Barroso-Munoz et al. (2007). These configurations were used for production of ethyl acetate. They have reported Petyuk column as structure requires lowest amount of energy. The basic concept of heat integration consists on the utilization of hot process streams to exchange heat with cold process streams. To improve the energy efficiency of separation processes, several heat integrated techniques have been proposed.

Wang et al. (2008) have investigated the design and control strategies of a reactive distillation process with partially thermal coupling for the production of methanol and n-butyl acetate by transesterification reaction of methyl acetate and n-butanol. Partially thermal coupling can be used to eliminate the condenser of the second column. Not only energy reduction but also better operability and controllability can be obtained for the thermally coupled reactive distillation process.

A simple control scheme with three temperature control loops is sufficient to maintain product purities and stoichiometric balance between the reactant feeds.

Miranda-Galindo et al. (2009) have explored the esterification of lauric acid and methanol using a thermally coupled distillation sequence with a side rectifier and the Petlyuk distillation column. The study was conducted using as a design tool a multi objective genetic algorithm with restrictions. The product of the esterification can be used as biodiesel. It was found that the thermally coupled distillation sequence involving a side rectifier can produce biodiesel with a high purity (around 0.999) and also pure water, and the excess of methanol is recovered in a side rectifier. The results indicate that the energy consumption of the complex distillation sequence with a side rectifier can be reduced significantly by varying operational conditions.

Recently, Gomez-Castro et al. (2010) have modified supercritical process for biodiesel production; they proposed two alternatives of process involves the use either of reactive distillation or thermally coupled reactive distillation (Petyluk column). These processes ware compared in term of total energy consumption, resulting to the Petlyuk column achieve to obtain minimum total energy consumption. Continuously, they have proposed additional process of reactive thermally coupled (side-stripper) direct sequence is one of the configurations requires lowest thermal energy consumption for esterification step implying higher energy saving than others.

Kiss (2010) has presented a novel heat-integrated process based on reactive distillation that aims to reduce the energy requirements for biodiesel production from esterification, Steady-state and dynamic simulation results are given for a plant producing 10 ktpy fatty acid methyl esters (FAME) from methanol and waste vegetable oil with high free fatty acids (FFA) content, using sulfated zirconia as green catalyst. Such process eliminates all conventional catalyst related operations, efficiently uses the raw materials and the reactor volume offering complete conversion of the fatty acids and allowing significant energy savings. Remarkably, compared to previously reported RD processes, the energy requirements of this process are about 45% lower – only 108.8 kW h/ton biodiesel – while the capital investment cost remains the same as no additional equipment is required.

Nguyen and Demirel (2011) have studied the production of methyl dodecanoate (biodiesel) using lauric acid and methanol with a solid acid catalyst of sulfated zirconia using two distillation sequences such as conventional RD and thermal coupling RD, as well as heat integration of processes. The thermally coupled side-stripper reactive distillation and eliminate the condenser of the reactive distillation column is studied. Both the sequences are optimized by using the thermal and hydraulic analyses of the Column Targeting Tools of Aspen Plus simulator. Comparisons of the optimized sequences show that in the thermally coupled sequence, the energy consumption is reduced by 13.1% in the reactive distillation column and 50.0% in the methanol recovery column. The total exergy losses for the columns are reduced by 281.35 kW corresponding to 21.7% available energy saving in the thermally coupled sequence. In addition, the composition profiles indicate that the thermally coupled reactive distillation column operates with the lower concentration of water in the reaction zone which reduces catalytic deactivation.

Moreover, this integrated RD alternative offers the significant benefits over conventional biodiesel processes (Kiss, 2011). It eliminates all conventional catalyst-related operations such as catalyst neutralization, separation and disposal of waste salts, waste water treatment, efficient usage of raw materials, complete conversion, significantly high unit productivity, multifunctional plant suitable for a large range of feedstock with very high FFA content, such as palm fatty acid distillate, frying oils, animal tallow and waste vegetable oil, and reduced capital and operating costs. Compared to the base case, the heating and cooling requirements of this process are significantly decreased, by 43% and 47% respectively.

CHAPTER III

THEORY

3.1 Biodiesel

Biodiesel, which is known as a fatty acid alkyl ester (FAAE), is one of several promising types of alternative fuel. It can be direct used, or blended in any amount with diesel fuel for use in compression ignition engines due to the similarly fuel property of diesel and biodiesel as shown in Table 3-1. It is non-toxic, biodegradable, renewable fuel, environment friendly, has higher cetane number, and fuel efficient (Biofuel Phils, 2008). The several catalyzed process for biodiesel production (based on catalyst type) from vegetable oil and animal fats can be converted into biodiesel such as trans-esterification, enzyme lipase, supercritical fluid extraction, hydro-pyrolysis. Most of the methods for biodiesel production depend greatly on the quality and composition of the feedstock, especially with respect to free fatty acid content. The most alcohol used is usually methanol due to its viabilities of economic and chemical properties.

3.1.1 Biodiesel feedstock

Feedstock of biodiesel is derived from renewable, sustainable and biodegradable materials. Generally all types of vegetable oil and animal fat could be used as feedstock in the biodiesel process. They contain triglycerides; composing of three long-chain fatty acids of 8 to 22 carbons attached to a glycerol backbone, which are useful in the biodiesel process (O'Brien, 2004; Sharma et al., 2008). Moreover, it is divided into two types; edible and non-edible type. Vegetable oil of edible type has long been used in the conventional biodiesel process, largely due to the abundance availability of edible vegetable oil in the global market. Various vegetable oils and animal fats have been used in different countries as

feedstock in the biodiesel process owing to its availability (Sharma et al., 2008). Examples of edible oil that are being studied in the biodiesel process are soybean oil, rapeseed oil, sunflower oil, palm oil, and coconut oil. Examples of non-edible oil in the biodiesel process are waste, jatropha oil, cottonseed oil, rubber seed oil, algae oil and tobacco oil (Kansedo, 2009). Biodiesel feedstocks are classified based on their free fatty acid content as follows:

- Refined oils, such as soy bean or refined canola oil (FFA <1.5%)
- Low free fatty acid yellow greases and animal fats (FFA<4%)
- High free fatty acid greases and animal fats (FFA ≥ 20%)

Table 3-1 Fuel properties of diesel versus biodiesel (Kiss et at., 2008)

Fuel property	Diesel	Biodiesel
Fuel standard	ASTM D975	ASTM D6751
Fuel composition	C_{10}-C_{21} HC[a]	C_{12}-C_{22} FAME[a]
Kinetic viscosity, mm^2/s (at 40 ^oC)	1.3-4.1	1.9-6.0
Specific gravity, kg/L	0.85	0.88
Boiling point, ^oC	188-343	182-338
Flash point, ^oC	60-80	100-170
Cloud point, ^oC	-15 to 5	-3 to12
Pour point, ^oC	-35 to -15	-15 to 10
Cetane number (ignition quality)	40-55	48-65
Stoichiometric air/fuel ratio (AFR)	15	13.8
Life-cycle energy Balance (energy units produced per unit energy consumed)	0.83/1	3.2/1

[a] HC, hydrocarbons; FAME, fatty acid methyl ester

Table 3-2 Typical fatty acid composition of common oil sources (Kincs, 1985)

Lipid	Fatty acid composition, % by weight						
	Lauric	Myristic	Palmitic	Stearic	Oleic	Linoleic	Linolenic
	12:00	14:00	16:00	18:00	18:01	18:02	18:03
Soybean	0.1	0.1	10.2	3.7	22.8	53.7	8.6
Cottonseed	0.1	0.7	20.1	2.6	19.2	55.2	0.6
Palm	0.1	1	42.8	4.5	40.5	10.1	0.2
Lard	0.1	1.4	23.6	14.2	44.2	10.7	0.4
Tallow	0.1	2.8	23.3	19.4	42.4	2.9	0.9
Coconut	46.5	19.2	9.8	3	6.9	2.2	0

Biodiesel nomenclature depends on the feedstock and alcohol used to make it, but is sometimes called fatty acid methyl esters or FAME. Providing alcohol as methanol, alkyl group becomes methyl likewise ethanol to ethyl group. For instance, a biodiesel made from palm oil using methanol is called Palm Methyl Ester. A biodiesel made from soya oil using ethanol is therefore called Soya Ethyl Ester. Furthermore, it may be called following feedstock composition such as triglyceride and free fatty acid. For example, methyl oleate is produced from the most triolein/oleic acid feedstock with methanol. Ethyl lauriate made from the trilaurin/lauric acid feedstock using ethanol. Table 3-2 shows typical fatty acids, which vary in carbon chain and in the number of unsaturated bonds, found in various crude oil sources.

The main raw material for biodiesel in Thailand is palm oil due to its high availability and cheapest price of those vegetable oils. There are few biodiesel plants is using cooking oil as feedstock (APEC Thailand). Moreover, usage of palm oil feedstock is all capable of producing several gallons of fuel per acre that can power an unmodified diesel engine. Palm oil's chemical compositions are within the range of those types of fatty acids (Table 3-2); the level of saturated fatty acids is almost equal to that of the unsaturated fatty acids. Its major components are palmitic acid and oleic acid. Commercially, palm oils with relatively low free fatty acid content are known as soft oils, whereas those with a high acidity are hard oils. Palm fruit contains the oil content of 45-50%, since crude palm oil includes high free fatty acid content of 4-5%

that it may be pretreated before feeding to the transesterification process. In addition, Jatropha is seen as an alternative feedstock for biodiesel production in Thailand.

3.1.2 Biodiesel production

Biodiesel is produced through the reaction of a vegetable oil with alcohol (i.e. methanol or ethanol) in the presence of a catalyst. There are some common methods used convert feedstock triglycerides and free fatty acids into the fatty acid alkyl including the base-catalyzed transesterification of triglycerides (Figure 3.1), the acid-catalyzed esterification of free fatty acids (Figure 3.2), and an acid/base combination of catalysts for sequential esterification/transesterification reactions. Most of the methods and procedures for biodiesel production depend greatly on the quality and content of the feedstock, especially with respect to free fatty acid content [Babcock]. The transesteri- fication produces biodiesel and glycerin reacting triglyceride and alcohol in the presence of alkali catalyst (commonly KOH or NaOH) that is effective in transesterifying the triglycerides present, but is ineffective in esterifying free fatty acids. This method is inappropriate for high free fatty (FFA) acid feedstock due to undesired saponification formed soap (Figure 3.3). The esterification is used for feedstock had high contend of free fatty acid that produces biodiesel and water using acid catalyst (commonly sulfuric acid). Moreover, the two-step method, the first step of the process is to reduce FFA content in vegetable oil by esterification with methanol and acid catalyst. The second step is transesterification process, in which triglyceride (TG) portion of the oil reacts with methanol and base catalyst to form ester and glycerol (Chongkhong et al, 2007). However, such method is disadvantage on higher capital and operating costs likewise combination of first two methods together. Alternatively, when oil feedstocks contain an excess of FFA they are pretreated through hydrolysis reaction (Figure 3.4), oil feedstock (triglyceride) is hydrolyzed with water so as to produce FFA and glycerol that pure glycerol is obtained from this. Hydrolysis pretreatment is held the best sequence for rich FFA feedstock before feeding to the esterification process. Furthermore, this sequence of hydrolysis and esterification is still appropriate applying for wide range feedstocks.
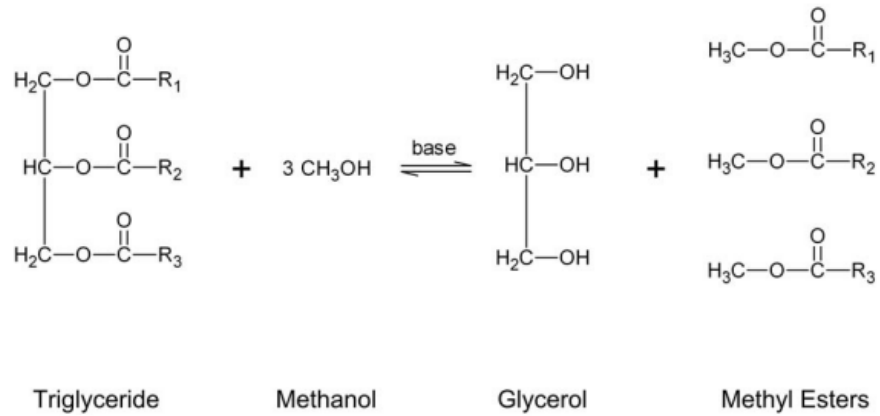
Fig. 3-1 Base-catalyzed transesterification reactions (Babcock, 2005)
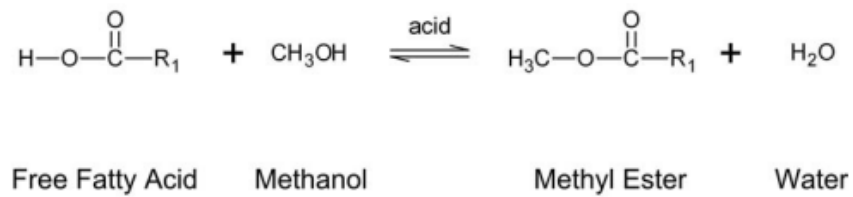
Fig. 3-2 Acid-catalyzed esterification reactions (Babcock, 2005)
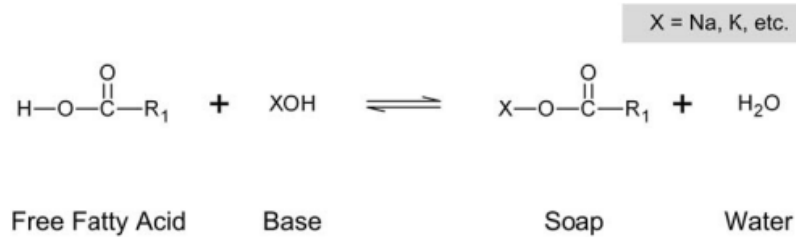
Fig. 3-3 Undesired saponification reactions (Babcock, 2005)
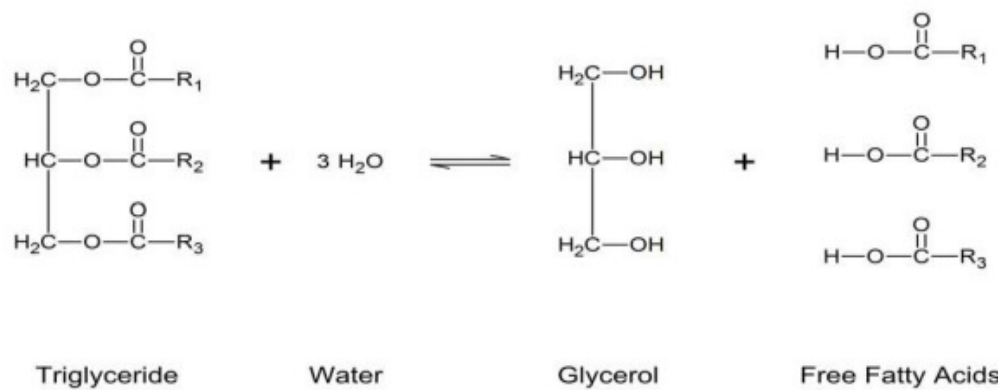
Fig. 3-4 Hydrolysis of triglyceride (Babcock, 2005)

3.1.3 Advantages and disadvantages of biodiesel

Biodiesel is a sustainable energy that is made from renewable sources such as vegetable oils and animal fats. These sources could always be re-planted or grown to ensure its sustainability. Other than that, biodiesel is a non-toxic and clean energy. The emissions from vehicles that are using biodiesel contains lower harmful gases such as carbon monoxide, sulfur dioxide and aromatic content compared to that of using petroleum derived diesel. Biodiesel could also reduce the emission of particulate matters (PM). Biodiesel also acts as a good lubricant to diesel engines. This could therefore prolong the self-life of the engines. Biodiesel also has higher flash point which makes it safer to handle compared to diesel. Other advantages of biodiesel as diesel fuel are liquid nature portability, readily available, renewability, higher combustion efficiency, higher cetane number and higher biodegradability. On the other hand, disadvantages of biodiesel include increased emission of NOx gas, higher cloud and pour points and also costlier compared to diesel due to high price of vegetable oils especially those of edible type. However, the cost of biodiesel could vary depending on the source of feedstock. Biodiesel can also dissolve certain parts of the diesel engines, especially those made of elastomers. Nevertheless, the advantages of biodiesel superseded the disadvantages generally on the environmental aspects, making it a very popular alternative to petroleum derived-diesel oil. (Kansedo, 2009)

3.2 Kinetic model (Tesser et al., 2005)

The feedstocks with high content of free fatty acid (more than 1- 2%), esterification process is usually applied to produce biodiesel. Oleic acid was assumed to represent a free fatty acid in wide range feedstocks. The esterification reaction between oleic acid and methanol can be represented in the following schematic form:

Oleic acid + methanol ↔ methyl oleate + water
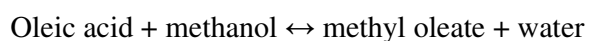
under the presence of an acid sulfonic resin as the catalyst is shown in Eq. (3-1)

$$C_{17}H_{33}COOH + CH_3OH \leftrightarrow C_{17}H_{33}COOCH_3 + H_2O \tag{3-1}$$

Tesser et al. (2005) studied the kinetics of esterification reaction of oleic acid and methanol in presence of acid sulfonic resin and proposed a pseudo homogeneous second-order kinetic model to describe such a reaction. The modeling of the experimental runs has been used with an expression of the reaction rate, for Eq. (3-2), that is as follows:

$$r = k_c x_A x_M (1 - \frac{1}{k_c} \frac{x_E x_W}{x_A x_M}) C_{cat} \tag{3-2}$$

where x_A, x_M, x_E, and x_W are mole of fraction of free oleic acid, methanol, methyl oleate and water, respectively, and k_c and k_e are kinetic and equilibrium constants which are temperature dependent following the Arrhenius equation.

Table 3-3 shows the kinetic parameters of esterification of oleic acid and methanol.

Table 3-3 Kinetic parameters for the esterification of oleic acid and methanol

Parameter	ln k_0	E_a (kcal/mol)
k_c	12.93	14.00
k_e	4.17	2.68

3.3 Reactive distillation

The conventional processes of esterification and transesterification consist of a reactor followed by a sequential distillation column obtaining purities of products, by-product and remaining reactants. This usually takes place in several separation devices. It is noted that the conventional process (Figure 3.5a) involves two steps of chemical reaction and subsequent separation. A common intensification alternative to those operations involves a reactive distillation (RD) that it is a technique which combines chemical reactions and product separations in one unit (Figure 3.5b). Currently RD has attracted more and more attention and been used widely due to its

many advantages over conventional sequential processes, such as a fixed-bed-reactor followed by a distillation column that it offers several potential benefits over the conventional sequential processes including increased yield, improved selectivity, reduced energy consumption, avoidance of hot spots and ability to separate close boiling species. One of the most important advantages of RD is that conversion limitation is avoided by continuous in situ product removal for equilibrium-controlled reactions. Like esterification, tranesterification is a typical equilibrium-limited reaction. Therefore, RD is used to improve conversion. The usage of RD column, both reaction and distillation are carried out simultaneously within a single vessel operating at some pressure, the temperatures of reaction and separation are not independent, that one process unit is eliminated; it leads to a reduction of capital investment and operating costs, significantly. RD has become one of the extensively researched process intensification methods (Wang et al., 2008; Mali and Jana, 2009; Qui et al., 2010; Gómez-Castro et al., 2010). In most cases, the reaction is catalyzed homogeneously or preferably heterogeneously so that it is often cited as catalytic distillation (Sundmacher and Qi, 2003). In general, both exothermic and endothermic reactions can be implemented in RD. However, the exothermic reactions are preferable as the heat released from the reactions can be used for product separation resulting in a reduced operation cost.

In conventional distillation design, tray holdup has no effect on steady-state composition. In reactive distillation, tray holdup (or amount of catalyst) has a profound effect on conversion, product composition, and column composition profiles. So, in addition to the normal design parameters of reflux ratio, number of trays, feed tray location, and pressure, reactive distillation columns have the additional design parameter of tray holdup. If there are two reactant feedstreams, an additional design parameter is the location of the second feed.

Pressure in conventional distillation design is usually set by a minimum temperature in the reflux drum (so that cooling water can be used) or a maximum temperature in the reboiler (to prevent fouling or thermal decomposition). Establishing the optimum pressure in a reactive distillation column is more complex because of the interplay between reaction and phase separation. Most VLE

relationships show an increase in volatility with decreasing temperature. On the other hand, reaction rates decrease with decreasing temperature. If the reaction is exothermic, the chemical equilibrium constant increases with decreasing temperature. So, low operating pressure or temperature, which facilitates the phase separation, may require lots of catalyst or liquid tray holdup to compensate for the low reaction rates (Luyben).

3.3.1 Configuration of reactive distillation

By considering a reversible reaction scheme A+B⇔C+C where the boiling points of the components follow the sequence A, C, D and B. The traditional flow-sheet for this process consists of a reactor followed by a sequence of distillation columns; see Fig. 3.5 (a). The mixture of A and B is fed to reactor, where the reaction takes place in the presence of catalyst and reaches equilibrium. A distillation train is required to produce pure product C and D. The unreacted components, A and B, are recycled back to the reactor. In practice the distillation train could be much more complex than the one portrayed in Fig. 3.5 (a) if one or more azeotropes are formed in the mixture. The alternative RD configuration is show in Fig. 3.5 (b). The RD column consists of reactive section in the middle with non-reactive rectifying and stripping sections at the top and bottom. The task of the rectifying section is to recovery reactant B from the product stream C. In the stripping section, the reactant A is stripped from the product D. In the reactive section the product s are separated in-situ, driving the equilibrium to the right and preventing any undesired side reactions between the reactants A (or B) with the product C (or D). For a properly designed RD column, virtually 100% conversion can be achieved. (Baur, 2000)

(a) Conventional process   (b) Reactive distillation
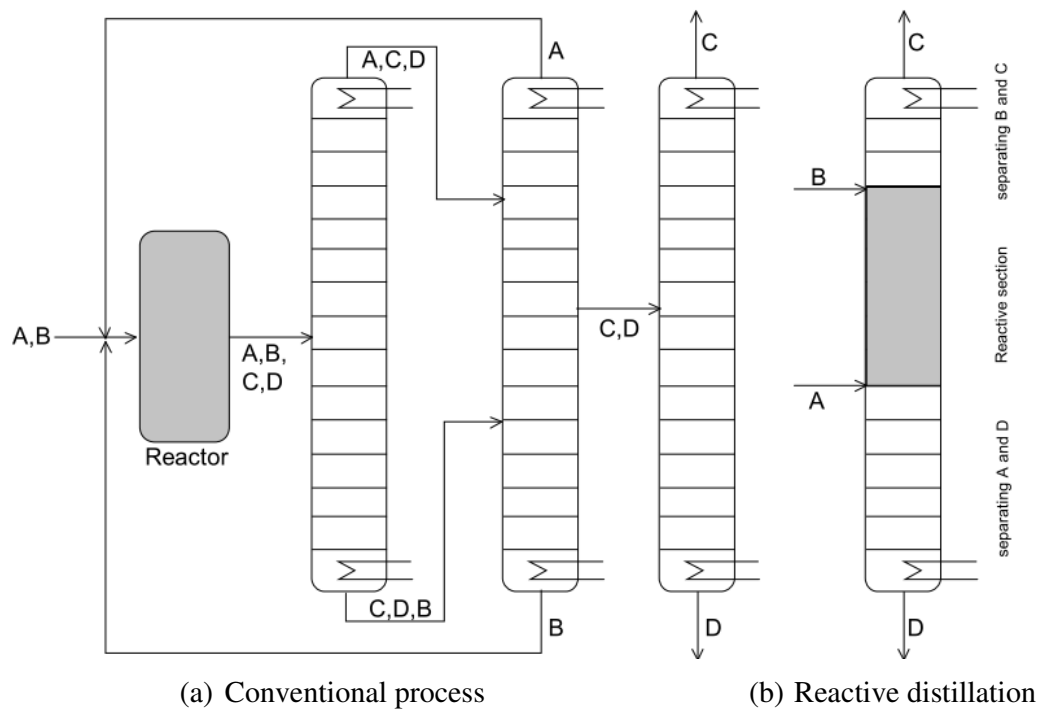
Fig. 3-5 Processing scheme for a reaction sequence A + B <=> C+D where C and D are both desired products. (a) Typical configuration of a conventional process. (b) The reactive distillation configuration. The reactive sections are indicated by gray areas. [Baur, 2000]

3.3.2 Advantages and disadvantages of reactive Distillation

The benefits of using RD can be summarized as follows (Baur, 2000; Qui, 2010; Tuchlenski et al., 2001):

1. Simplification or elimination of the separation system can lead to significant capital saving.

2. Improved conversion of reactant approaching 100% for equilibrium-limited reaction due to shifting of the equilibrium to the right. This increase in conversion gives a benefit in reduced recycle cost.

3. Improved selectivity. Removing one of the products from the reaction mixture or maintaining a low concentration of one of the reagents can lead to

reduction of the rates of side reactions and hence improved selectivity for the desired products.

4. Significantly reduced catalyst requirement for the same degree of conversion.

5. Avoidance azeotropes. RD is particularly advantageous when the reactor product is a mixture of species that can form several azeptropes with each other RD conditions can allow the azeotropes to be reacted away in a single vessel.

6. Reduced by-product formation.

7. Heat integration benefit. If the reaction is exothermic, the heat of reaction can be used to provide the heat of vaporization and reduce the reboiler duty. Endothermic reactions are not suitable for the RD technology because of vapor condensation. Although endothermic reactions require more reboiler duty and therefore exhibit no large energy savings, there are no restrictions to the application of RD.

8. Avoidance of hot spots and runaways using liquid vaporization as thermal fly wheel.

However applying RD technology in industrial scale, three constraints has to be fulfilled:

1. The use of RD technology is only possible, if the temperature window of the vapor liquid equilibrium is equivalent to the reaction temperature. By changing the column operating pressure, this temperature window can be altered. However, the thermal stability of the catalyst can limit the upper operation temperature of the distillation column.

2. Because of the necessity of wet catalyst pellets the chemical reaction has to take place entirely in the liquid phase.

3. As it is very expensive to change the catalyst in a structured catalytic packing catalysts with a long lifetime are strongly required.

3.4 Design of distillation column

The design objective of distillation column is to separate the mixture obtaining required purity of any component. The distillation column can be design by simulating in HYSYS that originates the calculations of Fenske's equation for minimum number of plates, Underwood's equation for minimum reflux ratio, and Gilliland's correlation for number of ideal plates at operating reflux.

3.4.1 Minimum number of plates

Fenske's equation is used to calculate N_{min} which is the number of plates required to make a specified separation at total reflux. The Fenske total reflux equation can be written as

$$N_{min} = \frac{ln\left[(x_{Di}/x_{bi})/(x_{Dj}/x_{Bj})\right]}{ln\alpha_{ij}}$$

Where i is any component and j is an arbitrary selected reference component in the definition of relative volatilities,

$$\alpha_{ij} = \frac{K_i}{K_j} = \frac{y_i/x_i}{y_j/x_j}$$

3.4.2 Minimum reflux ratio

An approximate but fairly accurate method of determining R_{DM} was developed by Underwood. The relative volatility for each component is taken to be the same in the upper and lower invariant zones, and constant molal over flow is assumed The equations for the invariant zones are written terms of the relative volatility α_i, where α_i = K_i/K_{ref}, with the heavy key generally generally taken as the reference component. The two equations are combined with an overall material balance and the feed quality

equation to give an equation that must be solved by trial. The correct root $\emptyset$ of this equation lies between the values of α for the key. The equation is

$$1 - q = \sum \frac{\alpha_i x_{Fi}}{\alpha_i - \emptyset}$$

The value of $\emptyset$ is then used to get R_{DM}

$$R_{DM} + 1 = \sum \frac{\alpha_i x_{Di}}{\alpha_i - \emptyset}$$

Then q has the following numerical limits for the various conditions:

Cold feed $q > 1$

Feed at bubble point (saturated liquid), $q = 1$

Feed partially vapor, $0 < q < 1$

Feed at dew point (saturated vapor), $q = 0$

Feed superheated vapor, $q < 0$

3.4.3 Number of ideal plates at operating reflux

The empirical correlation of Gilliland then used these values to give N for any specified. Limitations of the Gilliland correlation are discussed by Henley and Seader. The following equation, developed by Molokanov et al. satisfies the end points and fits the Gilliland curve reasonably well:

$$\frac{N - N_{min}}{N + 1} = 1 - exp\left[\left(\frac{1 + 54.4\psi}{11 + 117.2\psi}\right)\left(\frac{\psi - 1}{\psi^{0.5}}\right)\right]$$

Where $\psi = (R - R_{DM})/(R+1)$

3.4.4 HYSYS for design of distillation column

The reflux ratio was calculated by determining the minimum reflux ratio using a model of shortcut distillation column, and multiplying by 1.5 to obtain the optimum reflux ratio (McCabe et al., 2001). The required data for simulation of shortcut model is feed condition and composition and specified design parameters including light and heavy key components in bottom and distillate, respectively, pressure of condenser and reboiler. The minimum reflux ratio is appeared achieving then the reflux ratio, as well as the the number of stage, feed stage, and rates of distillate and bottom. These data is taken to design on distillation in the rigorous model.

CHAPTER IV

CONVENTIONAL REACTIVE DISTILLATION PROCESSES FOR BIODIESEL PRODUCTION

4.1 Simulation of reactive distillation process for biodiesel production

There are many studies on the reactive distillation process; some of them deal with the design of reactive column for mixture up to 4 components, and some others analyze reactive distillation column with equilibrium and non-equilibrium stage models (Buar et al, 2000). In this chapter, the production of biodiesel from esterification reaction in reactive distillation process is studied. The oleic acid is assumed as fatty acid and esterified by methanol for biodiesel production. This study has been focused on the esterification step to produce methyl ester (biodiesel product) from oleic acid using reactive distillation column and considered energy consumption. Simulations of the reactive distillation processes are performed by using HYSYS commercial software to investigate the effects of key operating parameter on the performance of the reactive distillation for biodiesel production. The activity coefficient model of UNIQUAC is used to estimate the thermodynamic properties and phase equilibrium, and also the usage of the rigorous equilibrium stage model. Oleic acid, a major component in palm oil, is represented as fatty acid. Methyl oleate (biodiesel) is taken as the product of esterification reaction whereas water is considered as a by-product. Reactive distillation column, T-100 shown in Fig.4-1 (a) has 30 stages, rectifying section located at the top, reaction zone located at the middle, and stripping section located at the bottom of the column. The column operates with a total condenser. The column is operated at different pressure between condenser and reboiler of 0.5 bars, stage efficiency of 70% is assumed.

The esterification reaction takes place in the reaction zone from stages 3 to 29 with heterogeneous catalyst of acid sulfonic resin. Methyl oleate and water are formed

in the reactive zone where the esterification of oleic acid and methanol is carried out. The reverse hydrolysis reaction is negligible and kinetic rate constants are given by Tesser et al. (2005). The bottom separation zones, reboiler stage, separates the desired product, methyl oleate, while the top separation zone, stages of 1 tray and condenser, remove the water and unreacted methanol.
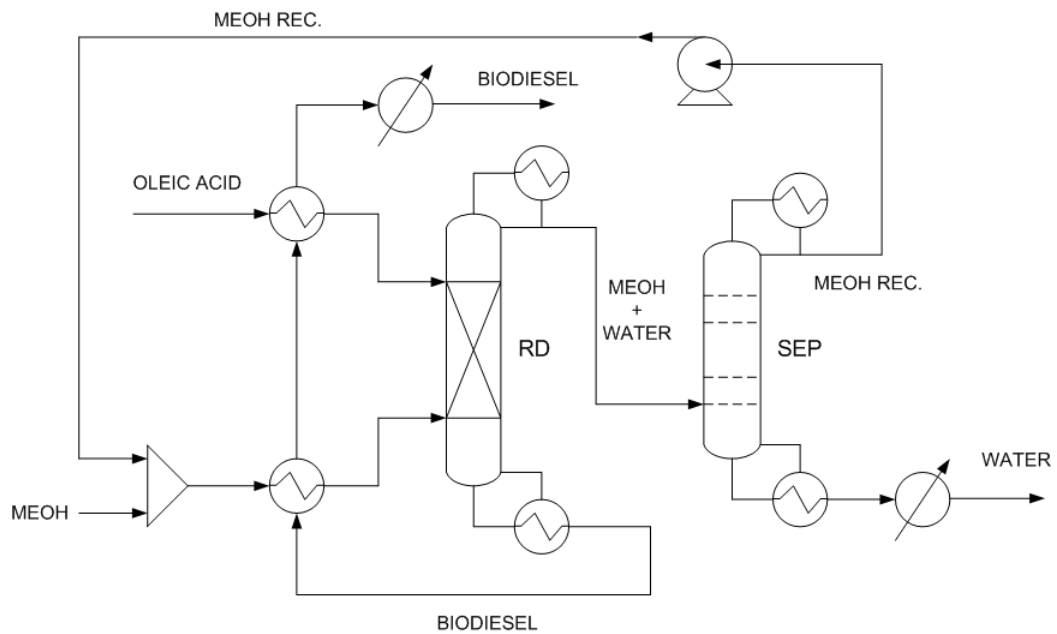
(a)
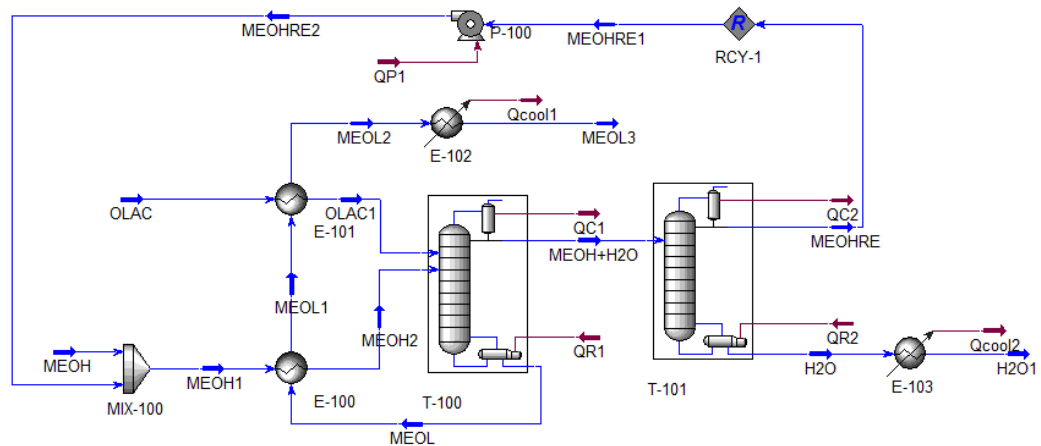
(b)

Fig. 4-1 (a) Schematic diagram and (b) Flowsheet of a conventional reactive distillation for biodiesel production.

4.1.1 Model validation

The model of biodiesel process using the reactive distillation is taken from the research of Nguyen and Demirel (2011). Because the Nguyen and Demirel model (N&D model) considered a dodecanoic acid as the fatty acid whereas oleic acid is chosen for this work. The validations of the model for this work are carried out to present that the N&D model can be applied. The referred configuration of biodiesel process is shown as flowsheet in Fig. 4-1 (b). The biodiesel production using reactive distillation process requires at least two columns for biodiesel separation and methanol recovery. The reference condition is shown in Table 4-1 for N&D model. Reactive distillation column, the feeds streams consisting of fatty acid and methanol at the flow rate of 20,032.14 and 3364.43 kg/h, respectively; are fed to the both ends of the reaction zone to maximize conversion. The reactive distillation is operated at the pressure of 5.5 to 6 bars with molar reflux ratio of 0.1 and the reboiler duty of 5635 kW. Fig. 4-2 shows the temperature profile and Fig. 4-3 to 4-6 show component profiles within the reactive distillation column for N&D model and validated model. They can be seen that both N&D model and validated model are obtain the similar tends in profiles of temperature, methanol, methyl ester, water compositions, whereas composition profile of fatty acid is obviously different in stage of 3 to 8 because reaction of oleic acid and methanol for validated model is lower reaction of dodecanoic acid and methanol for N&D model. The temperature profile (Fig. 4-2) is seen that the validated model used oleic acid as feedstock utilizes the higher reboiler temperature than N&D model used dodecanoic acid as feedstock because they are obtain the methyl oleate and methyl dodecanoate, respectively; boiling point of methyl oleate higher than methyl dodecanoate. For methanol profile in Fig. 4-4 is seen that the validated model require the amount of methanol in esterifying fatty acid less than the N&D model causing the lower formation of methyl ester, as well as the lower purity of biodiesel product (Fig. 4-5). Considering the composition profile of all components as shown in Fig. 4-7 is seen that there is a large amount of methanol in the top of column while less amount of fatty acid, methyl ester (biodiesel product), and water are observed. The bottom products consist of mostly methyl ester and slightly water as a by-product. Under this condition, the conversion of fatty acid is

99.99% for N&D model. The water and unreacted methanol, the lowest boiling point substances, is withdrawn from the reactive distillation column as distillate stream whereas the biodiesel product, methyl ester is removed as a bottom stream with purity of 96.14%. Table 4-2 shows the simulation results of validated model comparing to N&D model. It is seen that the values of bottom rate, boilup rate, and boilup ratio are more relatively error because the component properties of methyl ester (methyl dodecanoate / methyl oleate).

Table 4-1 Operating conditions and configuration of reactive distillation column T-100 and methanol distillation column T-101 (Nguyen and Demirel, 2011)

Condition & Configuration	Design	
	RD (T-100)	MD (T-101)
Number of stages	30	12
OLAC1 feed stage	3	-
MEOH2 feed stage	29	-
MEOH+H2O feed stage	-	9
OLAC1 temperature, °C	100	-
MEOH2 temperature, °C	110	-
Molar reflux ratio	0.1	1.55
Reaction stages	3-29	-
Distillate rate, kmol/h	196	95
Condenser duty, kW	-2168.38	-2375.23
Condenser temperature, °C	124.12	64.36
Condenser pressure, bar	5.5	1
Reboiler duty, kW	5634.95	2136
Bottom rate, kmol/h	104	101
Reboiler temperature, °C	311.29	97.59
Reboiler pressure, bar	6	1
Total conversion, mol%	99.99	-
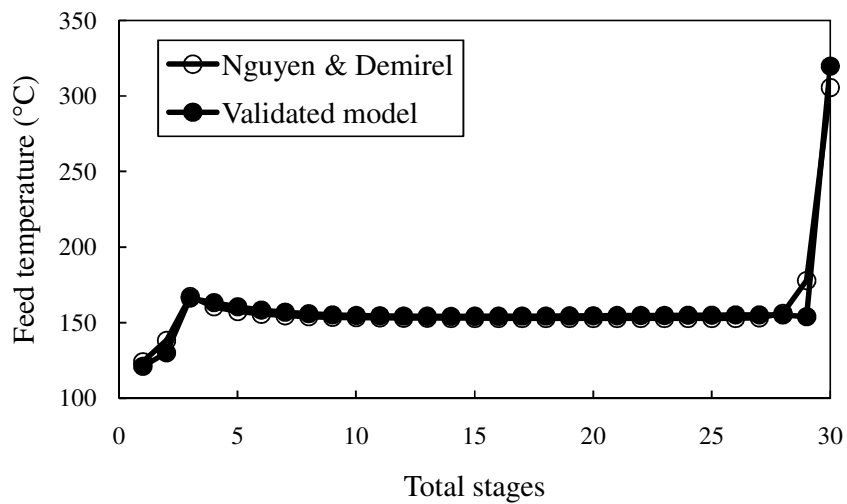
Fig. 4-2 Temperature profile in reactive distillation column.
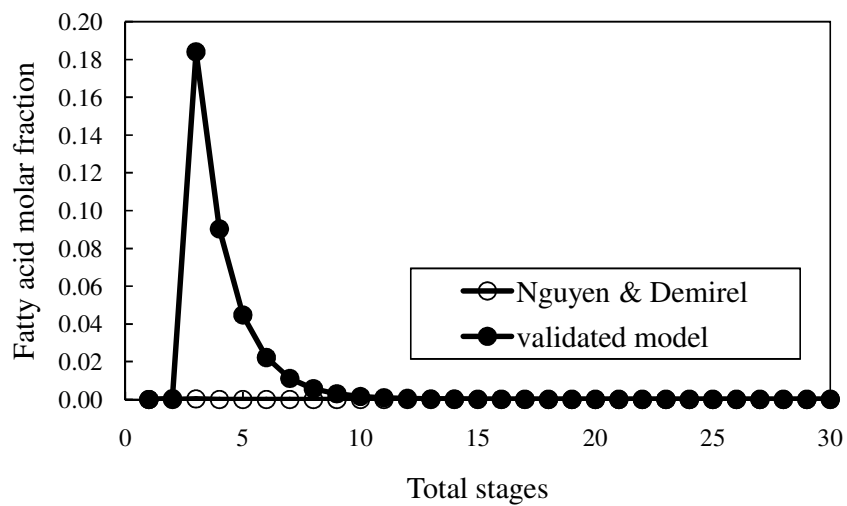
Fig. 4-3 Composition profile of fatty acid in reactive distillation column.
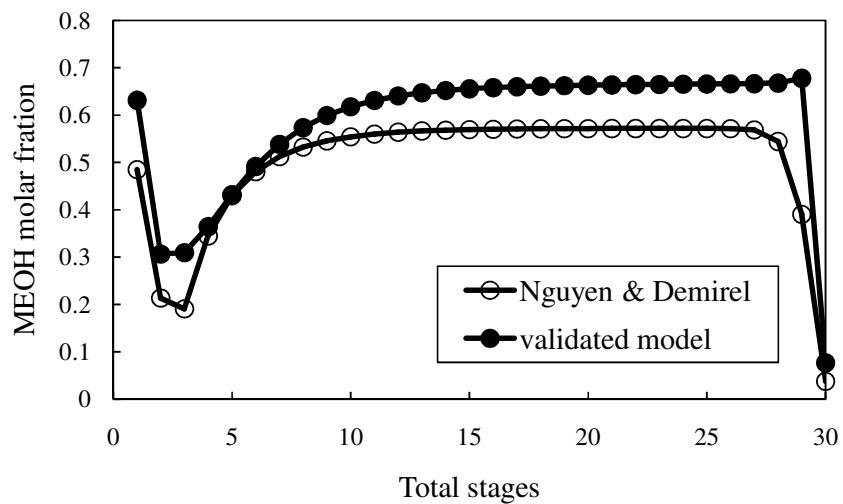
Fig. 4-4 Composition profile of methanol in reactive distillation column.
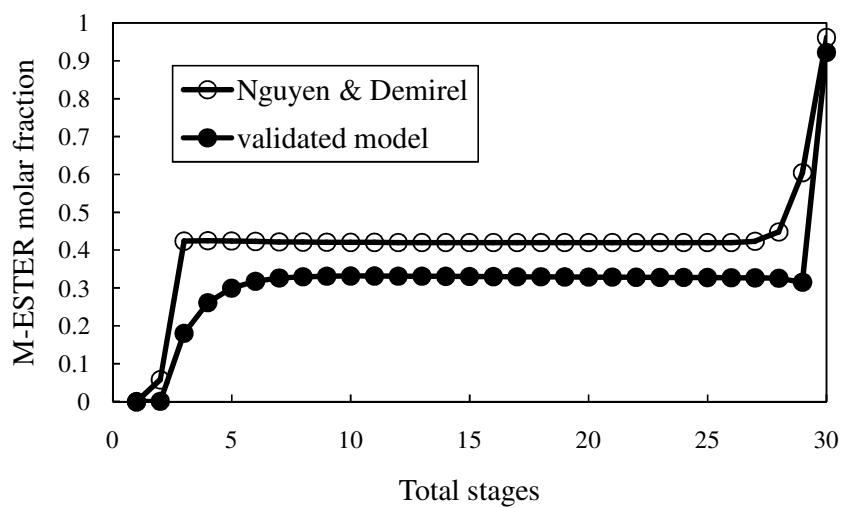
Fig. 4-5 Composition profile of methyl ester in reactive distillation column.
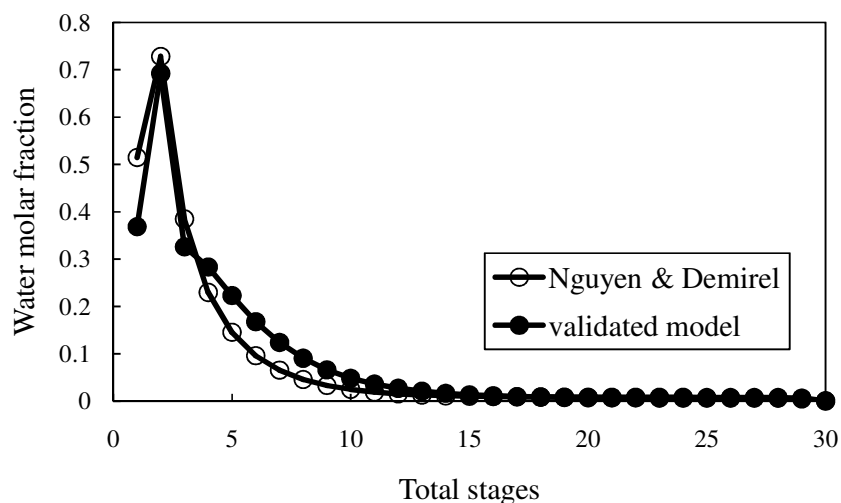
Fig. 4-6 Composition profile of water in reactive distillation column.

Table 4-2 Validation of the reactive distillation column model used in this study.

Operating condition	RD (T-100)		% error
	N&D model	Validated model	
Condenser temperature (°C)	124.07	121.1	2.39381
Condenser duty (kW)	-2176.04	-2049	5.838128
Distillate rate (kmol/h)	196.59	194.2	1.215728
Reflux rate (kmol/h)	19.7	19.4	1.522843
Reflux ratio	0.1	0.1	0
Reboiler temperature (°C)	311.26	321.8	3.38624
Reboiler duty (kW)	5634.95	5635	0.00089
Bottom rate (kmol/h)	103.41	76.72	25.80988
Boilup rate (kmol/h)	170.95	202	18.1632
Boilup ratio	1.65	2.64	60
%conversion	100	99.99	0.01
%purity	96.69	92.43	4.405833
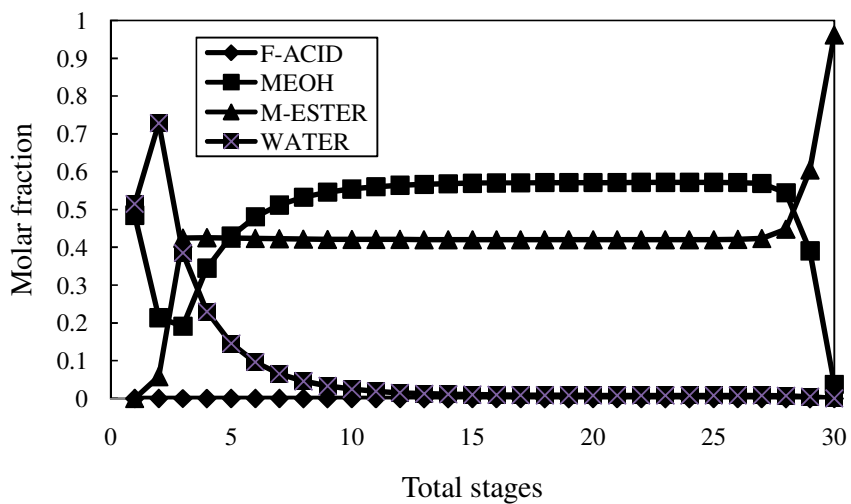
(a)
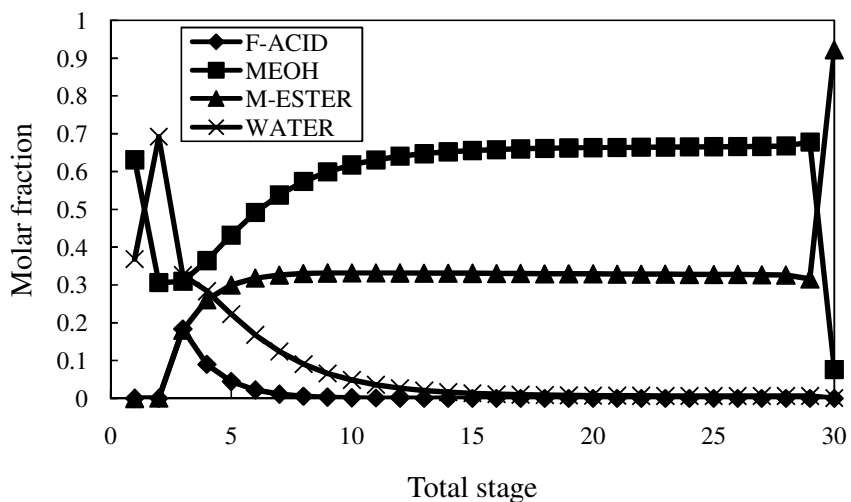
(b)

Fig. 4-7 Composition profiles of N&D model (a) and validated model (b).

For separation distillation column (T-101), the mixture of methanol and water from the top of reactive distillation column are separated to recover methanol in the top of column mixing to fresh methanol. It is fed to the column at the stage 9. The methanol distillation (MD) column is operated at the pressure of 1 bar with reflux ratio of 1.55 and the reboiler duty of 2136.23 kW. Fig. 4-8 shows the temperature profile and Fig. 4-9 and 4-10 show composition profiles of methanol and water,

respectively, within the column at the reference condition. It can be seen that the operating temperature within MD column of N&D model is higher than validated model causing MD column can separate methanol and water from mixture of methanol and water where the high purity of methanol and water are obtained. It is not the case of validated model that can be obtained only the high purity of methanol. The composition profiles can be seen that there is a large amount of methanol in the top of column while fewer amounts of oleic acid, methyl ester, and water are observed. The bottom products consist of mostly water and slightly methanol. Such condition, recovered methanol is obtained purity up to 99% in the top; however, mostly water in the bottom is still mixed with methanol. The range of operating temperature of column is 60 to 80°C for case of validated model. That is not high enough to separate water which boiling point of 100°C. The simulation results for methanol distillation column of validated model can be compared to N&D model as shown in Table 4-2.
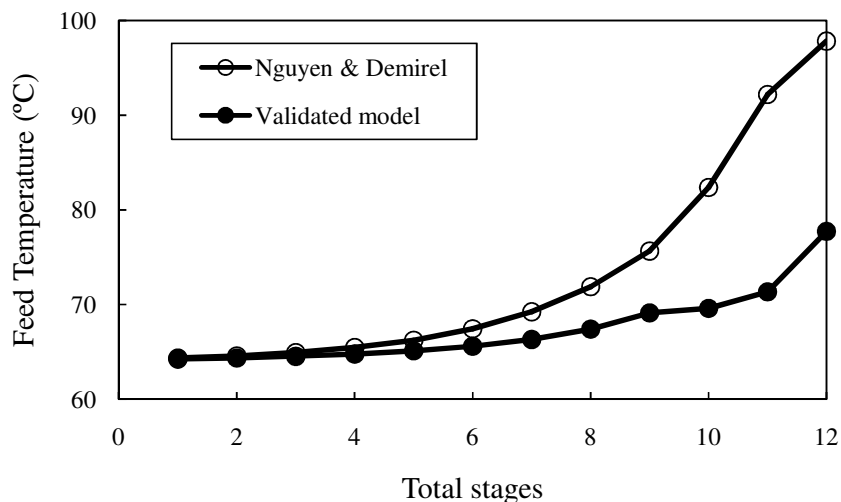
Fig. 4-8 Temperature profile in methanol recovery column.
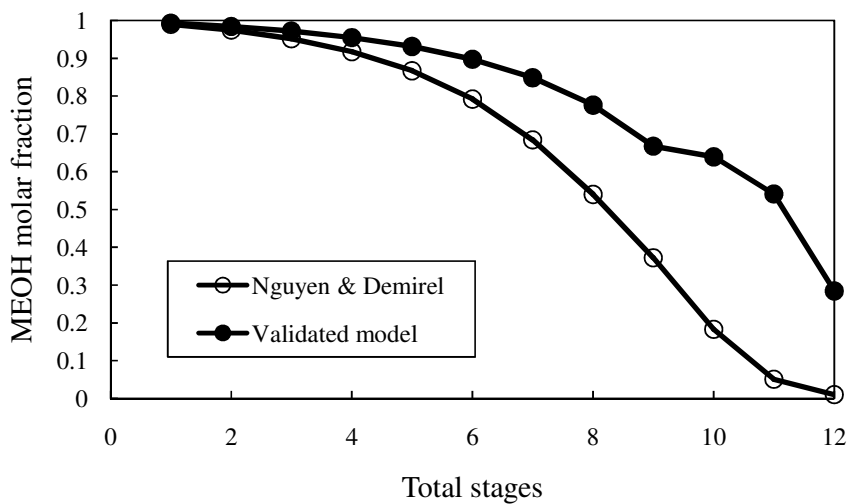
Fig. 4-9 Composition profile of methanol in methanol recovery column.
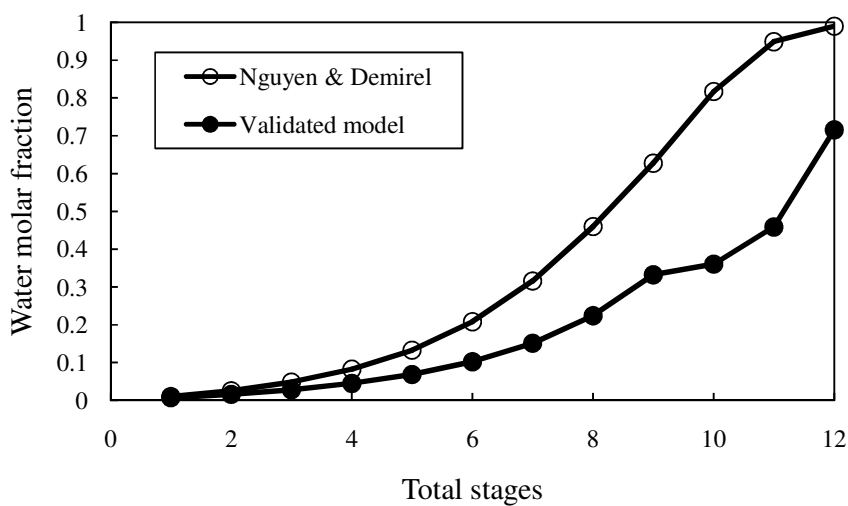
Fig. 4-10 Composition profile of water in methanol recovery column.

Moreover, in this process has been added pre-heating of product stream and feed streams via shell and tube heat exchanger (E-100 and E-101). The hot stream (stream MEOL) from the bottom in reactive distillation is cooled down with the cold streams (OLAC and MEOH1) to decrease temperature by E-100 and E-101, respectively, while cold feeds is heated up to increase temperature before fed into the column.

Table 4-3 Validation of the methanol distillation column model used in this study.

Operating condition	MD (T-101)		%error
	N&D model	Validated model	
Condenser temperature (°C)	64.34	64.23	0.170967
Condenser duty (kW)	-2377	-2437	2.52419
Distillate rate (kmol/h)	95.18	97.28	2.20635
Reflux rate (kmol/h)	147.5	151	2.37288
Reflux ratio	1.55	1.55	0
Reboiler temperature (°C)	96.93	77.62	19.92159
Reboiler duty (kW)	2136.23	2136.23	0
Bottom rate (kmol/h)	101.58	99.42	2.126403
Boilup rate (kmol/h)	186.68	204	9.27791
Boilup ratio	1.84	2.05	11.413

4.1.2 Performance of a conventional reactive distillation (CRD) process

In this section, the performance of reactive distillation for biodiesel production is investigated. The standard condition (Nguyen and Demirel, 2011) as esterification of dodecanoic acid and methanol is taken to simulate the base process from esterification of oleic acid and methanol. The reactive distillation column is evaluated the performance by considering the conversion of fatty acid and the purity of biodiesel product. The conversion of oleic acid is defined by Eqs. (4-1)

$$\text{Conversion} = \frac{F_{OLAC,i} - F_{OLAC,o}}{F_{OLAC,i}} \times 100 \qquad (4\text{-}1)$$

where $F_{OLAC,i}$ and $F_{OLAC,o}$ are molar flow rate of oleic acid in feed and outlet stream on reactive distillation column, respectively.

The reference condition has been taken to analyze the operating parameters on performance of reactive distillation for biodiesel production from esterification of oleic acid and methanol obtaining the optimum condition to be base case process was called that the conventional reactive distillation (CRD) process. The effect of

operating parameters such as column pressure, feed temperature, bottom rate, reactive stages, and feed locations are analyzed in term of the fatty acid conversion and methyl ester purity, as well as the reboiler duty.

4.1.1.1 Effect of column pressure for CRD process

The effect of column pressure on the performance of the reactive distillation in term of the oleic acid conversion and methyl oleate (biodiesel product) purity is studied where the difference of top and bottom pressure is 0.5 bar (i.e. top and bottom pressure of 3.5 and 4 bar). Fig. 4-11 and 4-12 show that when the bottom pressure is increased from 2 to 9 bar, the conversion of oleic acid and the purity of biodiesel are greatly increased from 2 to 3 bar and slightly increased from 3 to 4 bar, however, higher pressure of 4 bar, the performance of reactive distillation is not improved. Elevating the column pressure leads to higher temperatures and hence higher reaction rates for kinetically controlled reactions. Then the chemical equilibrium of reaction shift to a product side where oleic acid can be converted to methyl ester. Nevertheless, the too increase in bottom pressure (4 bar) is not affected to purify the biodiesel product because no changing in temperature of reboiler, while the unnecessarily increased utilization of reboiler duty. Otherwise, using acid sulfonic rasin it is not possible to operate at temperatures above 150 ℃ since this is the maximum operating temperature recommended by the manufacturer. Simulation studies show that temperatures below 150 ℃ can be realized when pressures up to 3 bar are realized. Therefore, the column pressure for CRD process is 3.5 - 4 bar obtaining highest oleic acid conversion and biodiesel purity. Moreover, it is shown that an increase in the column pressure results the increased reboiler duty as shown in Fig. 4-13.
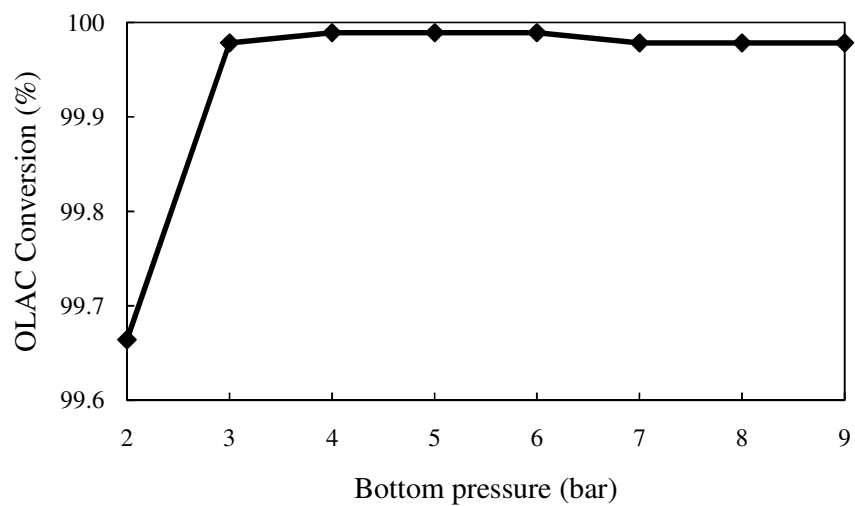
Fig. 4-11 Effect of pressure on conversion of oleic acid in reactive distillation column.
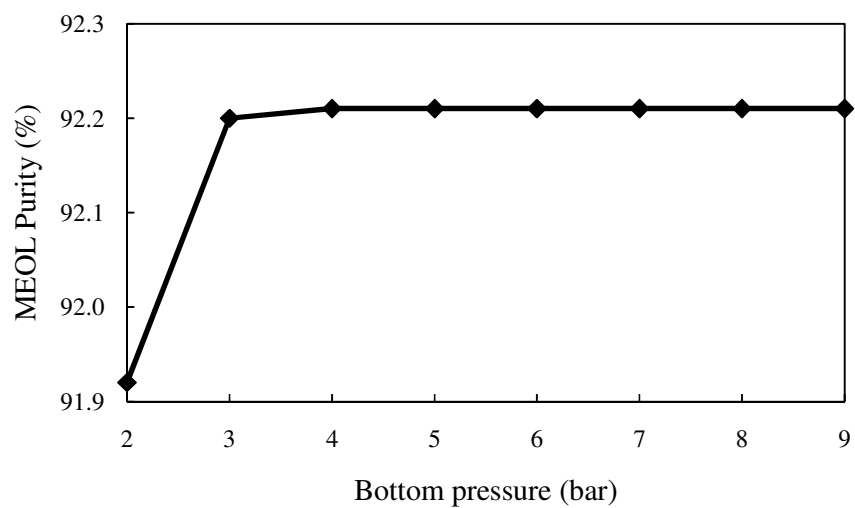
Fig. 4-12 Effect of pressure on purity of methyl oleate in reactive distillation column.
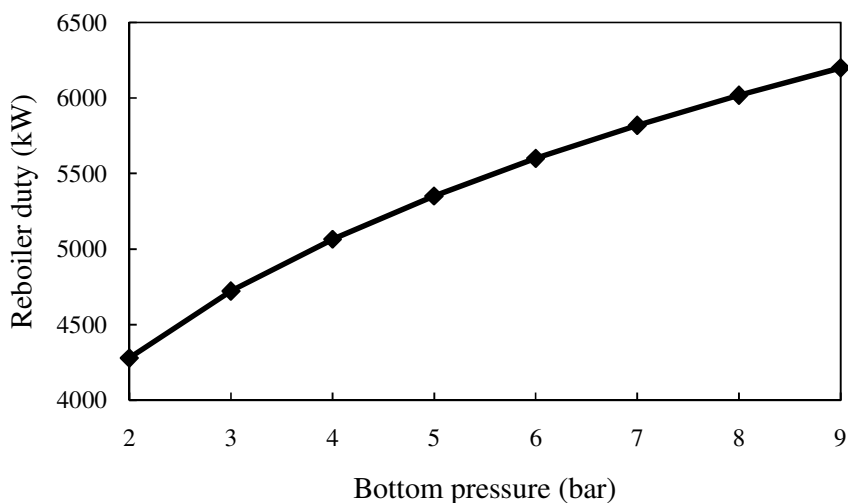
Fig. 4-13 Effect of pressure on reboiler duty in reactive distillation column.

4.1.1.2 Effect of feed temperature for CRD process

The effect of feed temperature on the performance of the reactive distillation in term of the conversion of oleic acid and purity of methyl oleate is studied. Figs. 4-14 and 4-15 show that when feed temperature of oleic acid is increased from 25 to 200°C while fixed methanol feed temperature of 110°C at the standard condition. It can be seen that the conversion of oleic acid and purity of methyl oleate are increased with increasing feed temperature of oleic acid until at more than 100°C of oleic acid feed temperature, the performance of reactive distillation is not improved. For exothermic reactions equilibrium shifts toward the reactants. Thus, a temperature increase often results in decline in conversion. Departure from chemical equilibrium also decreases with increasing temperature, thereby increasing the reaction driving force and eventually causing increase in the reaction rate. Moreover, the effect of feed temperature has been considered on reboiler heat duty as shown in Fig. 4-16. It can be seen that increasing temperature of oleic acid feed resulting the decrease in heat energy supplied to reboiler of reactive distillation. Therefore, the temperature of oleic acid obtaining the highest olaeic acid conversion and biodiesel purity with the achieved low reboiler duty is 175°C. Due to effect of the low ft correction factor in heat exchanger, the oleic acid feed temperature of 200°C is not chosen.

Fig. 4-14 Effect of feed temperature on conversion of oleic acid in reactive distillation column.

Fig. 4-15 Effect of feed temperature on purity of methyl oleate in reactive distillation column.

Fig. 4-16 Effect of feed temperature on reboiler duty in reactive distillation column.

4.1.1.3 Effect of bottom rate for CRD process

In this study, the effect of bottom rate on the performance of the reactive distillation are studied in term of the conversion of oleic acid and purity of methyl oleate as shown in Figs. 4-17 and 4-18, initially the bottom rate at standard condition is 76.9 kmol/h and then it is went on decreasing to 71 kmol/h. It is observed that decrease in bottom rate is not affect on the conversion of oleic acid as shown in Fig. 4-17 the average conversion of oleic acid is 99.98%, whereas the product purity is increased with decrease in bottom rate because methanol is more boiled up the top. However, the decrease in bottom rate causes the increase in reboiler duty as shown in Fig. 4-19 because the column is required more energy for vaporization of methanol to the top. Thereby, the bottom rate is important parameter on the product purity which the biodiesel purity up to 99% is achieved at 71.5% with reboiler duty of 7520 kW.

Fig. 4-17 Effect of bottom rate on conversion of oleic acid in reactive distillation column.

Fig. 4-18 Effect of bottom rate on purity of methyl ester in reactive distillation column.
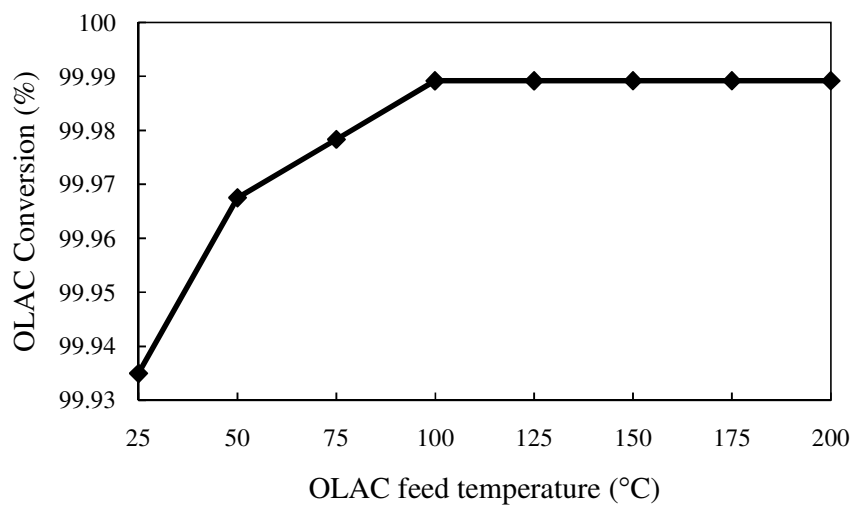
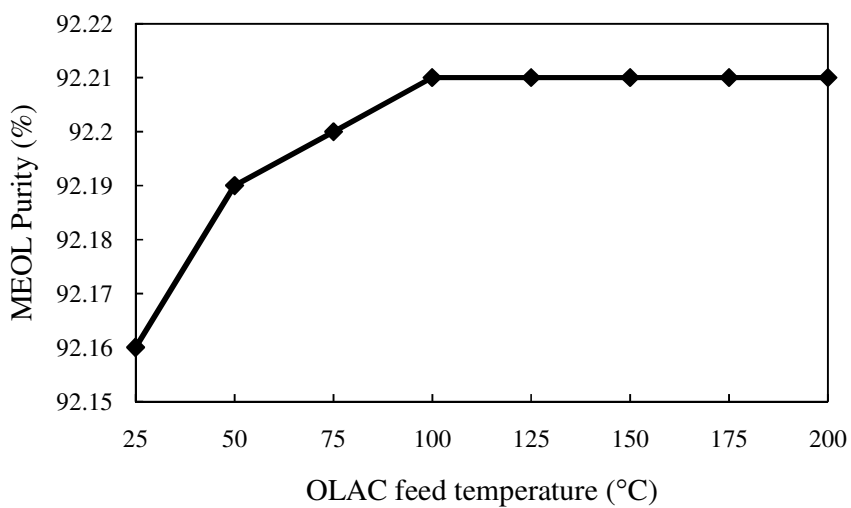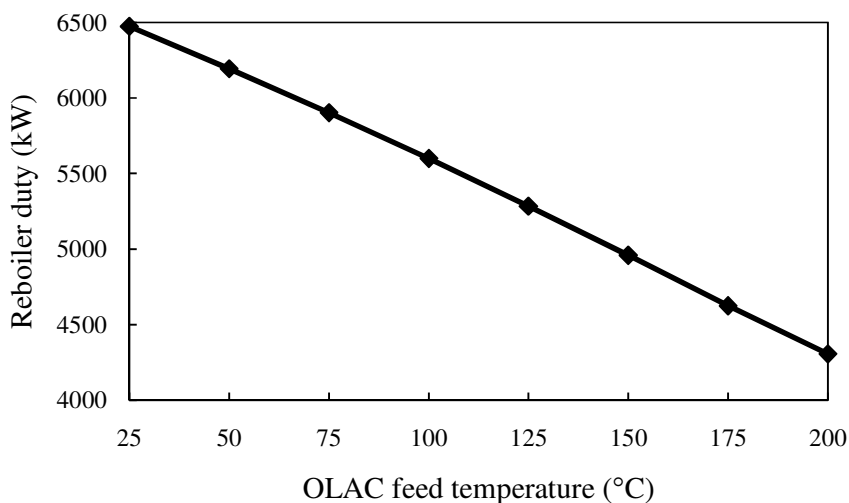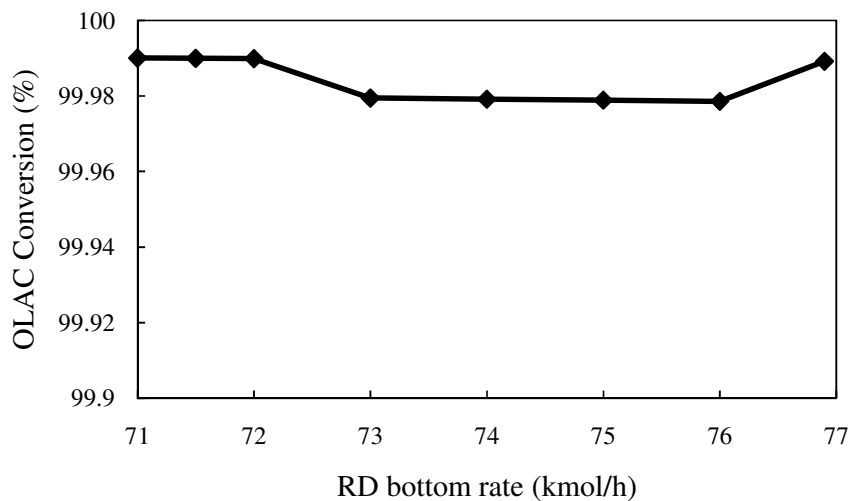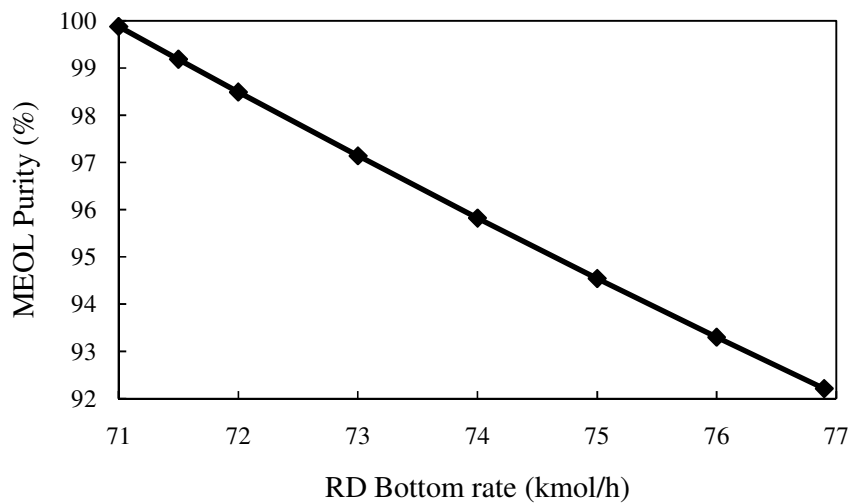**Fig. 4-19** Effect of bottom rate on reboiler duty in reactive distillation column.

4.1.1.4 Effect of reactive stages for CRD process

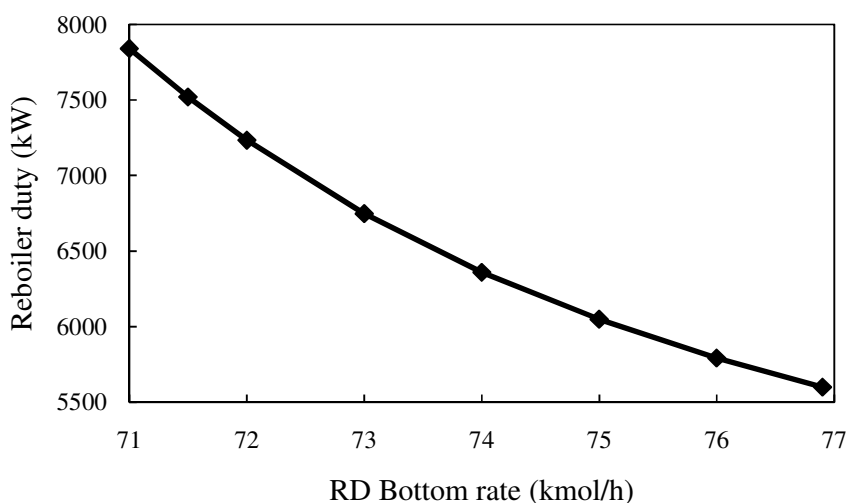The effect of reactive stage on the performance of the reactive distillation at the different stripping stages is demonstrated in term of the conversion of oleic acid and purity of methyl oleate. The acid sulfonic resin is considered as a heterogeneous catalyst for the biodiesel production from palm oil. It is installed on the stage of 3 to 29 where oleic acid and methanol are fed to both ends of reactive section; the reactive trays are minimally varied to 5 stages and specified rectifying section of 1 (stage 2). Height of the reactive section are assumed by reactive stage, which it is implied that decrease in reactive stage with decrease in height of reactive section and amount of solid catalyst. Figs. 4-20 and 4-21 show the simulation results were initially number of reactive stage of 27 at standard condition. It is found that decreasing less reactive stages does not improve the performance of reactive distillation until decreasing less than reactive stages of 12 affecting the decrease in oleic acid conversion and biodiesel purity because provides oleic acid and methanol to have less contracting area, thereby no enhancing the conversion of oleic acid. The separation efficiency is crucial for the success of the process since water has to be removed from the reactive section not only to shift the chemical equilibrium to higher conversions but also to avoid its detrimental sorption effect on reaction kinetics. At the specified reactive stage, there

are no change in conversion of oleic acid and purity of biodiesel product with increasing the stripping stage. Considering the number of reactive stages on the reboiler duty as shown in Fig. 4-22, it can be seen that the decreased reactive stage with increase in reboiler duty. And at the specified reactive stage, increasing the stripping stage causes increase in reboiler duty because the added stripping stage causing heat from reboiler is difficulty reached in reactive section, the external energy is more supplied to system. It has been shown that both separation efficiency of the packing and amount of catalyst offered by packing are important for the success of the process due to better separation efficiency. The number of reactive stages necessary to achieve conversions close to 100% has been determined. The number of non-reactive stages above and below the reactive section is of minor importance for the performance of the overall process. And at the specified reactive stage, increasing the stripping stage causes increase in reboiler duty because the added stage causing heat is reached difficulty in reactive section. Therefore, the number of reactive stages is 14 and no stripping stage due to the highest oleic acid conversion and biodiesel purity and the lowest reboiler duty are obtained.

Fig. 4-20 Effect of reactive stage on conversion of oleic acid in reactive distillation.

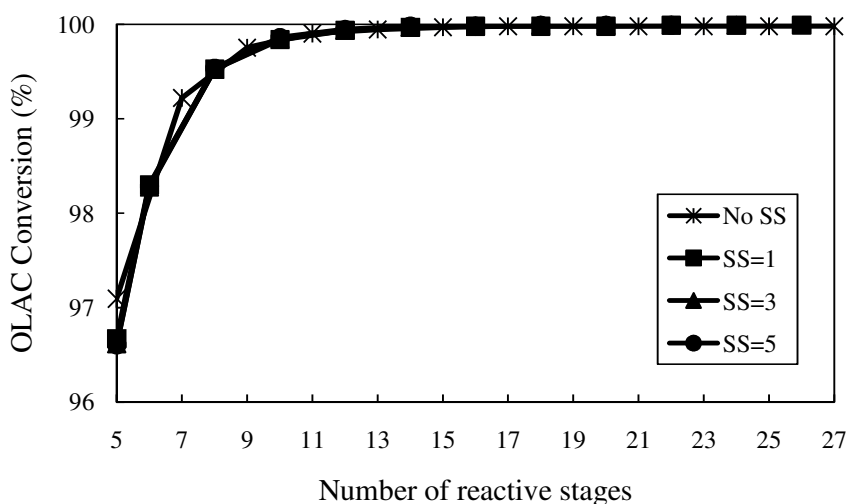**Fig. 4-21** Effect of reactive stages on purity of methyl ester in reactive distillation column.

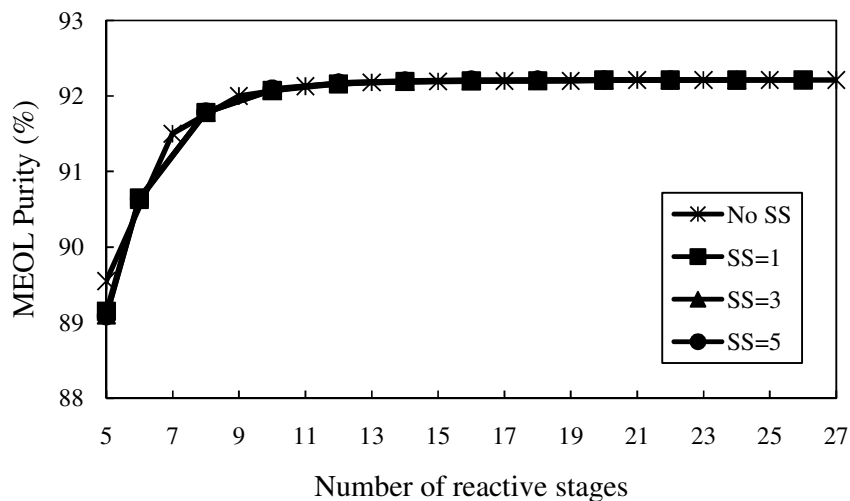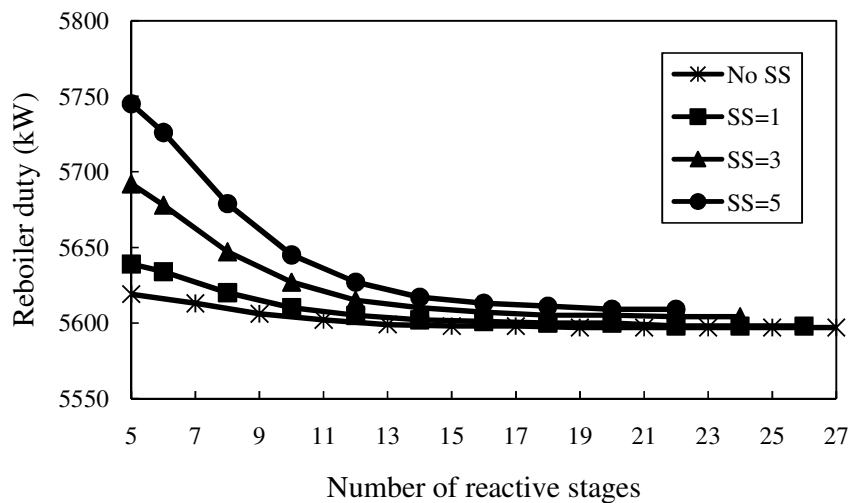**Fig. 4-22** Effect of reactive stages on reboiler duty in reactive distillation column.

4.1.1.5 Effect of feed locations for CRD process

In this study, the location of the two fresh feed streams is an important design parameter. For esterification reaction, the lighter reactant feed is fed on the bottom of the reactive tray. While the heavier reactant feed is fed on the top of the reactive tray. The performance of reactive distillation is investigated in the effect of feed locations as feed stages of oleic acid (heavier reactant) and methanol (lighter reactant) on oleic acid conversion and biodiesel purity as shown in Figs. 4-23 to 4-28. For oleic acid feed, it is fed from the top to bottom trays of the column when specified stage of methanol feed at tray 28 for standard condition. While methanol feed is fed from the bottom to top tray of the column after obtaining the optimum location of oleic acid feed. The simulation results have been shown that change in feed location of oleic acid affects to the performance of reactive distillation that is decrease in oleic acid conversion and biodiesel purity when location of oleic acid feed is changed from top to bottom tray as shown in Figs. 4-23 and 4-24. Considering the reboiler duty with oleic acid feed location in Fig. 4-25, it is shown that the optimum tray of oleic acid feed as tray 2 because the reboiler requires the minimum heat energy. For methanol feed, changing the feed location from bottom to top trays when oleic acid is fed at tray 2 is resulted that the oleic acid conversion and biodiesel purity are decreased as shown in Figs. 4-26 and 4-27. Considering the reboiler duty with methanol feed location as shown in Fig. 2-28, it is demonstrated that feeding methanol from the bottom to the top trays cause increase in reboiler duty because immediately vaporized methanol to the top of column, decreased an amount of methanol in reactive section, and the shorter reaction time between oleic acid and methanol. Changing the feed locations either oleic acid or methanol while one is specified, the contacting area of oleic acid and methanol is reduced affecting to kinetic reaction rate that uncompleted esterification reaction. This is caused the lower conversion and difficult separation of biodiesel product from impurities such as oleic acid and methanol. Thereby, the feed locations of oleic acid and methanol are tray of 2 and 28, respectively. However, the previous parameter of reactive stage has reported the number of reactive stage of 14 and no stripping stage then the reactive distillation column has total stage of 17 (include condenser and reboiler stages. Therefore, the feed locations of oleic acid and

methanol are shifted to follow on column stage where oleic acid and methanol are fed at tray of 2 and 15, respectively.
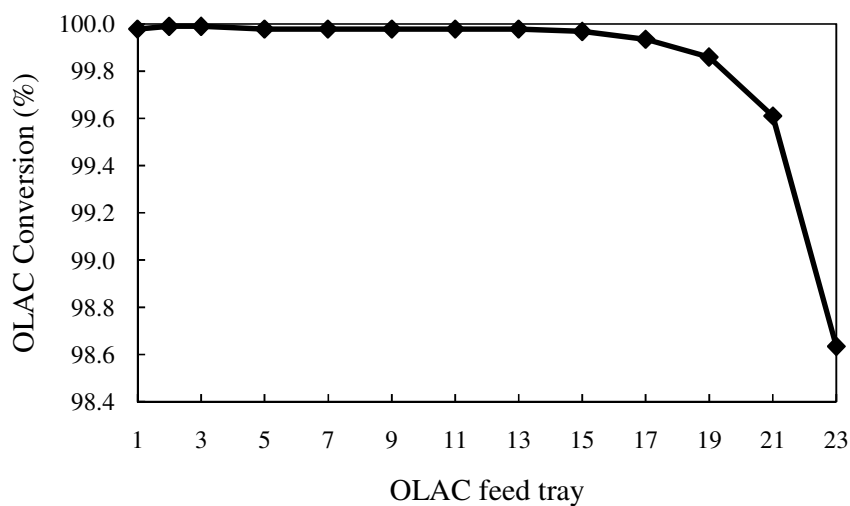
Fig. 4-23 Effect of oleic acid feed tray on conversion of oleic acid in reactive distillation column.
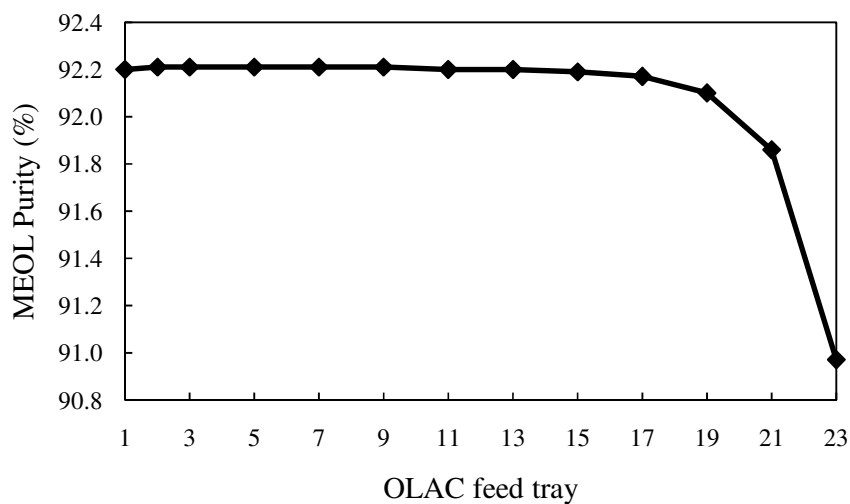
Fig. 4-24 Effect of oleic acid feed tray on purity of methyl ester in reactive distillation column.
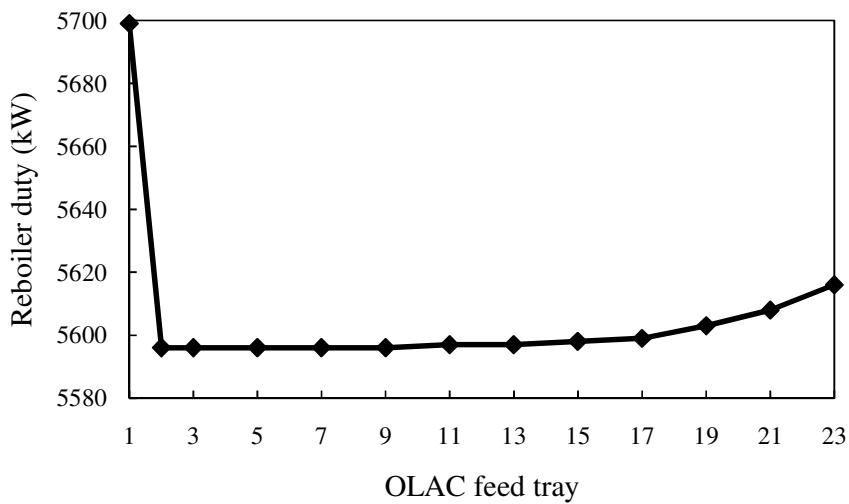
Fig. 4-25 Effect of oleic acid feed tray on reboiler duty in reactive distillation column.
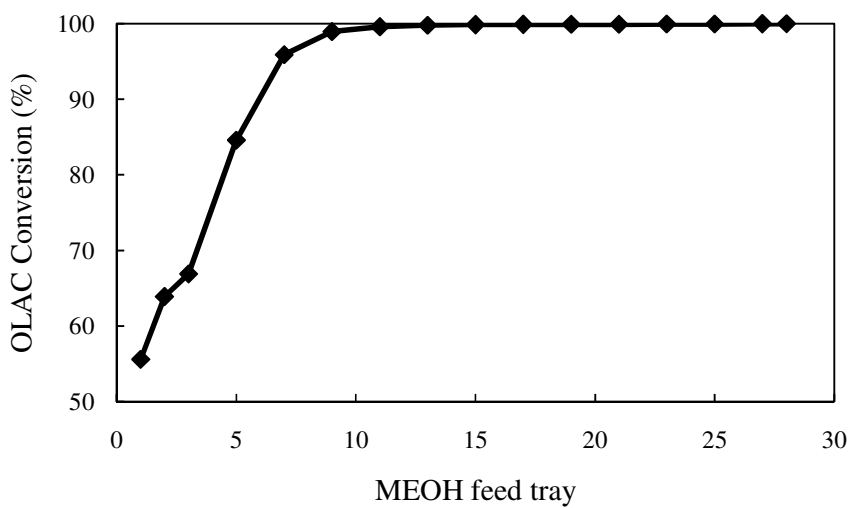
Fig. 4-26 Effect of methanol feed tray on conversion of oleic acid in reactive distillation column.
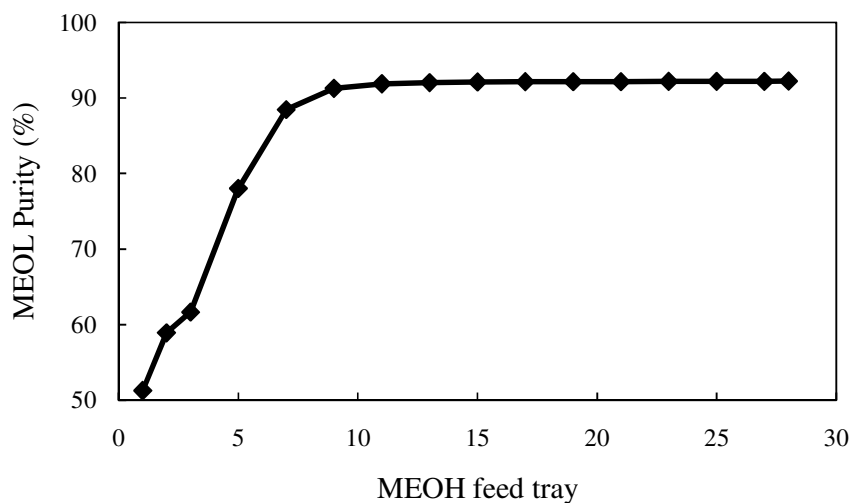
Fig. 4-27 Effect of methanol feed tray on purity of methyl ester in reactive distillation column.
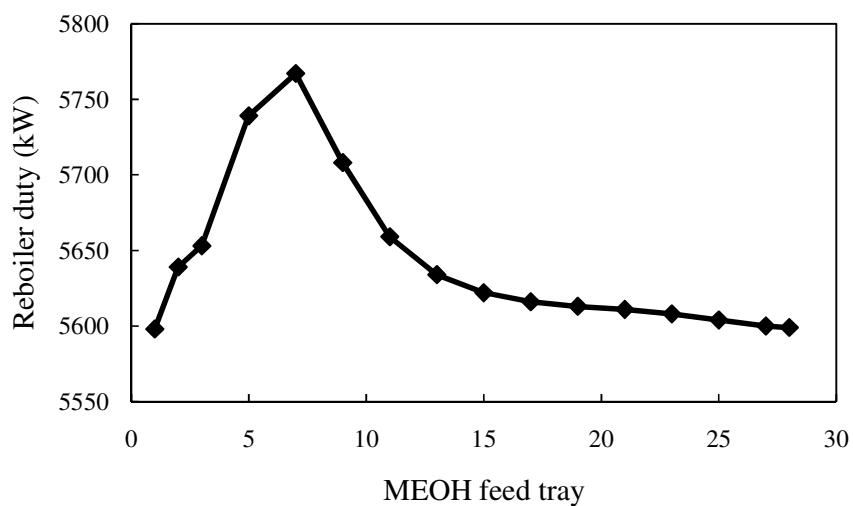
Fig. 4-28 Effect of methanol feed tray on reboiler duty of methyl ester in reactive distillation column.

4.1.1.6 The best conditions for CRD process

In the previous sections, the performance of reactive distillation is analyzed in term of the conversion of oleic acid and purity of biodiesel product. The effect of parameters such as column pressure, feed temperature, bottom rate, reactive stage, and feed locations are investigated. The best conditions for conventional reactive distillation are obtained including the column pressure of 3.5-4 bar, oleic acid feed temperature of 175°C, bottom rate of 71.5 kmol/h, the number of reactive stage of 14 and no stripping stage with the total column stage of 17 (include condenser; stage 0, and reboiler stages), and feed stages of oleic acid and methanol at tray of 2 and 15, respectively. The profiles of temperature and composition in reactive distillation column (T-100) are shown in Fig. 4-29 and 4-30, respectively. It can be seen that in the reactive zone, temperature remains almost constant whereas composition profile indicates that contains higher water concentration which causes liquid-liquid separation leading to solid catalyst deactivation.
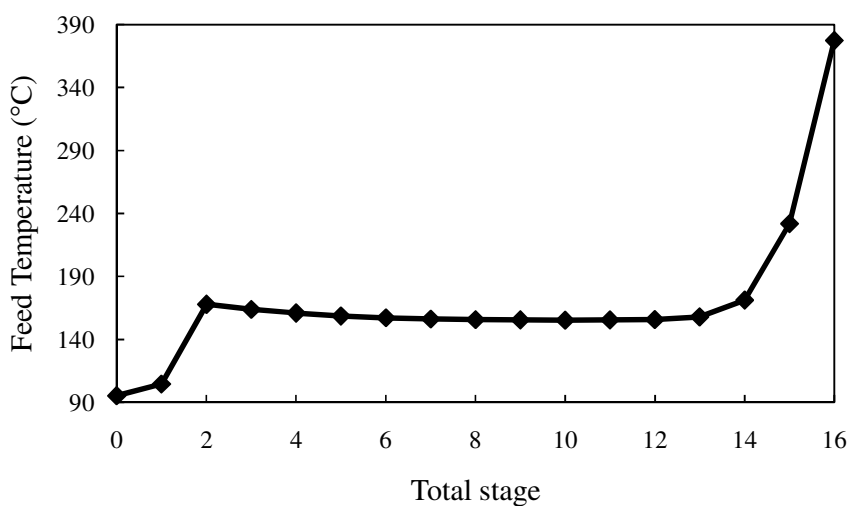
Fig. 4-29 Temperature profile in reactive distillation column for CRD process.
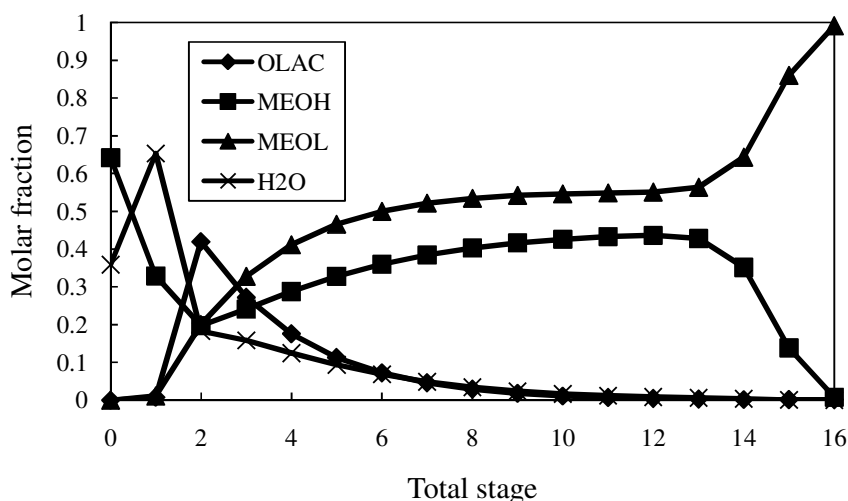
Fig. 4-30 Composition profile in reactive distillation column for CRD process.

4.1.3 Methanol distillation column for CRD process

The distillation column was used to recover the excess or unreacted methanol. From Fig. 4-1 (b), the distillate of reactive distillation column (T-100), the stream MEOH+H2O is fed to stage 9 of methanol separation column (T-101) with molar reflux ratio of 1.55 and distillate rate of 95 kmol/h which the high purity methanol is obtained in distillate while the water in bottom is not purified from methanol impurity. The methanol distillation column can be design from chapter 3 in section 3.4. The finished design has demonstrated that the column is specified by the total trays of 22, feed tray of 10, and reflux ratio of 1.55 with rates of distillate and bottom as 120 and 72.1 kgmol/h, respectively. The molar purities of methanol in distillate and water in bottom are achieved as 97.39% and 98.2%, respectively. The molar purities

of methanol in distillate and water in bottom are achieved as 99.97% and 99.50%, respectively. The temperature and composition profiles of methanol distillation column T-101 are presented in Fig. 4-31 and 4-32, respectively. Fig 4-31 (a) is shown that the column temperature is rather constant in stage 10-18 when considering composition profile in Fig 4-32 (a), it can be seen that the composition of methanol and water are nearly unchanged in such stage. Therefore, the separation tray of claim profiles should be reduced from 22 to 15, the obtained profiles as shown in Fig 4-31

(b) and 4-32 (b) achieving the high purity of methanol and water up to 99%. As well the recovery of methanol is 99.76%.
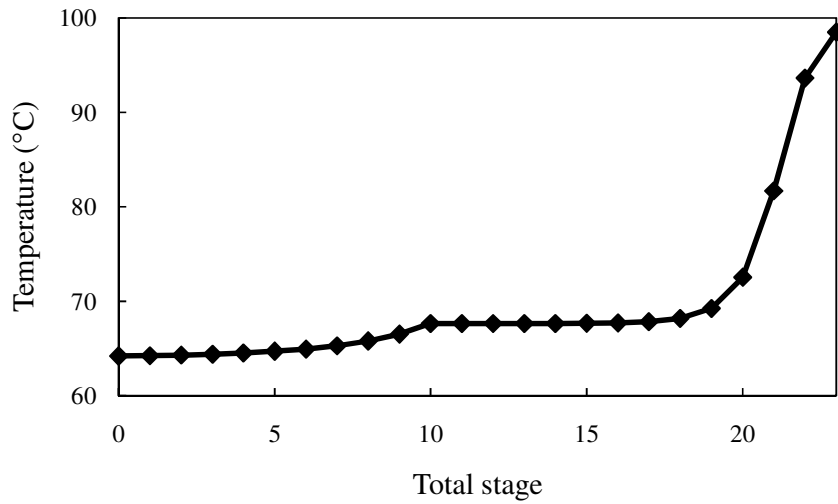
(a)
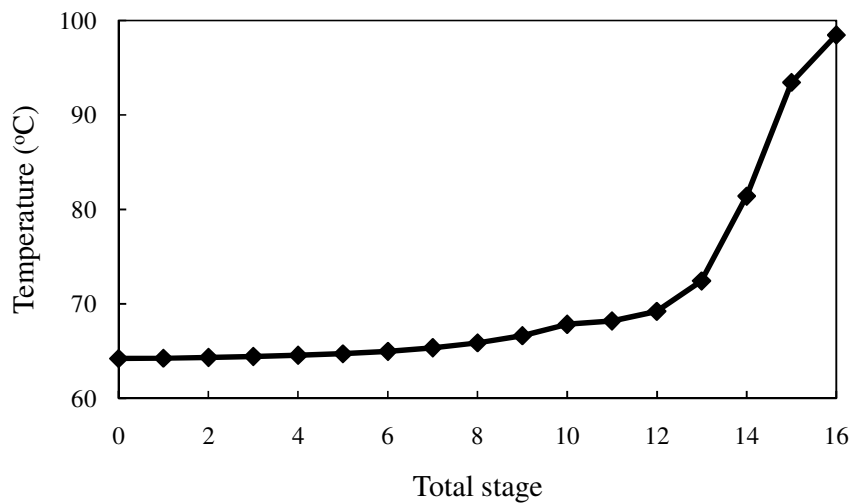
(b)

Fig. 4-31 Temperature profile in methanol distillation column for CRD process; (a) Total stage of 23 and (b) total stages of 16.
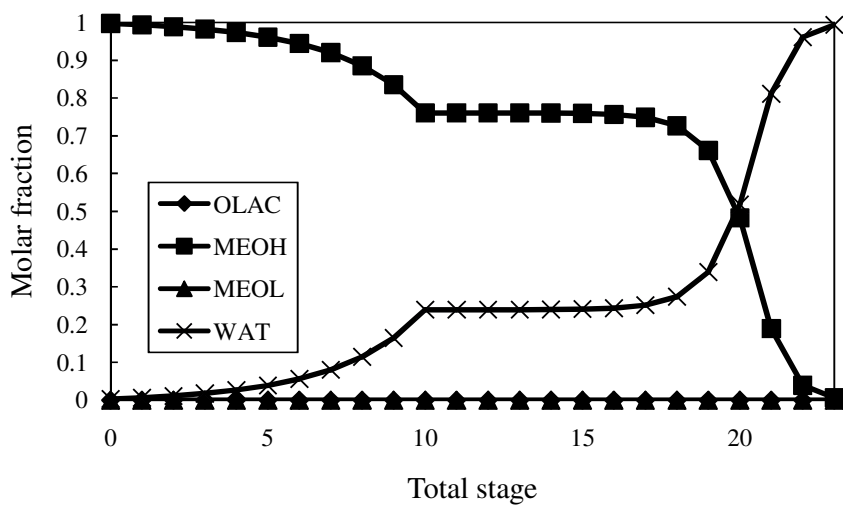
(a)
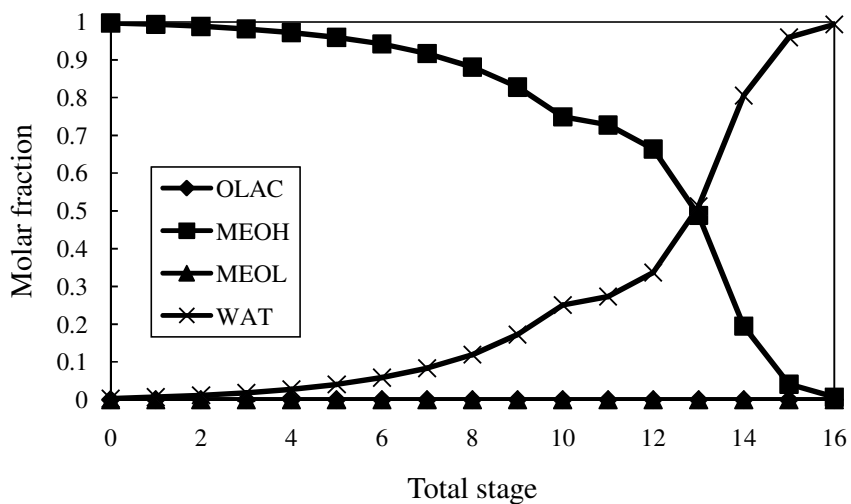
(b)

Fig. 4-32 Composition profile in methanol distillation column for CRD process; (a) Total stage of 23 and (b) total stages of 16.

CHAPTER V

THERMLLY COUPLED REACTIVE DISTILLATION PROCESSES FOR BIODIESEL PRODUCTION

5.1 Simulation of thermally coupled reactive distillation (TCRD) process

The conventional reactive distillation process has been presented in the previous section. Reactive distillation column is one of the unit required highest energy comparing to other units within CRD process for biodiesel production. To reduce the energy demand in reactive distillation processes, additional configurations have been taken to analyze. One of the most studied techniques is the thermal coupling in distillation systems. Generally, there are three well-known configurations of the thermal coupling such as thermally coupled side-stripper, side-rectifier and fully thermal coupling (Petlyuk column). Thermally coupled reactive distillation is possibly alternative for energy saving, it allows interconnecting vapor and liquid stream to achieve heat transfer by direct contact; then these interconnections avoid the need for a reboiler or a condenser or both. In this chapter, the processes of thermally coupled reactive distillation or TCRD for biodiesel production have been presented. The concept of thermal coupling is applied to different configurations for biodiesel production to reduce the energy usage of biodiesel process. Even so the thermal coupling from reactive distillation column and methanol distillation column is been possible as stripped-TCRD and rectified-TCRD by defining as s-TCRD ans r-TCRD, respectively as shown in Fig. 5-1. The TCRD processes include the two major units as reactive distillation (RD) column (production of methyl oleate) and separation (SEP) column (recovery of methanol); both RD column and SEP column are thermally coupled. The standard condition of these processes can be taken reference process in

the previous chapter. Likely, the methanol has been recovered from SEP column to RD column, as well as the preheating of feeds and product via heat exchanger.

(a) Stripped-TCRD (s-TCRD)   (b) Rectified-TCRD (r-TCRD)
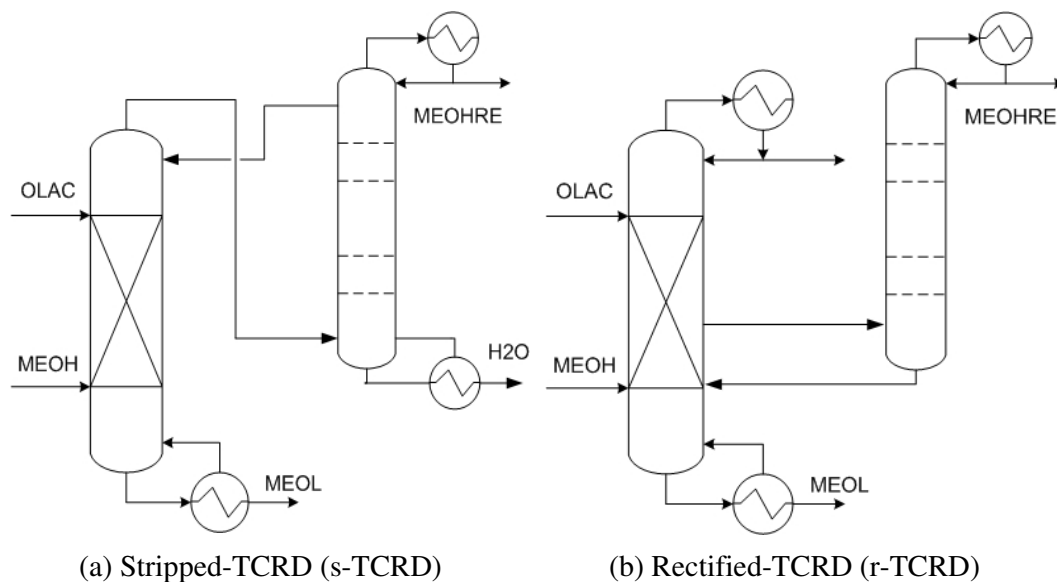
Fig. 5-1 Schematic diagram of thermal coupling for biodiesel production (a) stripped thermal coupling (b) rectified thermal coupling.

5.1.1 Performance of s-TCRD process

The s-TCRD process is configured in side-stripper thermal coupling as shown in Fig. 5-1 (a). Reactive distillation column is side-stripper column; no condenser at the top of column, vapor outlet is condensed by separation column (side-condenser for RD column) whereas stream SIDE in liquid phase is drawn from stage 1 of SEP column T-101 to top of RD column T-100 as shown in the process flowsheet (Fig. 5-2) due to on the stage 1 contains almost the composition of methanol no others contaminating come back to the RD column except methanol for heat transfer. The performances of this process is analyzed on parameters of column pressure, feed temperature, bottom rate, reactive stage, and feed locations in term of the oleic acid conversion and biodiesel purity.
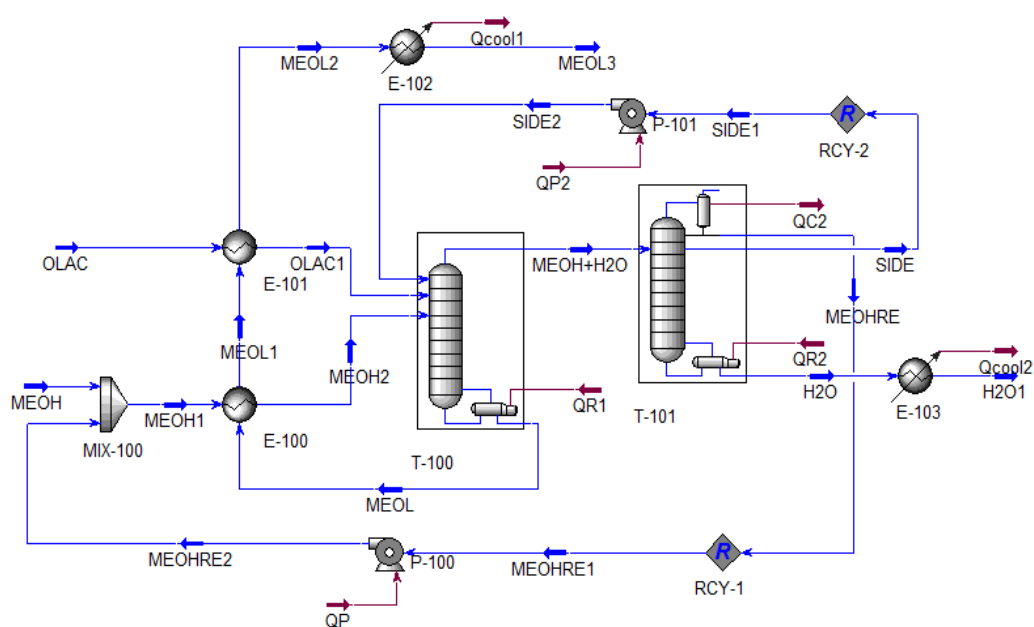
Fig. 5-2 Flowsheet of s-TCRD for biodiesel production.

5.1.1.1 Effect of column pressure for s-TCRD process

The effect of column pressure on the performance of reactive distillation in configuration of s-TCRD is investigated in term of conversion of oleic acid and purity of biodiesel as shown in Figs. 5-3 and 5-4. When the difference of the top and bottom pressure is 0.5 bar and the column pressure at standard condition is 5.5 – 6 bar (bottom pressure of 6 bar). The simulation result has demonstrated that the decrease in bottom pressure results the improved performance of the process, while increase in bottom pressure causes the poor performance of the process. However, decreasing the bottom pressure is lower than 3 bar causes a lot decrease in conversion of oleic acid and purity of biodiesel. Therefore, the column pressure obtaining the highest oleic acid conversion and biodiesel purity is 2.5 – 3 bar. Considering the reboiler duty as shown in Fig. 5-5, it is shown that such column pressure requires the heat energy of 4455 kW. For s-TCRD configuration, increase in column pressure causes the RD column is required the high operating energy, high reboiler duty, and high temperature of reboiler, as well as high column temperature. Such introduces the

reaction rate and purification of biodiesel. However, when the column pressure is increased results the more driving force within column, and the configuration of stripper column of reactive distillation has rapidly vaporized the methanol (lowest boiling point) to the top. The less amount of methanol in reactive section causes the decrease in conversion of oleic acid, and also the more formed water at higher column pressure results the lower purity of biodiesel product. Moreover, the biodiesel product is more than produced in reactive section at the lower column pressure.
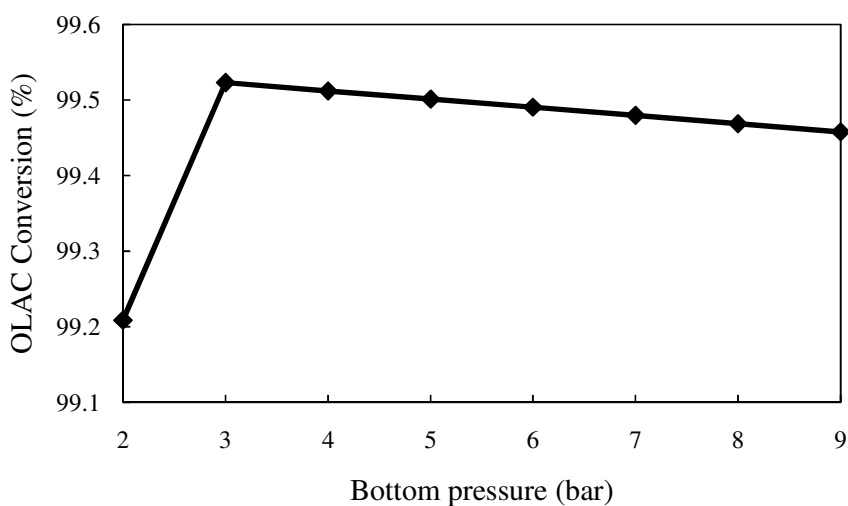
Fig. 5-3 Effect of pressure on conversion of oleic acid in reactive distillation column for s-TCRD process.
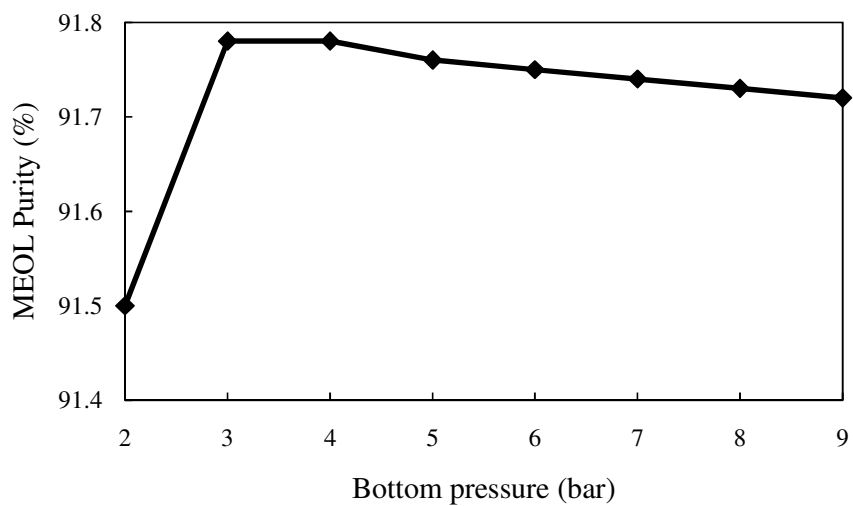
Fig. 5-4 Effect of pressure on purity of methyl ester in reactive distillation column for s-TCRD process.
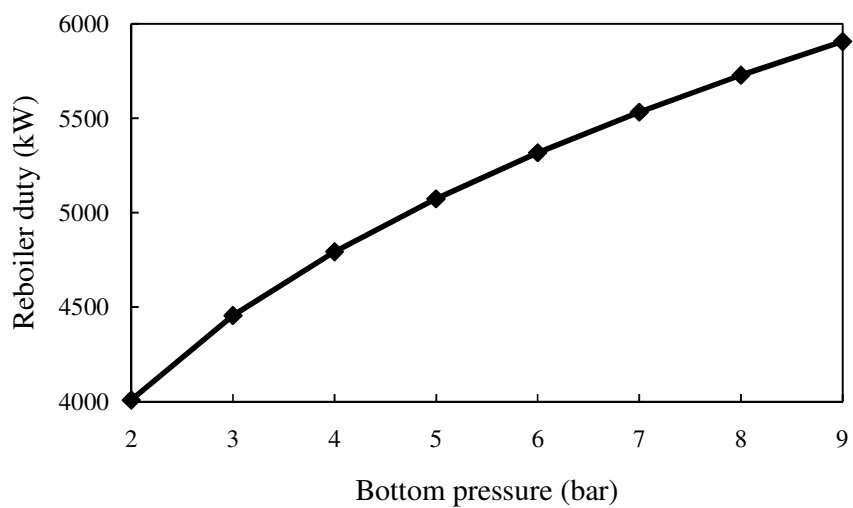
Fig. 5-5 Effect of pressure on reboiler duty in reactive distillation column for s-TCRD process.

5.1.1.2 Effect of feed temperature for s-TCRD process

In this section, the effect of oleic acid feed temperature on the performance of reactive distillation for s-TCRD configuration is studied in term of the conversion of oleic acid and purity of biodiesel product as shown in Figs. 5-6 and 5-7. When the temperature of oleic acid feed is 100°C at the standard condition. It is found that increase in temperature of oleic acid feed results the increased conversion of oleic acid and it is highest at 125°C. Considering the purity of biodiesel, it is shown that the increased temperature of oleic acid feed with increasing the purity of biodiesel where it is highest at 125°C and decreased after the increased temperature up to 125°C. When the reboiler duty is considered as shown in Fig. 5-8 with increase in oleic acid feed temperature results the reboiler duty is decreased. For s-TCRD configuration, increase in temperature of oleic acid affects the higher temperature in reactive section introducing the higher conversion of oleic acid, the more than formed biodiesel product in reactive section. However, the reboiler temperature is not increased while it is slightly decreased causing the decline in purity of biodiesel. Moreover, the methanol is more used to react at higher feed temperature, as well as the less than obtained water in reactive section. Therefore, the temperature of oleic acid feed is 150°C achieving the highest conversion of oleic acid and purity of biodiesel product.

Fig. 5-6 Effect of feed temperature on conversion of oleic acid in reactive distillation column for s-TCRD process.
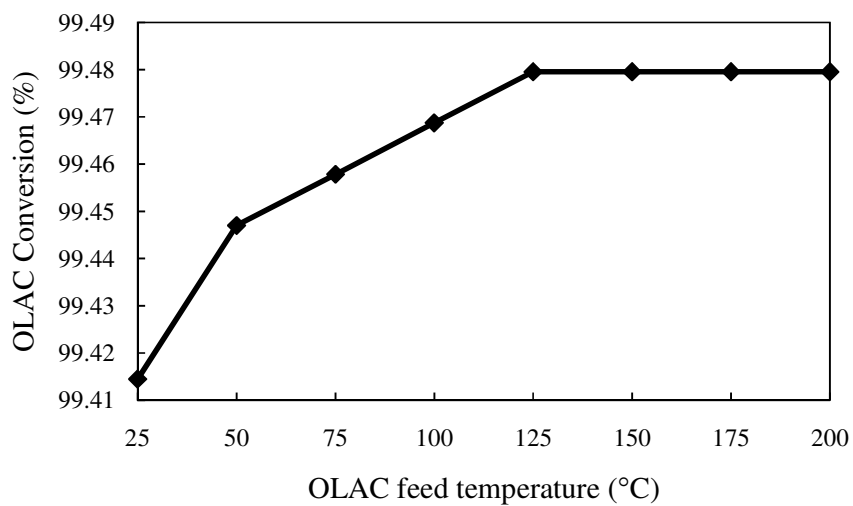

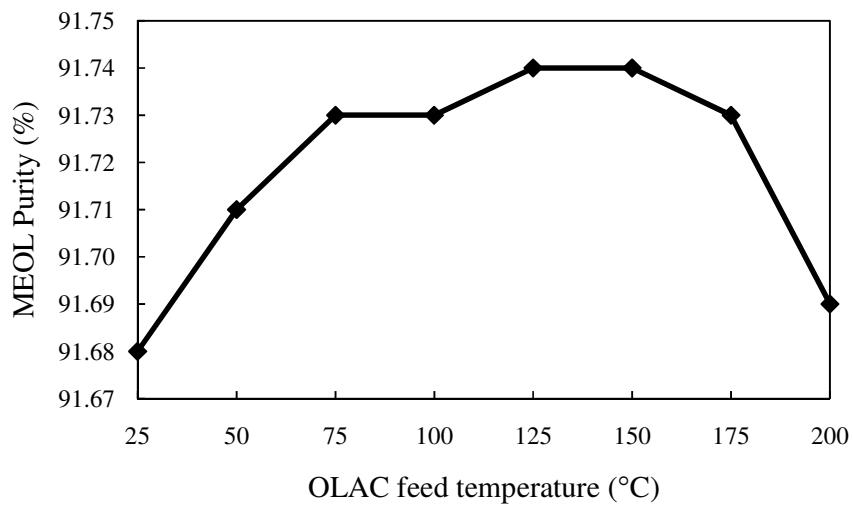**Fig. 5-7** Effect of feed temperature on purity of methyl oleate in reactive distillation column for s-TCRD process.

Fig. 5-8 Effect of feed temperature on reboiler duty in reactive distillation column for s-TCRD process.

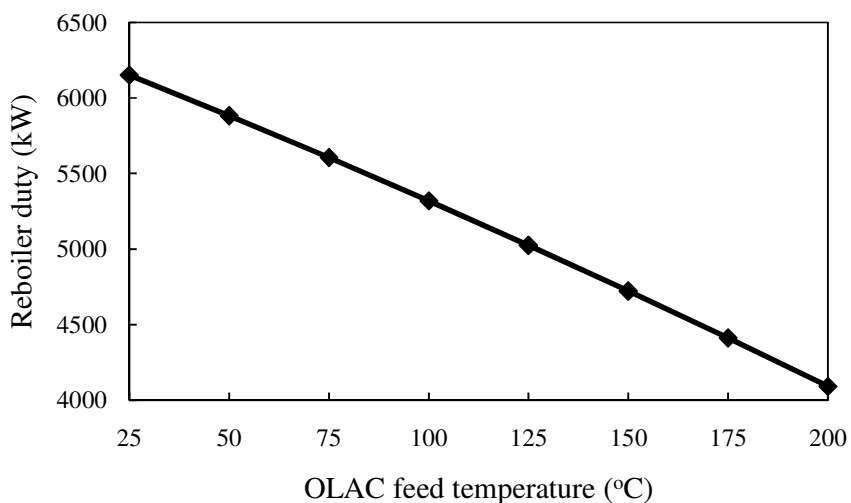### 5.1.1.3 Effect of bottom rate for s-TCRD process

In this study, the effect of the bottom rate in reactive distillation is investigated on performance of reactive distillation in term of the oleic acid conversion and biodiesel purity as shown in Figs. 5-9 and 5-10. The bottom rate in RD column at the standard condition is 76.9 kmol/h. It is shown that decrease in bottom rate results the increased conversion of oleic acid and purity of biodiesel product. Because there is the large amount of methanol in reactive section causes the more shifted chemical equilibrium to product side and there is amount of water as by-product is less formed due to the increased reboiler temperature with higher reboiler duty when lower bottom rate as shown in Fig. 5-11. However, the bottom rate should not too low because even more the increased reboiler duty. Thereby, the bottom rate for s-TCRD process achieving the oleic acid conversion and biodiesel purity up to 99% is 71 kmol/h.
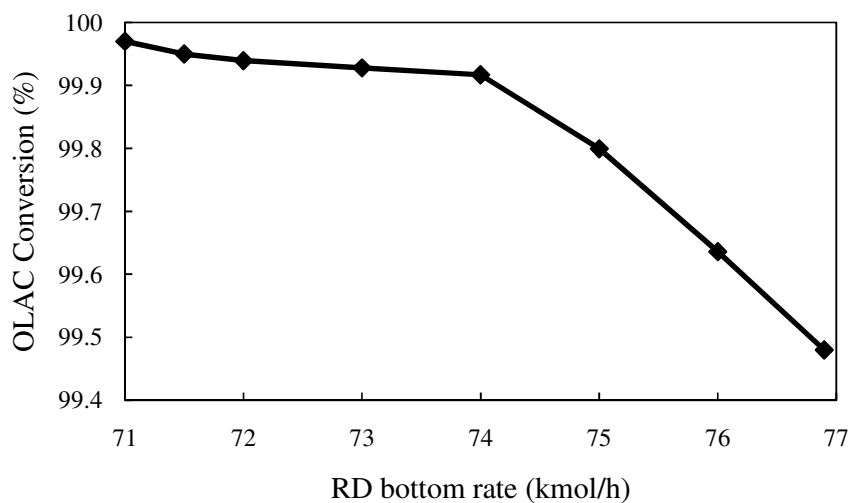
Fig. 5-9 Effect of bottom rate in reactive distillation column on conversion of oleic acid for s-TCRD process.

Fig. 5-10 Effect of bottom rate in reactive distillation column on purity of methyl ester for s-TCRD process.
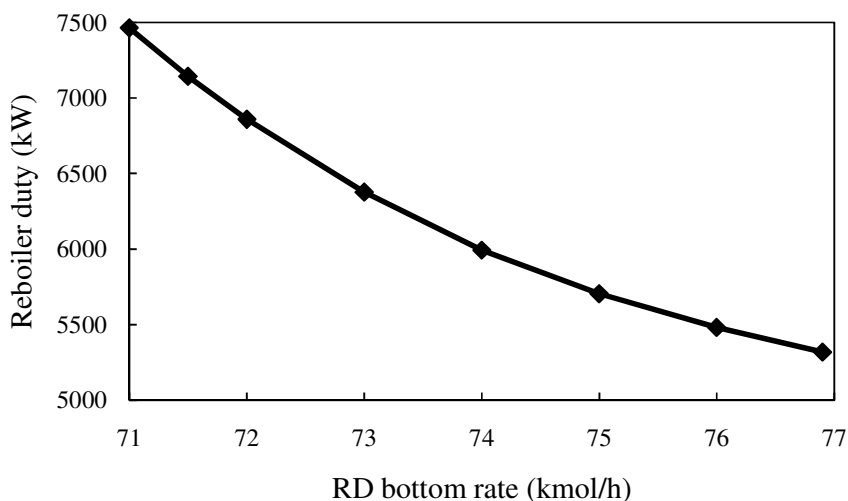
Fig. 5-11 Effect of bottom rate in reactive distillation column on reboiler duty for s-TCRD process.

5.1.1.4 Effect of reactive stages for s-TCRD process

In this study, the effect of reactive stage at the different stripping stages for s-TCRD process on the performance of reactive distillation in term of oleic acid conversion and biodiesel purity is demonstrated as shown in Figs 5-12 and 5-13. The simulation results have presented that the decreased conversion of oleic acid and purity of biodiesel with the decreased reactive stages less than 13 at the different stripping stages because the relatively constant temperature in reactive section results the amount of biodiesel product in reactive zone is generated with constant reaction rate. The amount of methanol is rapidly used in reactive section when the lower reactive stage, the oleic acid feed is incompletely converted to methyl oleate due to the too low contracting stage of reactants. When the specified reactive stage, it is shown that the increased conversion of oleic acid and purity of biodiesel with increasing the stripping stage because there is larger amount of methanol affecting the chemical equilibrium is more shifted to product side, the more converted oleic acid to biodiesel product, as well as obtaining the higher purity of biodiesel due to the less than generated water in reactive section. Considering the reboiler duty with change in reactive stage as shown in Fig. 5-14, it is found that the reboiler duty is relatively

constant on the reactive stage which the highest conversion of oleic acid and purity of biodiesel is obtained. Therefore, in study of this effect has illustrated that the reactive stage is 13 where the stripping stage of 7.
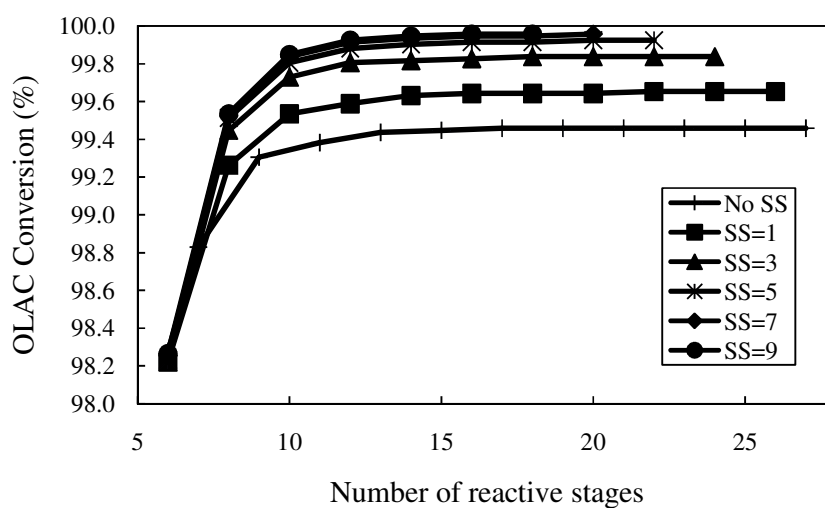
Fig. 5-12 Effect of reactive stages on conversion of oleic acid in reactive distillation column for s-TCRD process.

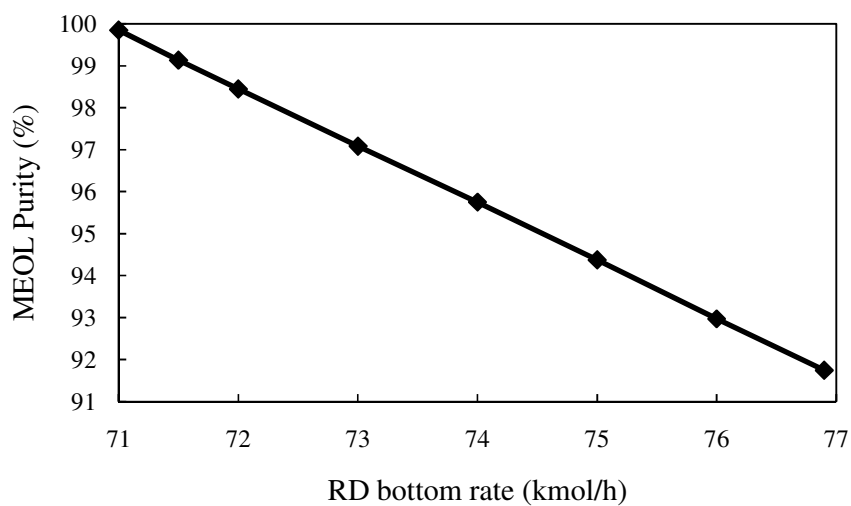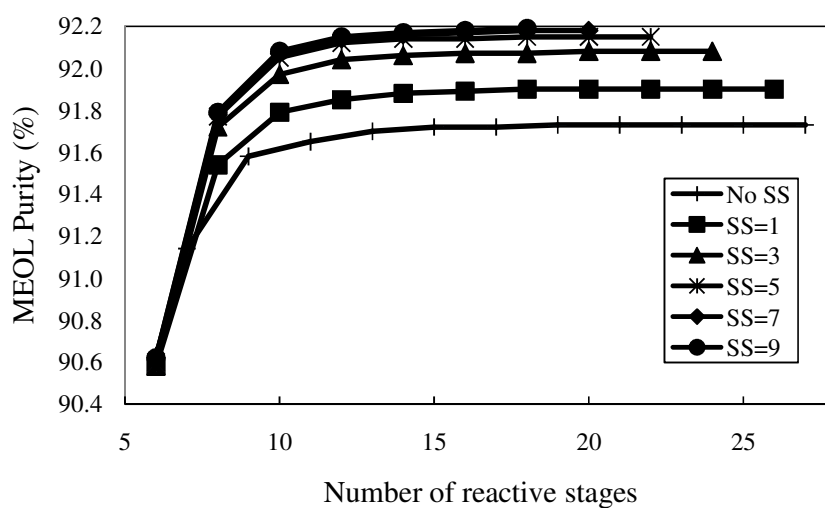**Fig. 5-13** Effect of reactive stages on purity of methyl oleate in reactive distillation column for s-TCRD process.
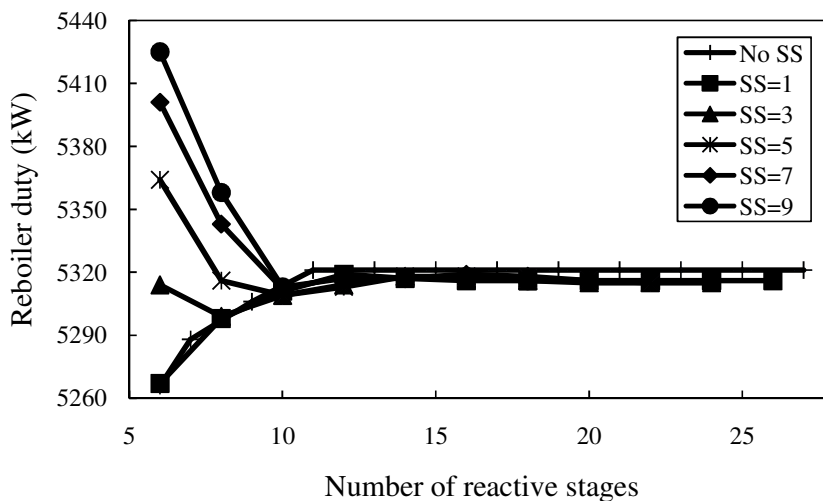
Fig. 5-14 Effect of reactive stages on reboiler duty in reactive distillation column for s-TCRD process.

5.1.1.5 Effect of feed locations for s-TCRD process

In this section, the effect of feed locations of oleic acid and methanol on the performance of reactive distillation in term of the oleic acid conversion and biodiesel purity are investigated as shown in Figs. 5-15 to 5-20. In the previous section, the s-TCRD process is illustrated with the reactive stage is 13 where the stripping stage of 7. Then, the variation of feed locations is carried out after the obtained best conditions from analyzed each effect of parameters and is taken to match in the s-TCRD model. For tray location of oleic acid feed when fixed methanol feed at tray of 14, it is shown that feeding the oleic acid from the top to the bottom trays results the decreases in conversion of oleic acid and purity of biodiesel as shown in Figs. 5-15 and 5-16. Considering the reboiler duty with oleic acid feed tray as shown in Fig. 5-17, it can be determined that the oleic acid feed should be fed on the tray of 2 due to obtaining the maximum conversion of oleic acid and purity of biodiesel while the minimized reboiler duty. Likewise, feeding the methanol from the bottom to the top trays when the fixed oleic acid feed at tray of 2, results the decreases in conversion of oleic acid and purity of biodiesel as shown in Figs. 5-18 and 5-19. And also considering the

reboiler duty with methanol feed tray (shown in Fig. 5-20) can be obtained that the methanol feed should be fed on the tray of 20.

Fig. 5-15 Effect of oleic acid feed tray on conversion of oleic acid in reactive distillation column for s-TCRD process.

Fig. 5-16 Effect of oleic acid feed tray on purity of methyl oleate in reactive distillation column for s-TCRD process.
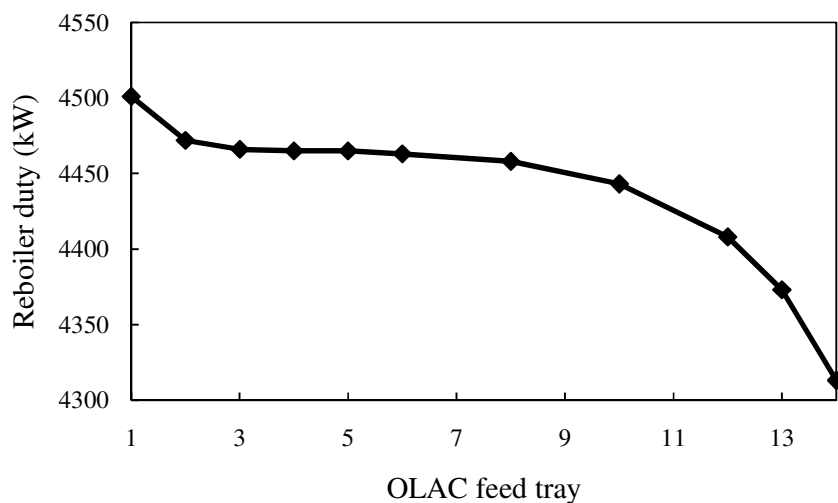
Fig. 5-17 Effect of oleic acid feed tray on reboiler duty in reactive distillation column for s-TCRD process.
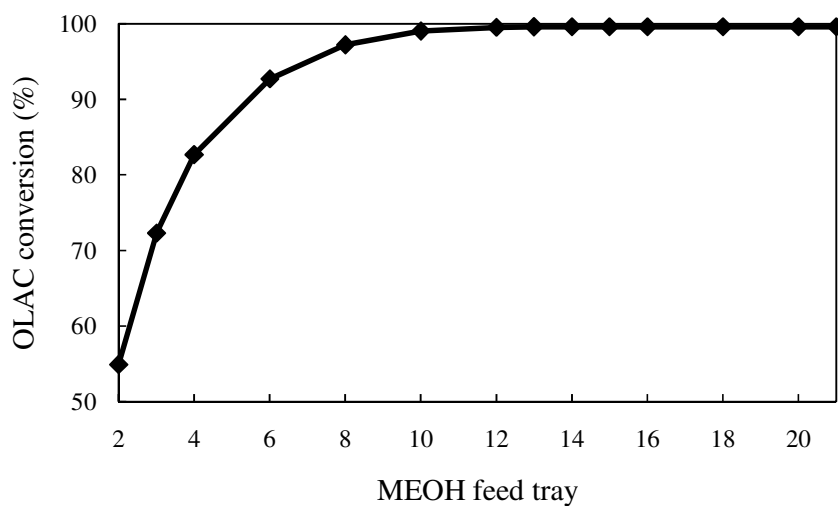
Fig. 5-18 Effect of methanol feed tray on conversion of oleic acid in reactive distillation column for s-TCRD process.
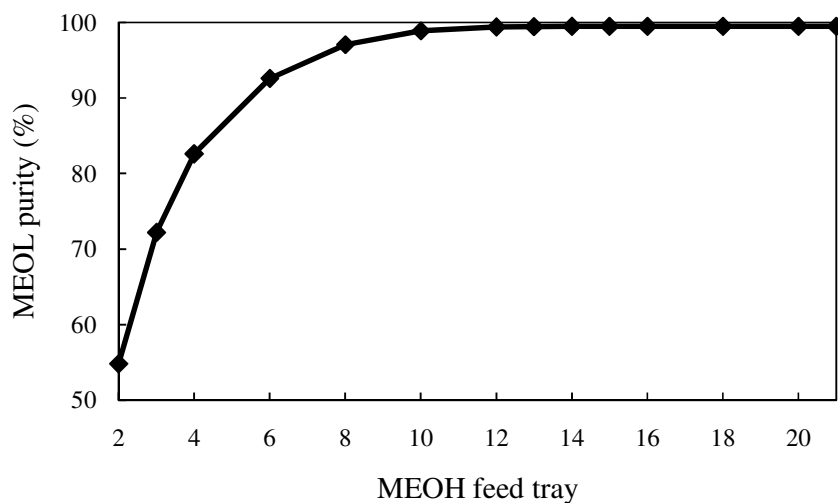
Fig. 5-19 Effect of methanol feed tray on purity of methyl oleate in reactive distillation column for s-TCRD process.
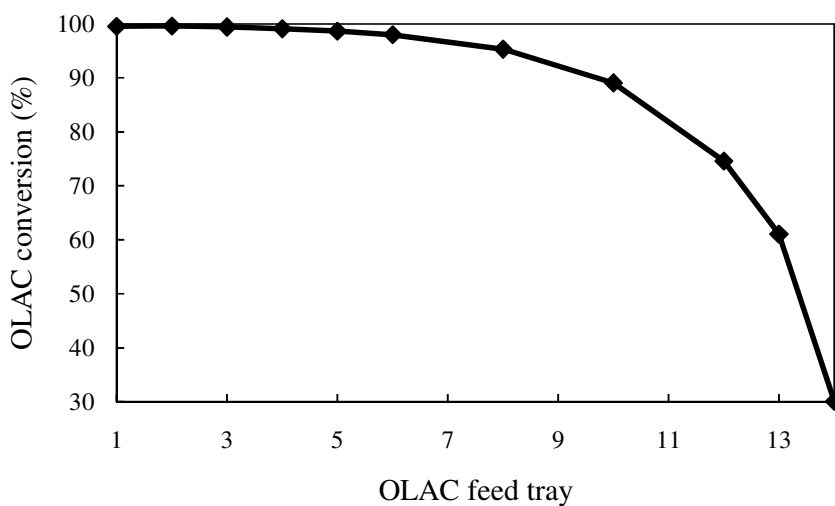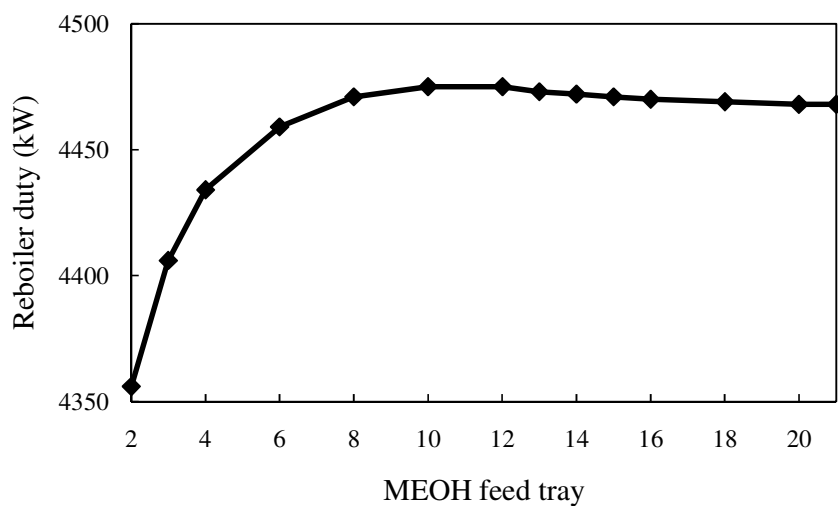

Fig. 5-20 Effect of methanol feed tray on reboiler duty in reactive distillation column for s-TCRD process.
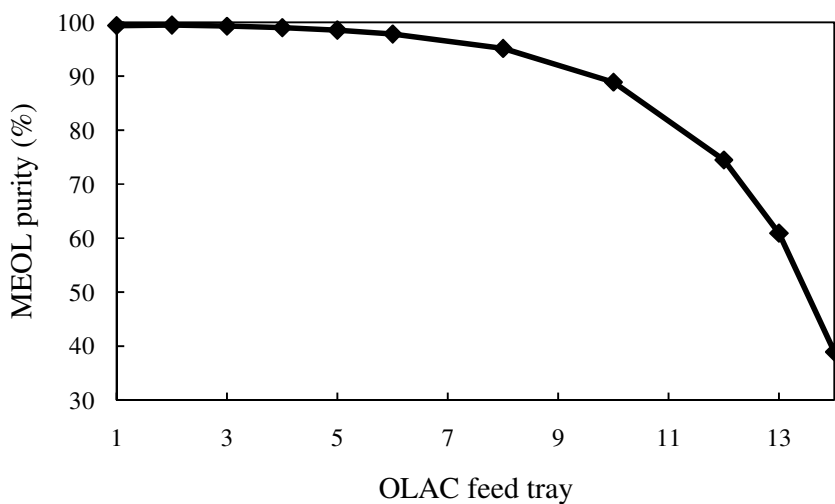
5.1.1.6 The best conditions for s-TCRD *process*

The best conditions for stripper-thermally coupled reactive distillation are obtained including the column pressure of 2.5-3 bar, oleic acid feed temperature of 150°C, bottom rate of 71 kmol/h, the number of reactive stage of 13 and stripping stage of 7 with the total column stage of 22 (include reboiler stage), and feed stages of oleic acid and methanol at tray of 2 and 20, respectively. The temperature and composition profiles in reactive distillation column T-100 are shown in Fig. 5-21 and 5-22, respectively. It can be seen that in the reaction zone, temperature remains almost constant from top to middle stages in reactive zone and increased sharply temperature from middle to bottom stages because in the middle of reactive zone start there is separation of methyl oleate from esterification reaction and unreacted methanol. For this reason, temperature in bottom of reactive zone is been suddenly high along the boiling poing of methyl oleate. Moreover, composition profile indicates that contains higher water concentration which causes liquid-liquid separation leading to solid catalyst deactivation look like the previous process.
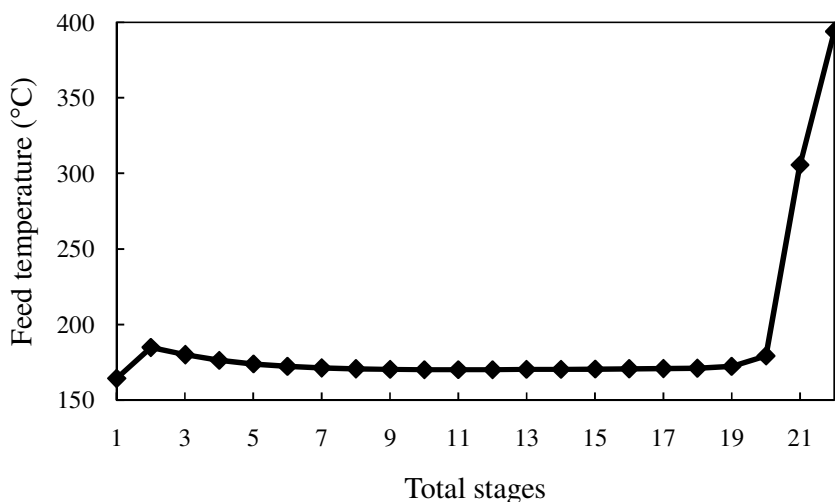
Fig. 5-21 Temperature profile in reactive distillation column for s-TCRD process.
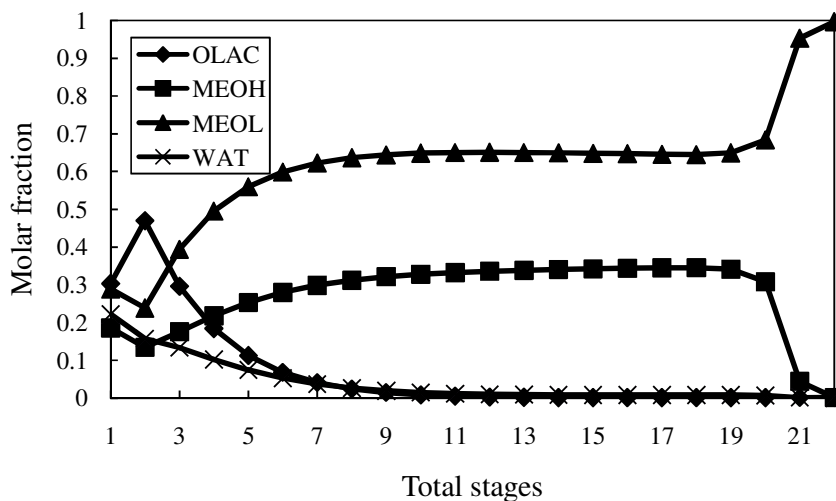
Fig. 5-22 Composition profile in reactive distillation column for s-TCRD process.

5.1.2 Methanol distillation column for s-TCRD process

The distillation column was used to recover the excess or unreacted methanol. Similar in the previous chapter , the distillate of reactive distillation column (T-100), the stream MEOH+H2O is fed to stage 9 of methanol separation column (T-101) with molar reflux ratio of 1.55 and distillate rate of 95 kmol/h which the high purity methanol is obtained in distillate while the water in bottom is not purified from methanol impurity. The methanol distillation column can be design from chapter 3 in section 3.4. For s-TCRD configuration, the methanol distillation column is configured to sidedraw on the stream SIDE in Fig. 5-2, then the coupling of shortcut and rigorous models are used to design the column T-101. The finished design has demonstrated that the column is specified by the total trays of 37 and feed tray of 17 when chosen reflux ratio of 1.55 (standard condition) with rates of distillate and bottom as 97.78 and 74.91 kgmol/h, respectively, and SIDE stream of 7 kmol/h. The molar purities of methanol in distillate and water in bottom are achieved as 99.05% and 94.53%, respectively. The temperature and composition profiles of methanol distillation column T-101 are presented in Fig. 5-23 and 5-24, respectively. Fig 5-23 (a) is shown that the column temperature is rather constant in stage 17-34 when considering composition profile in Fig 5-24 (a), it can be seen that the composition of methanol

and water are nearly unchanged in such stage. Therefore, the separation tray of claim profiles should be reduced from 37 to 16, the obtained profiles as shown in Fig 5-23 (b) and 5-24 (b) while the purity of methanol and water is still not changed. Moreover, the obtained recovery of methanol to the biodiesel process is 89.85% (no including methanol in stream SIDE).
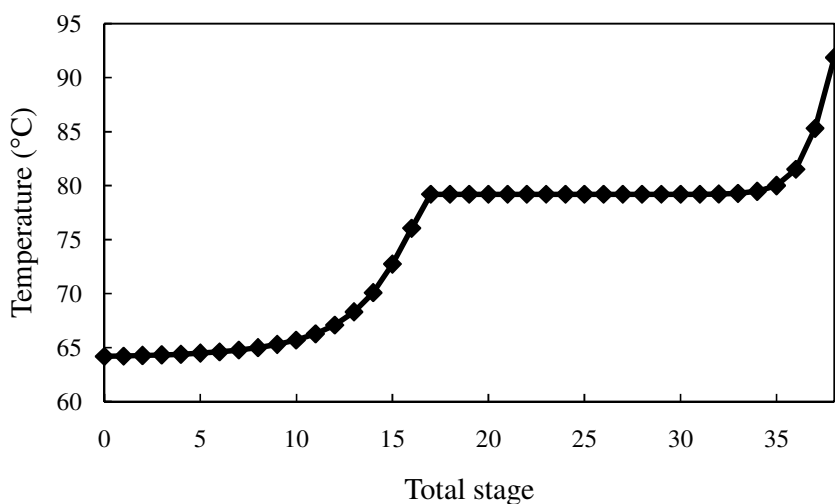
(a)
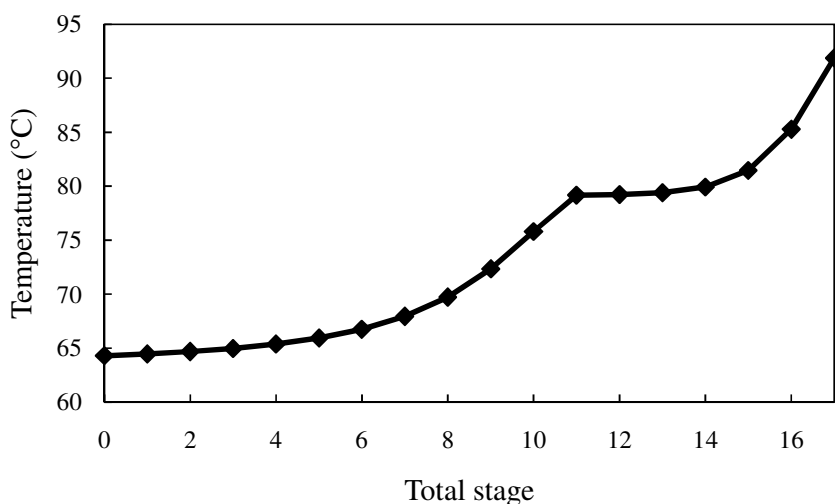
(b)

Fig. 5-23 Temperature profile in methanol distillation column for s-TCRD process; (a) Total stage of 39 and (b) total stages of 18.
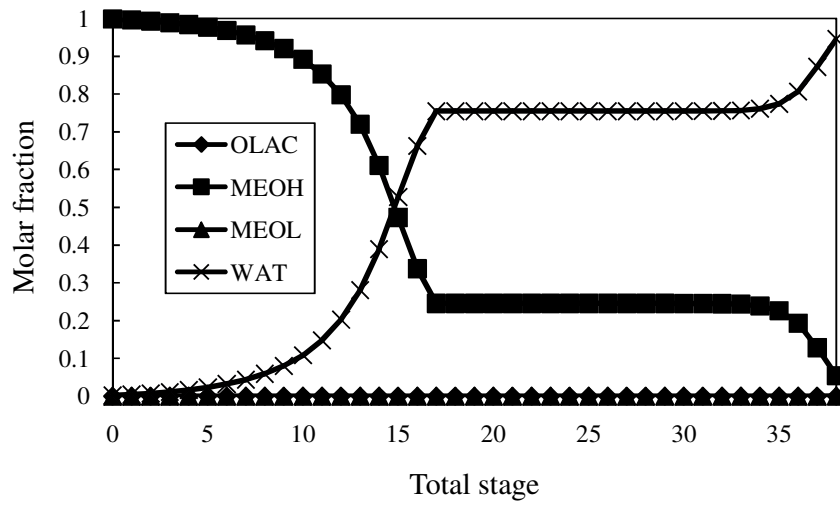
(a)
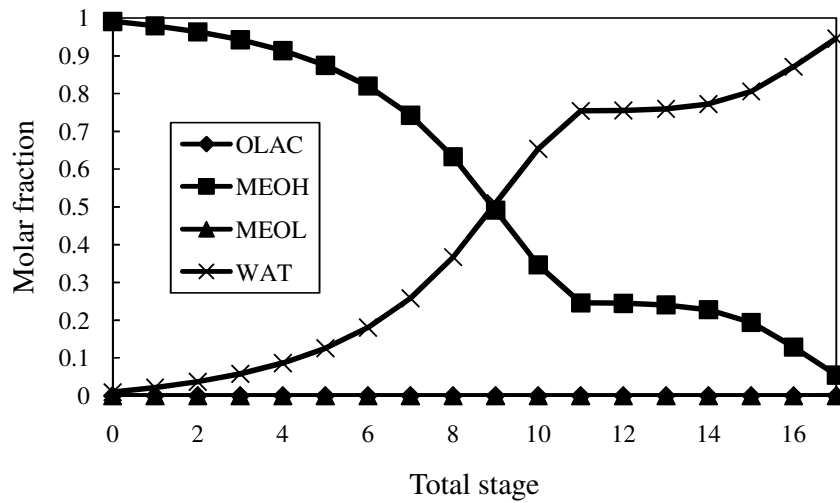
(b)

Fig. 5-24 Composition profile in methanol distillation column for s-TCRD process; (a) Total stage of 39 and (b) total stages of 18.

5.1.3 Performance of r-TCRD process

The r-TCRD process is configured in side-rectifier thermal coupling as shown in Fig. 5-1 (b). Methanol distillation column is rectifier column; no reboiler at the bottom of column. Both RD (T-100) and SEP (T-101) columns are thermally coupled; the vapor from RD column supplies the heat energy to the bottom of SEP column while the liquid from the bottom of the SEP column is transfer to the RD column. It can be performed using HYSYS as shown in process flowsheet (Fig. 5-25). The performances of this process is analyzed on parameters of column pressure, feed temperature, bottom rate, reactive stage, and feed locations in term of the oleic acid conversion and biodiesel purity. Because of the interlinking stages between the RD column and the SEP column are unknown. Then the effect of interlinking stages is additional analyzed.
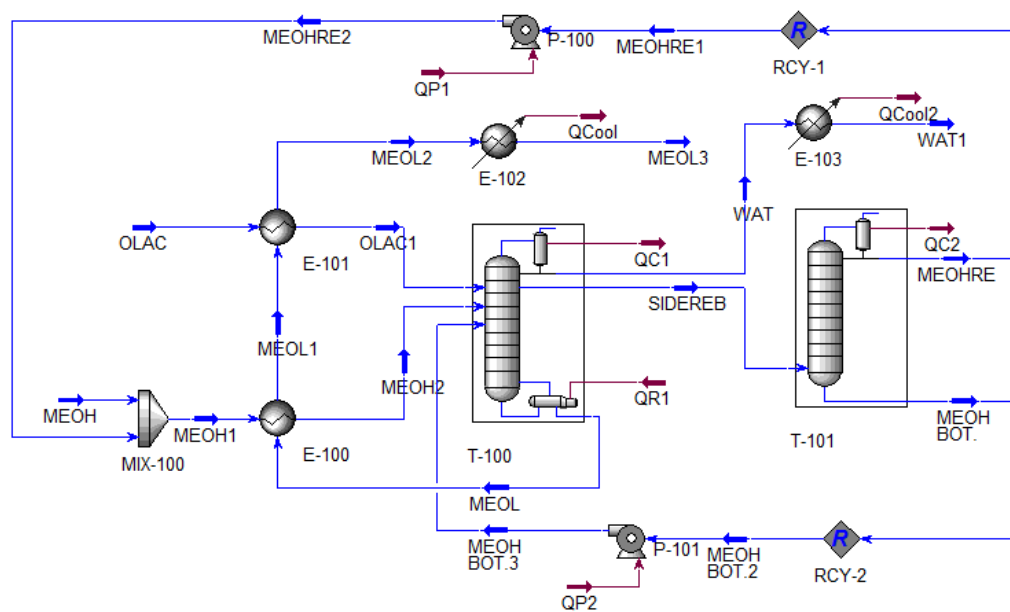
Fig. 5-25 Flowsheet of r-TCRD for biodiesel production.

5.1.2.1 Effect of interlinking stage for r-TCRD process

The interlinking stage is determined because of the vapor leaved RD stage to SEP column and liquid entered RD stage from SEP column need to known. In principle, when the vapor is withdrawn on stage n then the liquid is reached on stage n-1 of the RD column. The interlinking stage of RD column is varied from the bottom to top stage in the reactive zone, for example, RD stages of vapor outlet 19 (n) so the liquid inlet 18 (n-1). The performance of process is analyzed as shown in Fig. 5-26 and 5-27. The simulation results is demonstrated that the interconnecting stage should not be carried out at the top of the RD column causing the unimproved the conversion of oleic acid and purity of methyl oleate because in the top section of reactive zone is transition of the esterification reaction converted oleic acid to methyl oleate that incomplete reaction with withdrawn and entered reactants all the time. Considering on reboiler duty with varied interlinking stage as shown in Fig. 5-28, it be seen that withdrawing the stream SIDEREB from RD column at top of the reactive section results the high reboiler duty (i.e. reactive trays of 2). To minimize the reboiler duty, the optimal interlinking stage of 27 and 28 or bottom of reactive section should be chosen for liquid inlet and vapor outlet in RD column, respectively. Although at tray stage of 6 is seen that the lowest reboiler duty but it is not chosen, since the above reason about reactive interval.
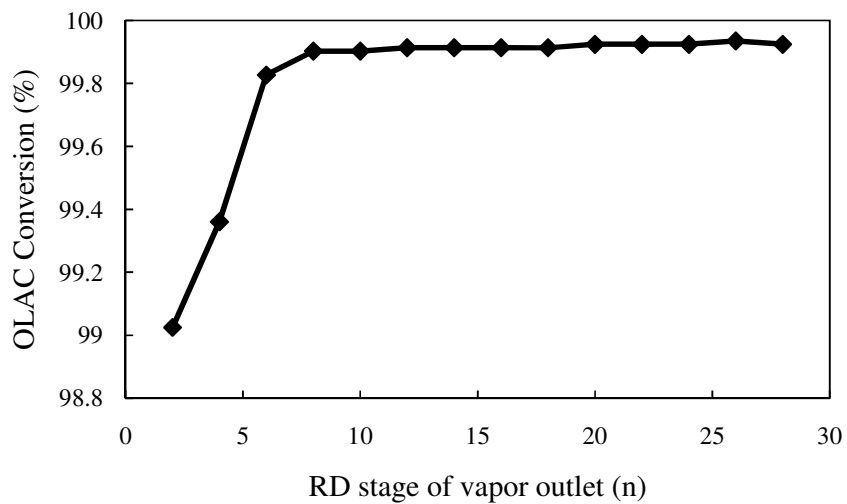
Fig. 5-26 Effect of interlinking stage on conversion of oleic acid in reactive distillation column for r-TCRD process.
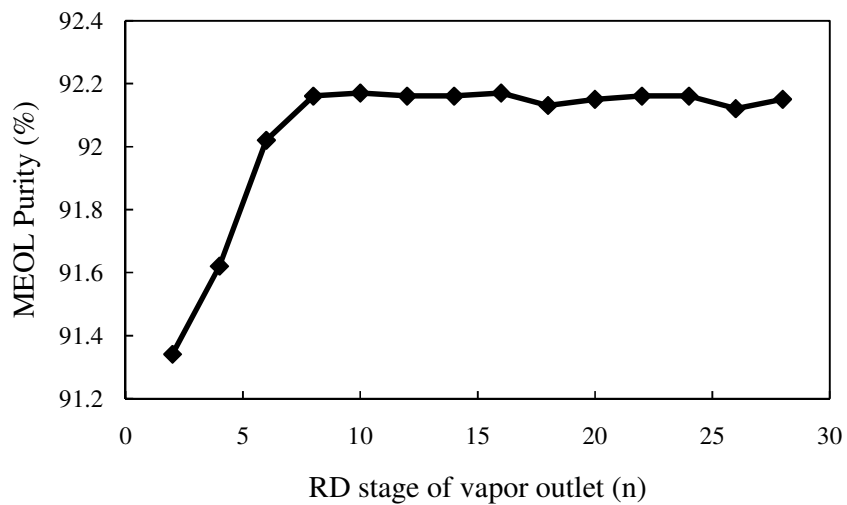
Fig. 5-27 Effect of interlinking stage on purity of methyl oleate in reactive distillation column for r-TCRD process.
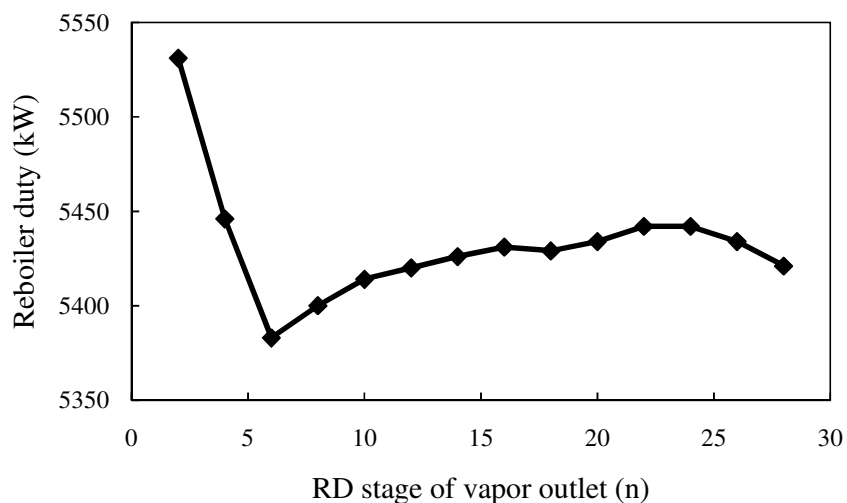
Fig. 5-28 Effect of interlinking stage on reboiler duty in reactive distillation column for r-TCRD process.

5.1.2.2 Effect of column pressure for r-TCRD process

In this section, the effect of column pressure on the performance of reactive distillation for r-TCRD configuration is studied in term of oleic acid conversion and biodiesel purity as shown in 5-29 and 5-30. The simulation results are demonstrated that the increased column pressure with increasing the conversion of oleic acid and purity of biodiesel from 2 to 4 bar, and a decrease of more than 4 bar. An increase in the column pressure results the higher temperature within reactive section and reboiler. However, at the too low column pressure (< 3 bar) affects the slowly reaction rate of oleic acid and methanol while the amount of methanol in reactive zone is rapidly decreased, and also the higher water fraction. At the too high column pressure (> 4 bar), the oleic acid is quickly used to react with methanol causing less than the generated biodiesel product while no change of water fraction. Therefore, the column pressure obtaining the maximum conversion of oleic acid and purity of biodiesel is 3.5 – 4 bar where the considered reboiler duty of 4807 kW as shown in Fig. 5-31.
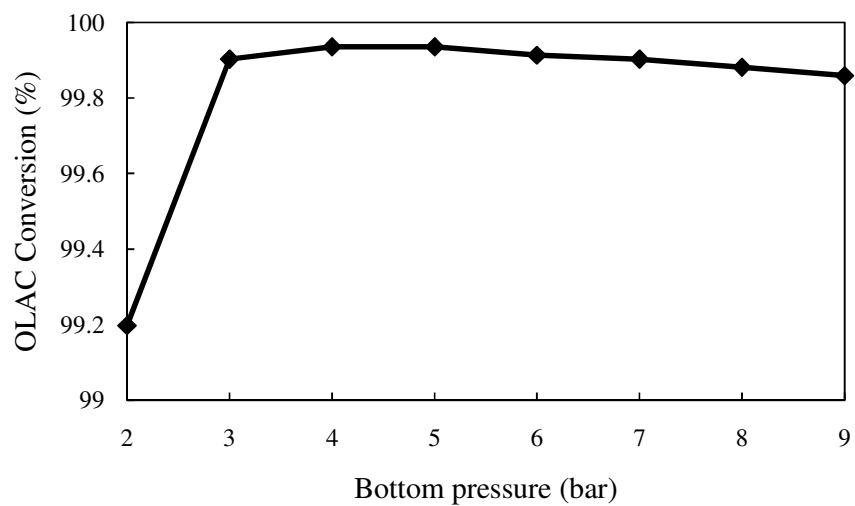
Fig. 5-29 Effect of pressure on conversion of oleic acid in reactive distillation column for r-TCRD process.

Fig. 5-30 Effect of pressure on purity of methyl oleate in reactive distillation column for r-TCRD process.

Fig. 5-31 Effect of pressure on reboiler duty in reactive distillation column for r-TCRD process.

5.1.2.3 Effect of feed temperature for r-TCRD process

The effect of oleic acid feed temperature on the performance of reactive distillation in term of oleic acid conversion and biodiesel purity for the r-TCRD configuration is investigated as shown in Figs. 5-32 and 5-33. It can be seen that the increased temperature of oleic acid feed with increasing conversion of oleic acid and purity of biodiesel because more than the generated biodiesel product and less than the formed water (by-product) in reactive section, and exactly lower reboiler duty (Fig. 5-34). Moreover, withdrawing of the stream SIDEREB (including methanol and methyl oleate components) from stage of 28 to transfer heat to SEP column (T-101) results the more purified methyl oleate component to the RD column. Thereby, the temperature of oleic acid feed obtaining the maximum conversion of oleic acid and purity of biodiesel is 175°C.

Fig. 5-32 Effect of feed temperature on conversion of oleic acid in reactive distillation column for r-TCRD process.

Fig. 5-33 Effect of feed temperature in reactive distillation column on purity of methyl oleate for r-TCRD process.

Fig. 5-34 Effect of feed temperature on reboiler duty in reactive distillation column for r-TCRD process.

5.1.2.4 Effect of bottom rate for r-TCRD process

The effect of the bottom rate in reactive distillation is investigated on performance of reactive distillation in term of the oleic acid conversion and biodiesel purity as shown in Figs. 5-35 and 5-36. Likewise, the bottom rate in RD column at the standard condition is 76.9 kmol/h. It is shown that decrease in bottom rate results the increased conversion of oleic acid and purity of biodiesel product with the similar reasons in the previous section. Therefore, the bottom rate for r-TCRD process achieving the oleic acid conversion and biodiesel purity up to 99% is 71.5 kmol/h. Considering the reboiler duty with decreasing the bottom rate as Fig. 5-37, it is shown that the reboiler is required the very high energy supply to achieve in the conversion and purity.

Fig. 5-35 Effect of bottom rate on conversion of oleic acid in reactive distillation column for r-TCRD process.

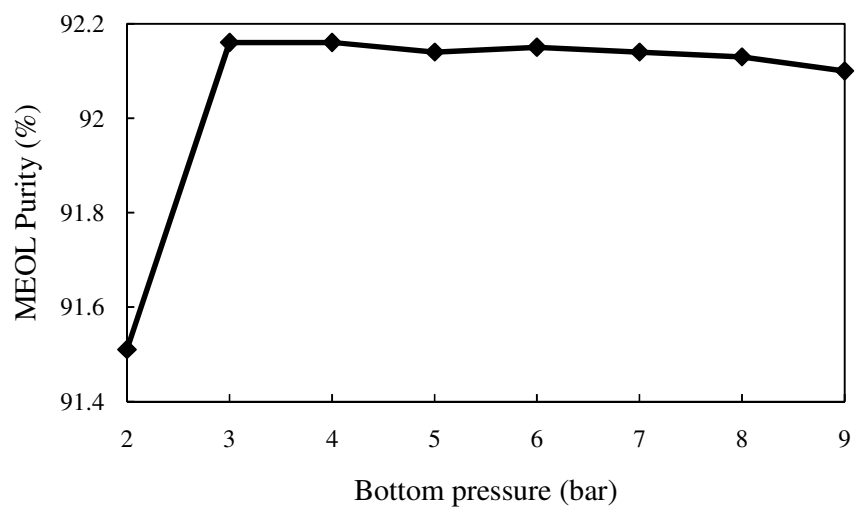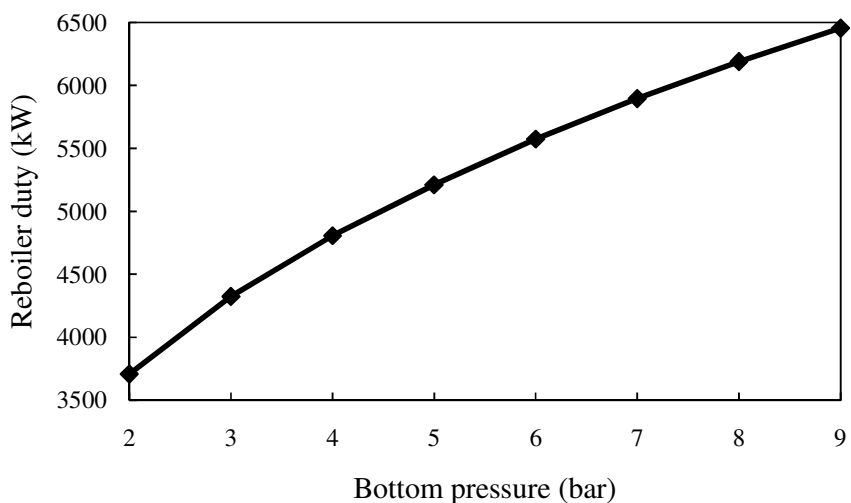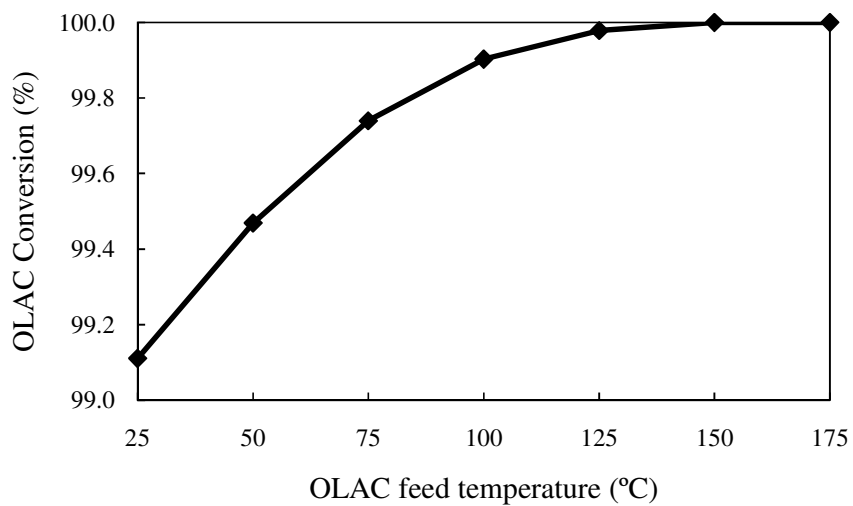**Fig. 5-36** Effect of bottom rate on purity of methyl oleate in reactive distillation column for r-TCRD process.
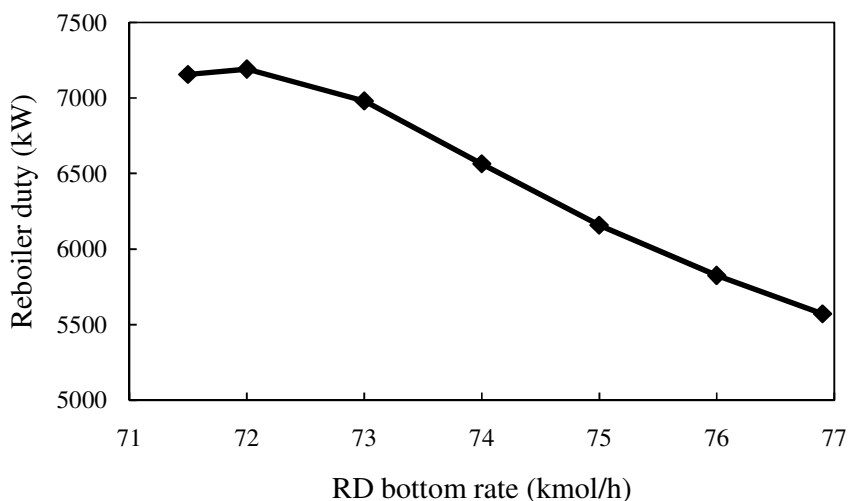
Fig. 5-37 Effect of bottom rate on reboiler duty in reactive distillation column for r-TCRD process.

5.1.2.5 Effect of reactive stage for r-TCRD process

In this study, the effect of reactive stage at the different stripping stages for r-TCRD process on the performance of reactive distillation in term of oleic acid conversion and biodiesel purity is investigated as shown in Figs. 5-38 and 5-39. It is demonstrated that the decreased conversion of oleic acid and purity of biodiesel with the decreased reactive stages less than 18 at the different stripping stages because the relatively constant temperature in reactive section results the amount of biodiesel product in reactive zone is generated with constant reaction rate. When the specified reactive stage, it is shown that increase in the stripping stage no affecting to improvement of system performance. However, the reboiler duty is increased as shown in Fig. 5-40, because heat from reboiler is difficulty reached in reactive zone, the external energy is more supplied to system. Therefore, in study of this effect has illustrated that the reactive stage is 18 where no stripping stage.

Fig. 5-38 Effect of reactive stage on conversion of oleic acid in reactive distillation column for r-TCRD process.

Fig. 5-39 Effect of reactive stage on purity of methyl oleate in reactive distillation column for r-TCRD process.
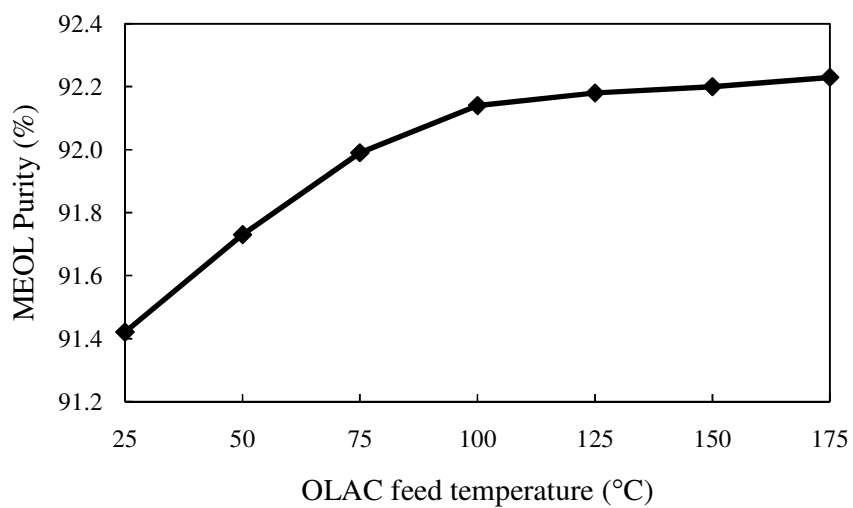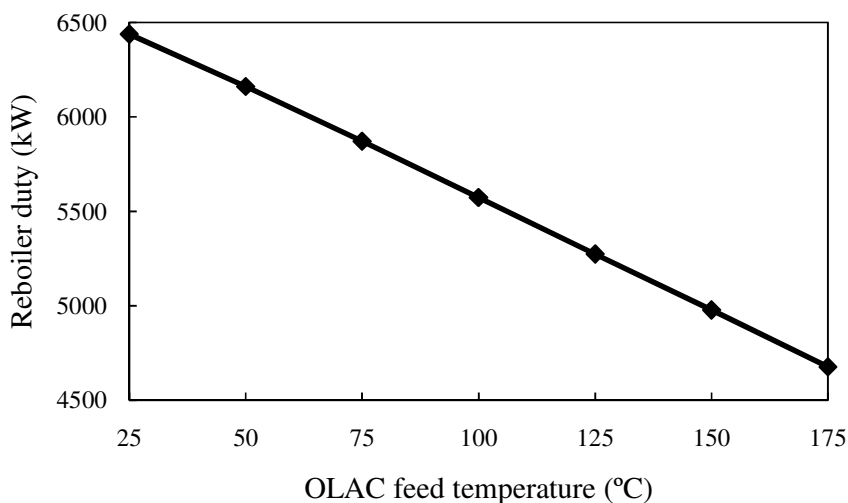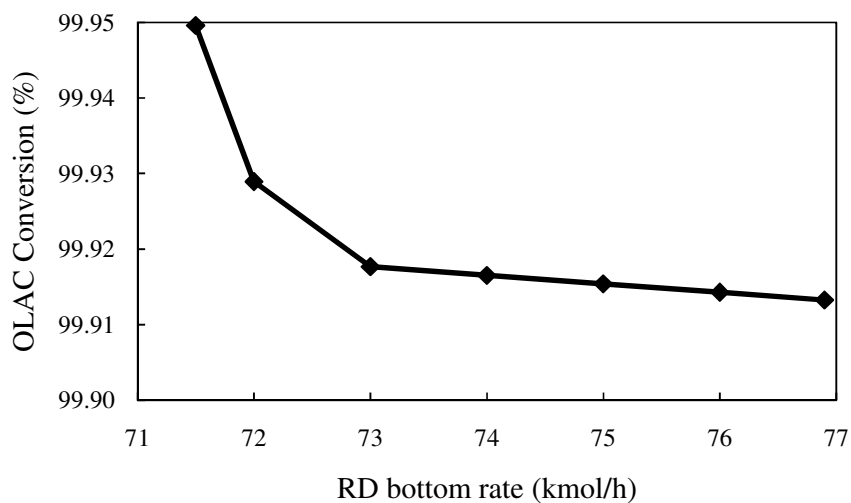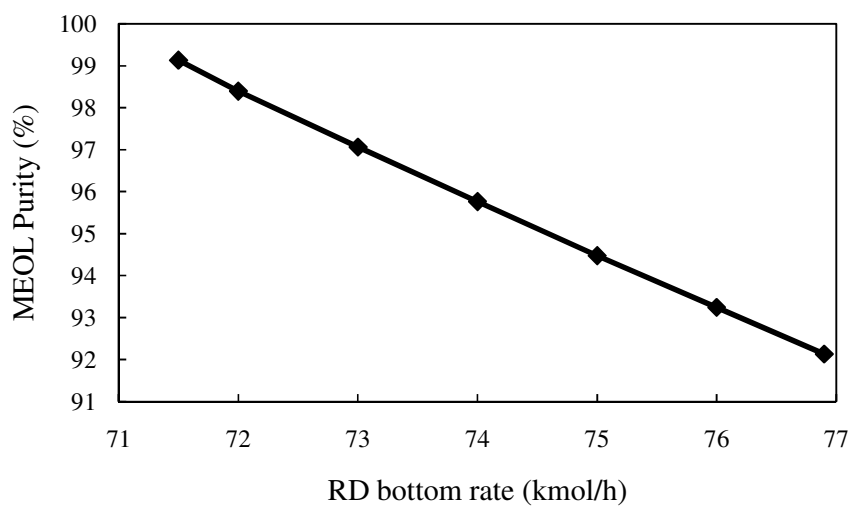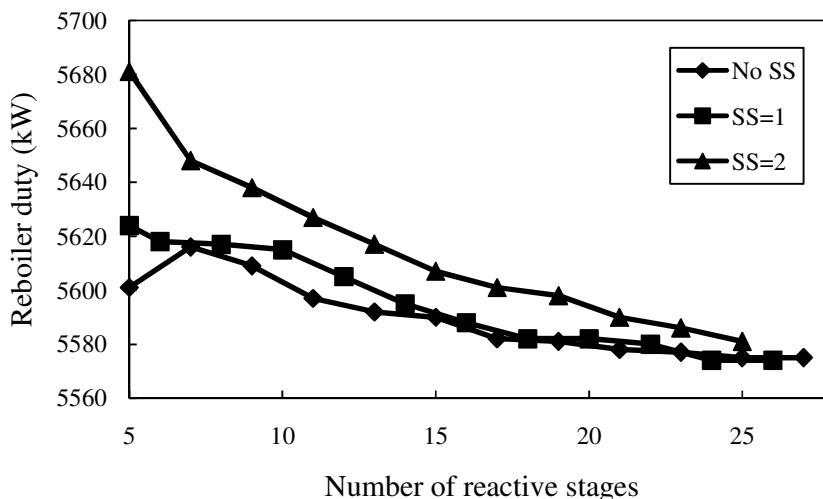
Fig. 5-40 Effect of reactive stage on reboiler duty in reactive distillation column for r-TCRD process.

5.1.2.6 Effect of feed location for r-TCRD process

Likewise, the effect of feed locations of oleic acid and methanol on the performance of reactive distillation in term of the oleic acid conversion and biodiesel purity are investigated for r-TCRD configuration as shown in Figs. 5-41 to 5-46. In the previous section, the r-TCRD process is illustrated with the reactive stage is 18 where no stripping stage. Like the chapter IV, the oleic acid feed, it is fed from the top to bottom trays of the column when specified stage of methanol feed at tray 28 for standard condition. While methanol feed is fed from the bottom to top tray of the column after obtaining the optimum location of oleic acid feed. The simulation results have been shown that change in feed location of oleic acid affects to the performance of reactive distillation that is decrease in oleic acid conversion and biodiesel purity when location of oleic acid feed is changed from top to bottom tray as shown in Figs. 5-41 and 5-42. Considering the reboiler duty with oleic acid feed location in Fig. 5-43, it is shown that the optimum tray of oleic acid feed as tray 2 because the reboiler requires the minimum heat energy and obtaining the maximum conversion and purity. For methanol feed, changing the feed location from bottom to top trays when oleic acid is fed at tray 2 is resulted that the oleic acid conversion and biodiesel purity are

decreased as shown in Figs. 5-44 and 5-45. Considering the reboiler duty with methanol feed location as shown in Fig. 5-46, it is demonstrated that feeding methanol from the bottom to the top trays cause increase in reboiler duty because immediately vaporized methanol to the top of column, decreased an amount of methanol in reactive section, and the shorter reaction time between oleic acid and methanol. By the reasons is similar in the previous chapter for this effect. However, the previous parameter of reactive stage has reported the number of reactive stage of 18 and no stripping stage then the reactive distillation column has total stage of 22 (include condenser and reboiler stages). Therefore, the feed locations of oleic acid and methanol are shifted to follow on column stage where oleic acid and methanol are fed at tray of 2 and 19, respectively.

Fig. 5-41 Effect of oleic acid feed tray on conversion of oleic acid in reactive distillation column for r-TCRD process.
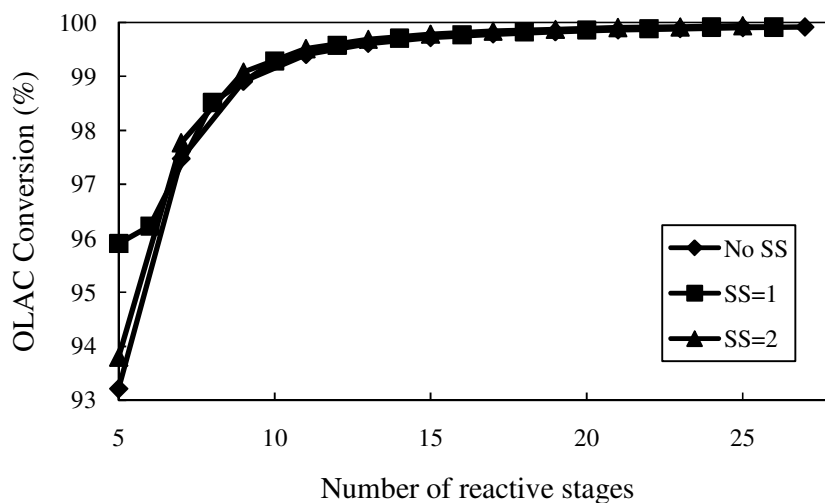
Fig. 5-42 Effect of oleic acid feed tray on purity of methyl oleate in reactive distillation column for r-TCRD process.
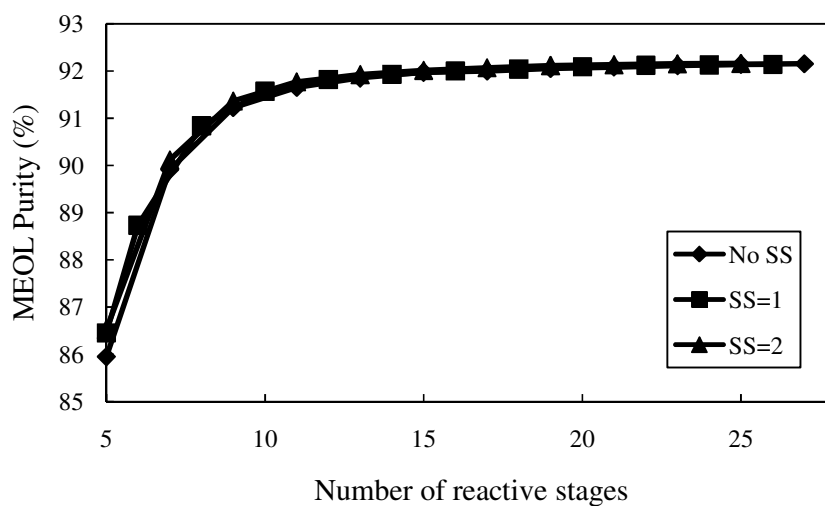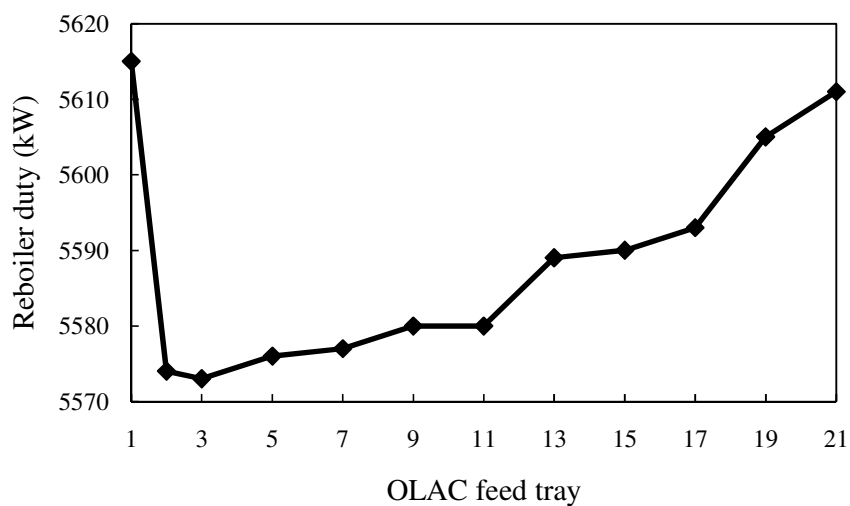

Fig. 5-43 Effect of oleic acid feed tray on reboiler duty in reactive distillation column for r-TCRD process.
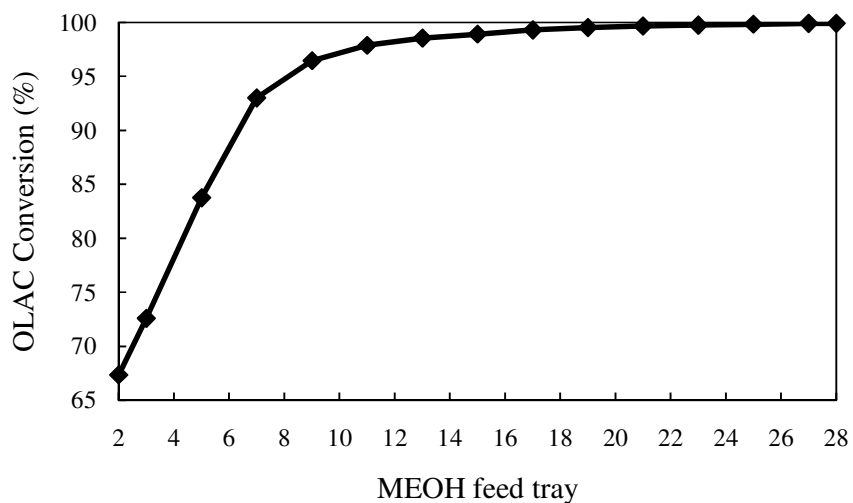
Fig. 5-44 Effect of methanol feed tray on conversion of oleic acid in reactive distillation column for r-TCRD process.
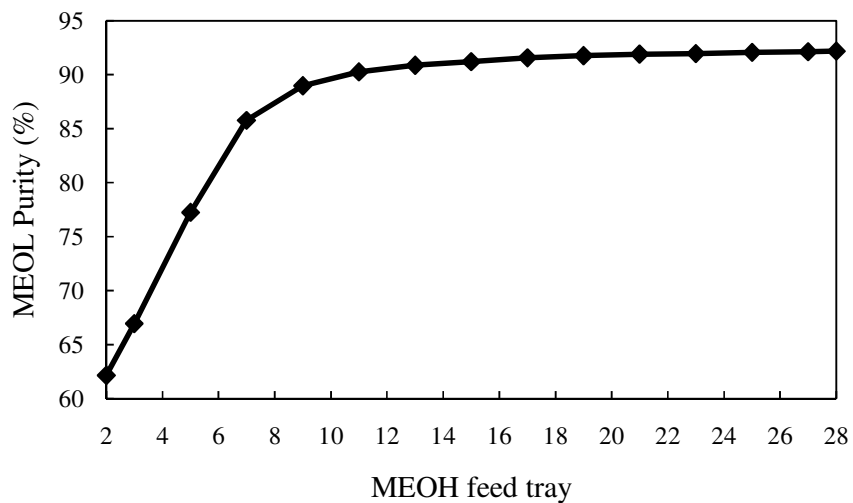
Fig. 5-45 Effect of methanol feed tray on purity of methyl oleate in reactive distillation column for r-TCRD process.
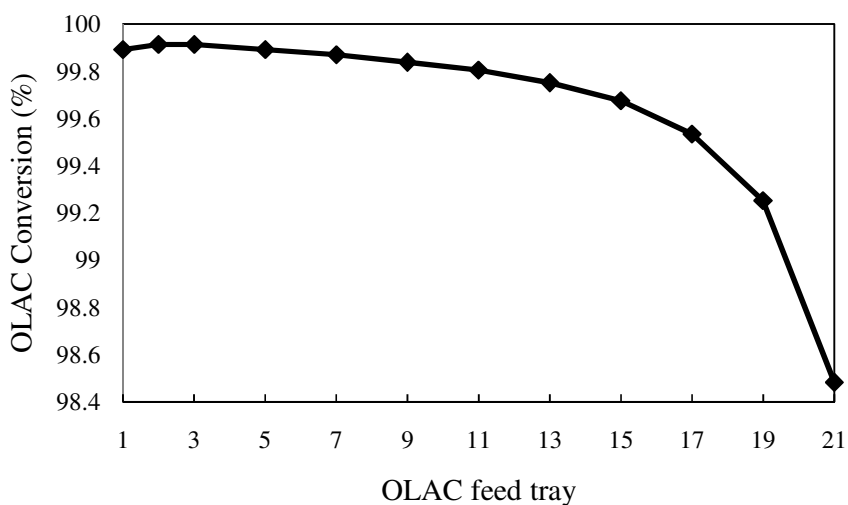
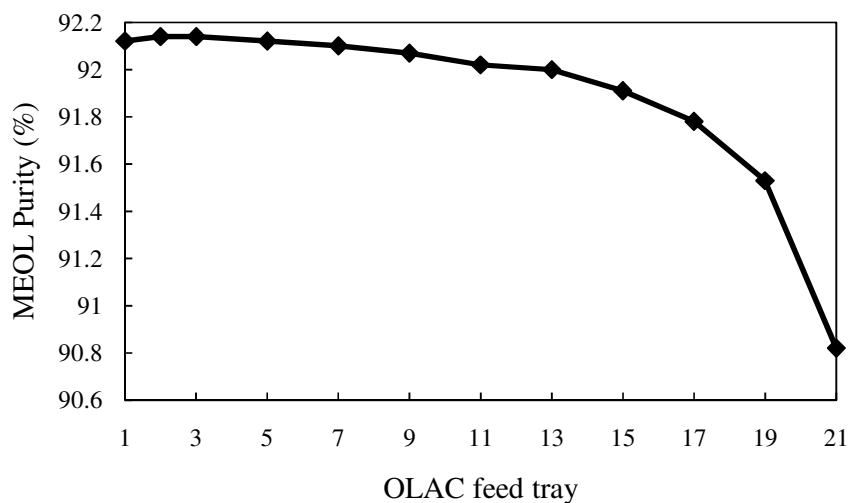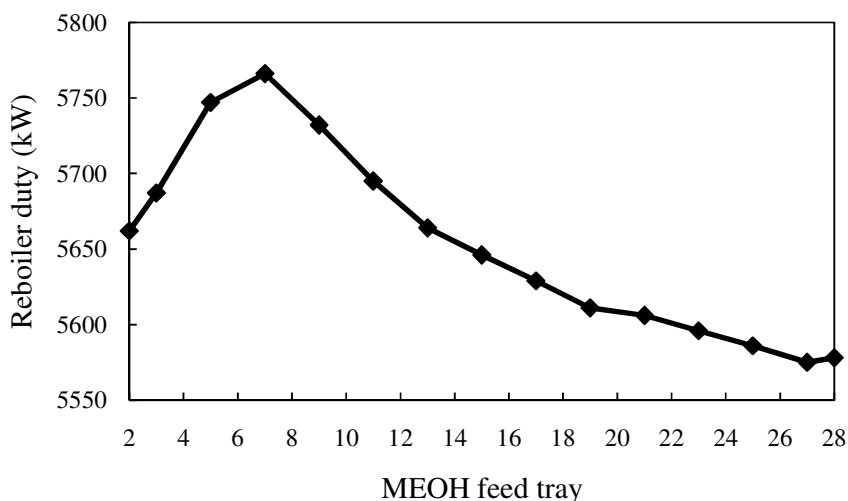**Fig. 5-46** Effect of methanol feed tray on reboiler duty in reactive distillation column for r-TCRD process.

5.1.2.7 The best condition for r-TCRD process

The best conditions for rectifier-thermally coupled reactive distillation are obtained including the column pressure of 3.5-4 bar, oleic acid feed temperature of 175°C, bottom rate of 71.5 kmol/h, the number of reactive stage of 18 with the total column stage of 21 (include condenser; stage 0, and reboiler stages), and feed stages of oleic acid and methanol at tray of 2 and 19, respectively. The temperature and composition profiles in reactive distillation column T-100 are shown in Fig. 5-47 and 5-48, respectively. It can be seen that in the reactive zone, temperature remains almost constant. The biodiesel product and unreacted methanol are continuously separated from the top of reactive zone unless the low purity until at the bottom of reactive zone that methyl oleate is purified and methanol is vaporized to the top. For this reason, temperature in bottom of reactive zone is been suddenly high along the boiling point of methyl oleate. However, contained water concentration in reactive zone is higher.
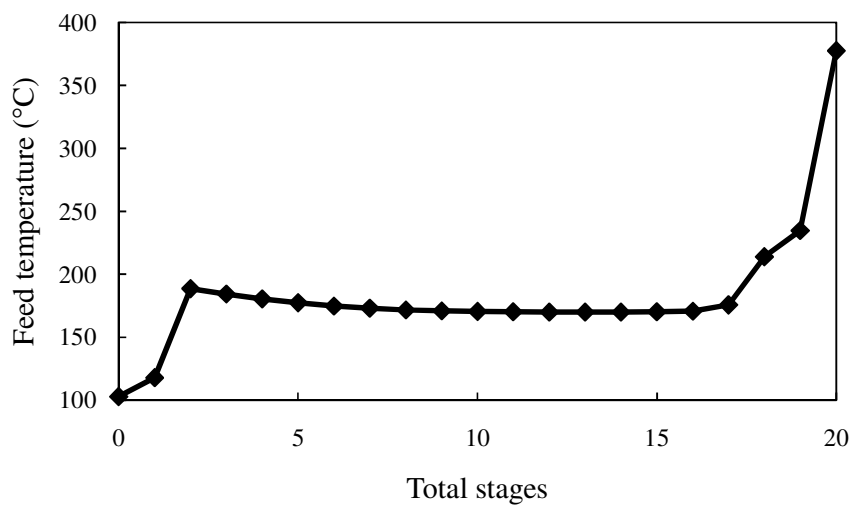
Fig. 5-47 Temperature profile in reactive distillation column for r-TCRD process.
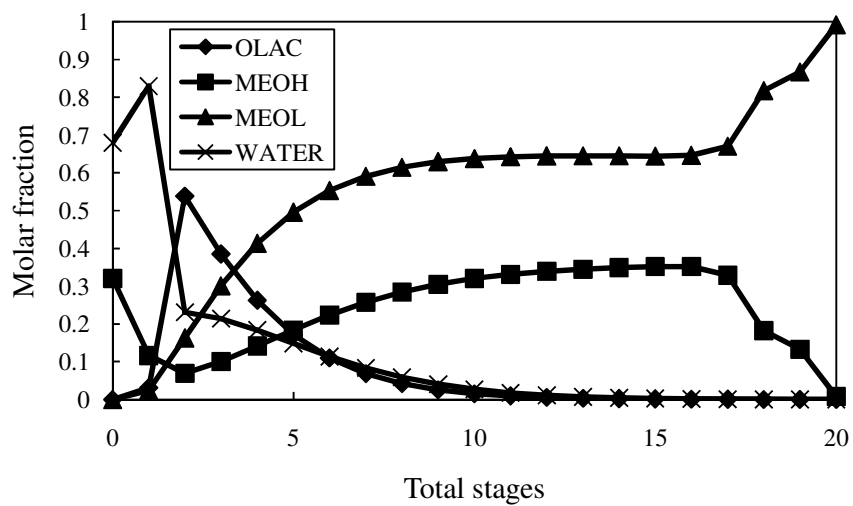
Fig. 5-48 Composition profile in reactive distillation column for r-TCRD process.

5.1.4 Methanol distillation column for r-TCRD process

The distillation column was used to recover the excess or unreacted methanol. From Fig. 5-25, the sidestream of reactive distillation column (T-100), the stream SIDEREB including methanol and methyl oleate components is fed to stage 9 of methanol separation column (T-101) with molar reflux ratio of 1.55. Like the previous process, the methanol distillation column can be design from chapter 3 in section 3.4. For r-TCRD configuration, the methanol distillation column is configured in the rectifier column as shown in Fig. 5-25, then the coupling of shortcut and rigorous models are used to design the column T-101. The finished design has demonstrated that the column is specified by the total trays of 3 and feed tray of 3, when specified the reflux ratio of 1.55 by obtained rates of distillate and bottom as 18.76 (methanol) and 175.2 (methyl oleate) kgmol/h, respectively. The molar purities of methanol in distillate and methyl oleate in bottom are achieved as 99.98 and 96.08%, respectively. The temperature and composition profiles of methanol distillation column T-101 are presented in Fig. 5-49 and 5-50, respectively. In this case, the boiling point of methanol and methyl oleate more differs separating easily methanol from methyl oleate with a few trays.
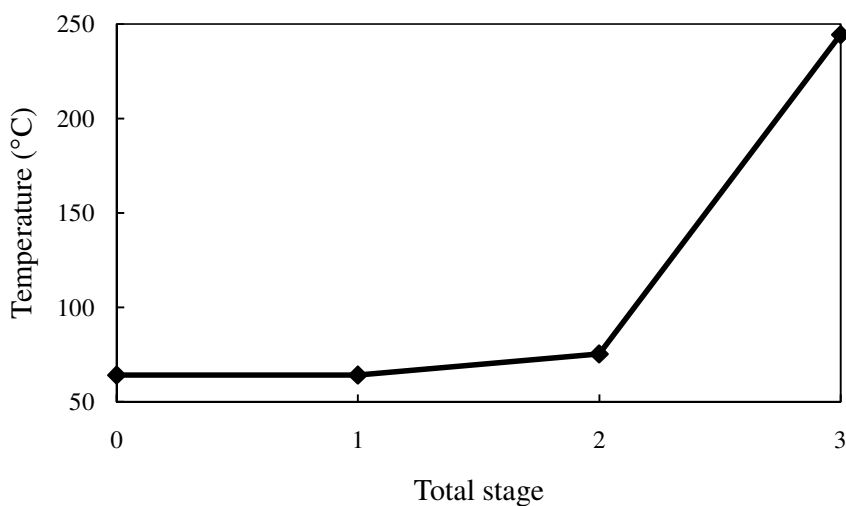
Fig. 5-49 Temperature profile in methanol distillation column for r-TCRD process.
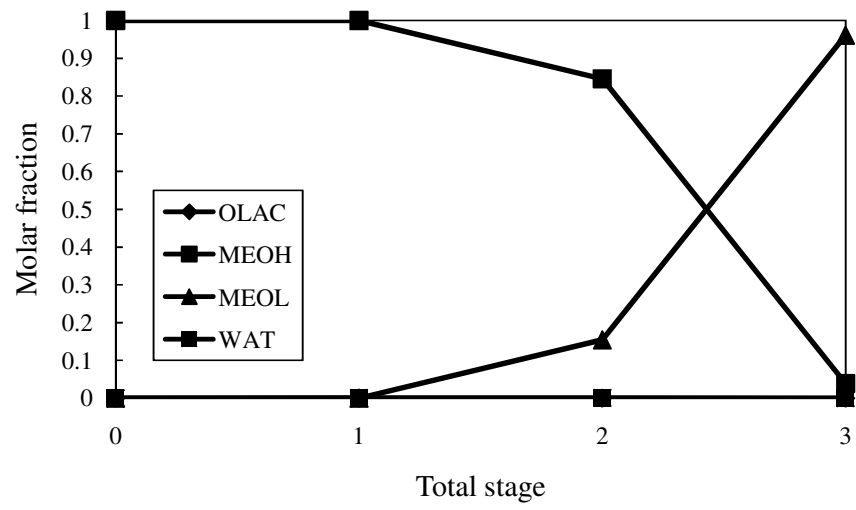
Fig. 5-50 Composition profile in methanol distillation column for r-TCRD process.

CHAPTER VI

HEAT INTEGRATED REACTIVE DISTILLATION PROCESS FOR BIODIESEL PRODUCTION

6.1 Simulation of heat integrated reactive distillation (HIRD) process

The previous chapter, the biodiesel processes of conventional reactive distillation and 2 types of thermally coupled reactive distillation is discussed the performances of reactive distillation. Heat integration is one of the techniques that can effectively reduce the energy consumption of the process. In this chapter, the heat integrated reactive distillation or HIRD for biodiesel production are proposed in concept of heat integrated distillation column (HIDC) as shown in Fig. 6-1. This configuration comprises two separate distillation columns, stripping and rectifying. It is applied to the reactive distillation column and separation column for biodiesel process. There is a pressure difference between the two columns; the overhead vapor of the stripper column is compressed before entering at the bottom of the rectifier column. The rectifying column therefore operates at a higher pressure (i.e., higher temperature). The liquid from the bottom of the rectifying column is fed into the top of the stripping column (Gadalla et al., 2007 and Horiuchi et al., 2008). The standard condition for HIRD process can be taken from the chapter 4. Likely, the methanol has been recovered from SEP column T-101 to RD column T-100, as well as the preheating of feeds and product via heat exchanger. Moreover, the methanol recovery is directly fed to the RD column instead of is mixed to methanol fresh feed, and also increased temperature of stream MEOHRE with stream of biodiesel product. The process flowsheet of HIRD configuration is shown in Fig. 6-2. The RD column is configured in the stripper column operated at the higher pressure, while the SEP column is rectifier column at atmospheric pressure. The both columns is integrated the heat where the stream MEOH+H2O in RD column has supplied the heat energy to

the SEP column, while the stream SIDE as remaining energy from SEP is recovered to the RD column.

Fig. 6-1 Heat integrated distillation column (Gadalla et al., 2007).

Fig. 6-2 Flowsheet of HIRD for biodiesel production.

6.1.1 Performance of HIRD process

As the previous chapters, the performances of HIRD process is analyzed on parameters of column pressure, feed temperature, bottom rate, reactive stage, and feed locations in term of the oleic acid conversion and biodiesel purity.

6.1.1.1 Effect of column pressure for HIRD process

The effect of column pressure on the performance of reactive distillation for HIRD configuration is studied as the previous chapters. The simulation results have been demonstrated as shown in Fig. 6-3 to 6-5; it is resulted like the CRD and r-TCRD processes. An increase in column pressure from 2 to 4 bar, the system performance is improved while the too high column pressure causes the slightly bad performance. By the reasons have been discussed as the previous processes. At the lower column pressure, the oleic acid and methanol are more than consumed in reaction on the reactive section affecting the higher production of methyl oleate. For HIRD process, the column pressure obtaining the maximum conversion of oleic acid and purity of biodiesel is 3.5 – 4 bar.
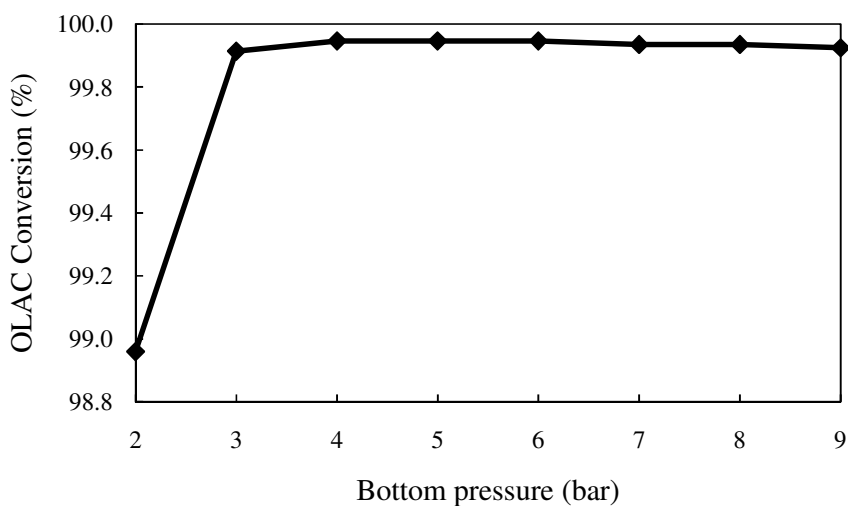
Fig. 6-3 Effect of pressure on conversion of oleic acid in reactive distillation column for HIRD process.
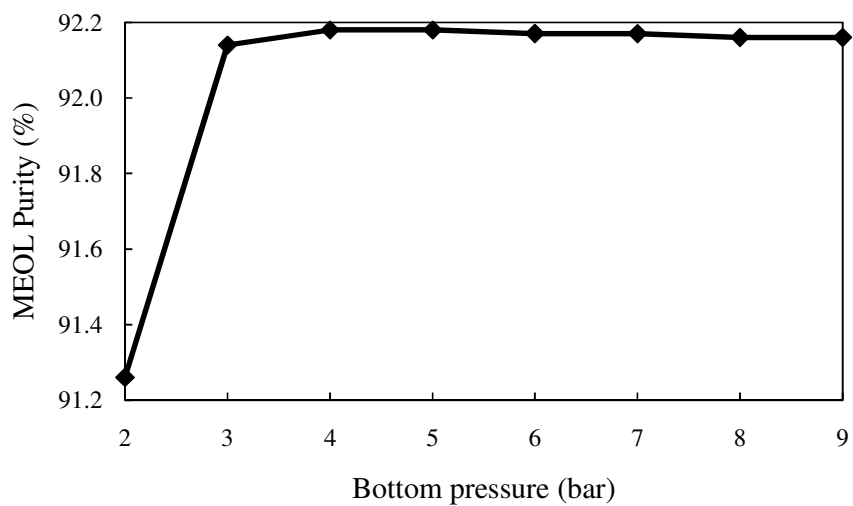
Fig. 6-4 Effect of pressure on purity of methyl oleate in reactive distillation column for HIRD process.
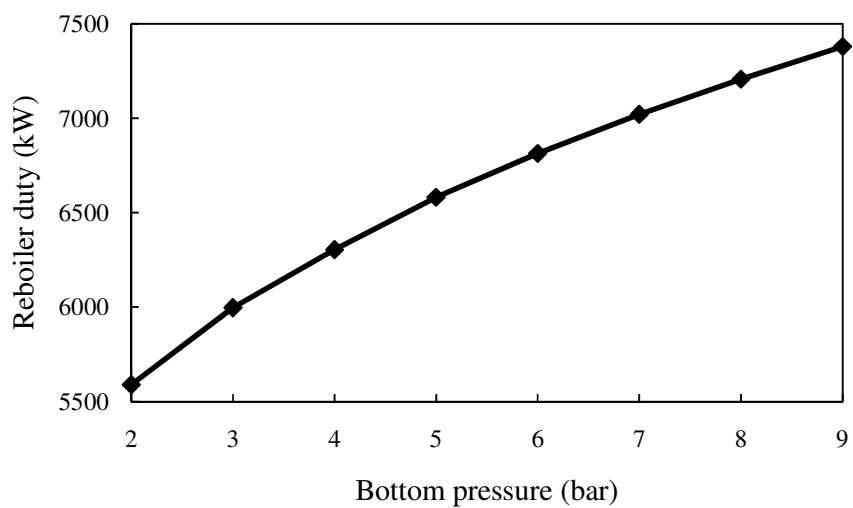
Fig. 6-5 Effect of pressure on reboiler duty in reactive distillation column for HIRD process.

6.1.1.2 Effect of feed temperature for HIRD process

Likewise, the effect of oleic acid feed temperature on the performance of reactive distillation for HIRD process is investigated as shown in Figs. 6-6 to 6-8. It is similarly shown in the r-TCRD process, an increase in temperature of oleic acid results the improved performance of system, as well as the decreased reboiler duty. The higher temperature of oleic acid feed results the higher temperature in reactive section, more than consumed methanol in reaction, the more generated biodiesel product, and also the less than formed water in reactive zone. Therefore, the temperature of oleic acid feed obtaining the maximum conversion of oleic acid and purity of biodiesel is 175°C.
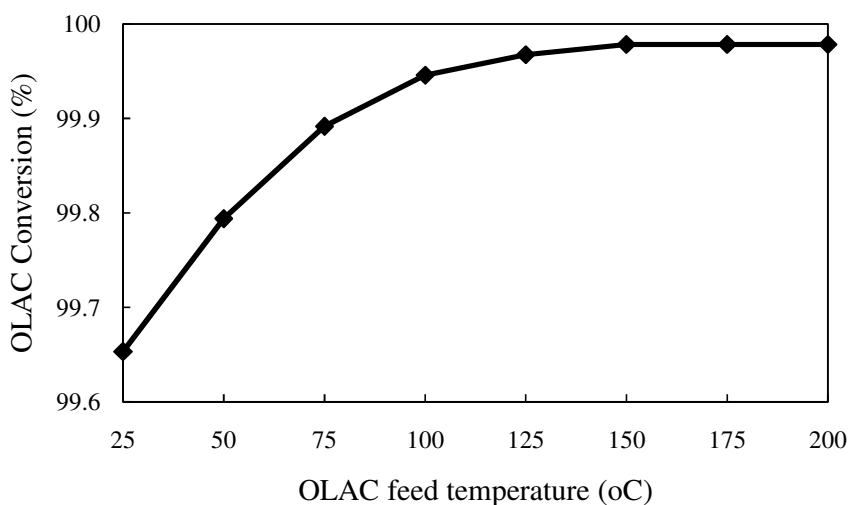
Fig. 6-6 Effect of feed temperature on conversion of oleic acid in reactive distillation column for HIRD process.
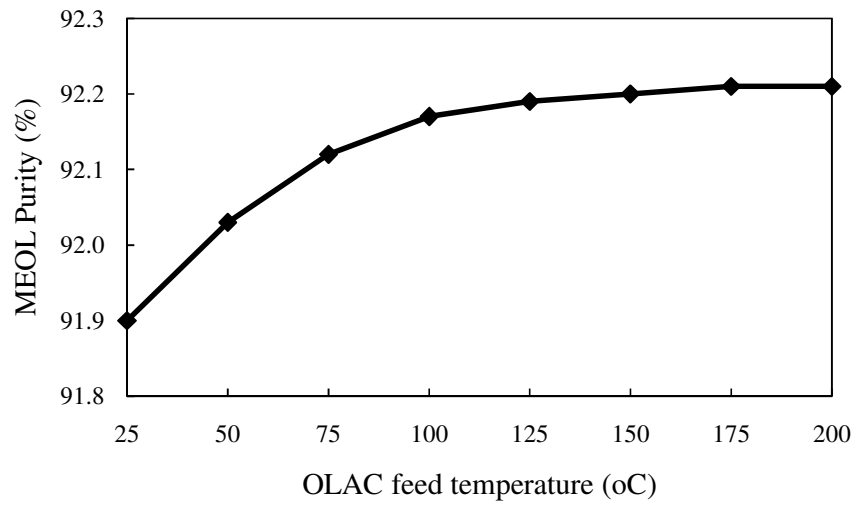
Fig. 6-7 Effect of feed temperature on purity of methyl oleate in reactive distillation column for HIRD process.

Fig. 6-8 Effect of feed temperature on reboiler duty in reactive distillation column for HIRD process.

6.1.1.3 Effect of bottom rate for HIRD process

In this study, the effect of bottom rate in reactive distillation column on the performance of reactive distillation is investigated as shown in Figs. 6-9 to 6-11. It is known that the more purified biodiesel product with decrease in the bottom rate and the improved performance of reactive distillation although the required higher reboiler duty. The lower bottom rate results the higher reboiler temperature while no change in the consumed composition of oleic acid and methanol in reactive section causing the generated product of methyl oleate in the same fraction at all of the bottom rate. Thereby, the bottom rate of RD column obtaining the maximum conversion of oleic acid and the purity of biodiesel up to 99% is 71.5 kmol/h.
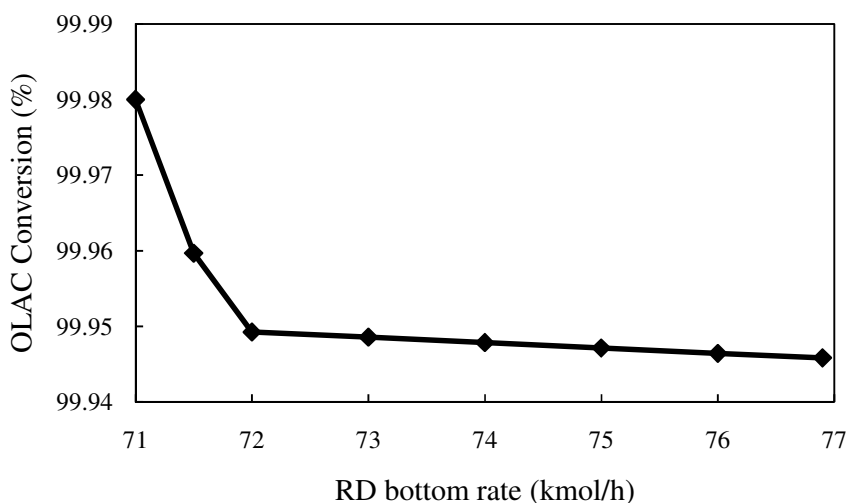
Fig. 6-9 Effect of bottom rate on conversion of oleic acid in reactive distillation column for HIRD process.
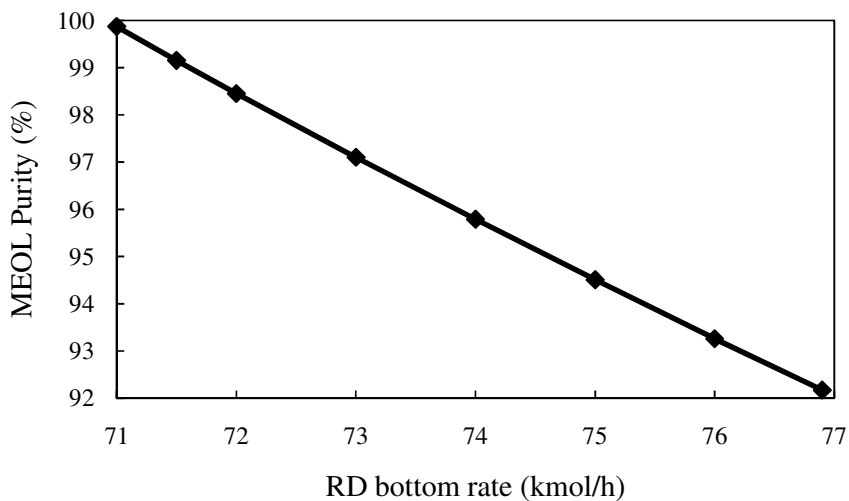
Fig. 6-10 Effect of bottom rate on purity of methyl oleate in reactive distillation column for HIRD process.
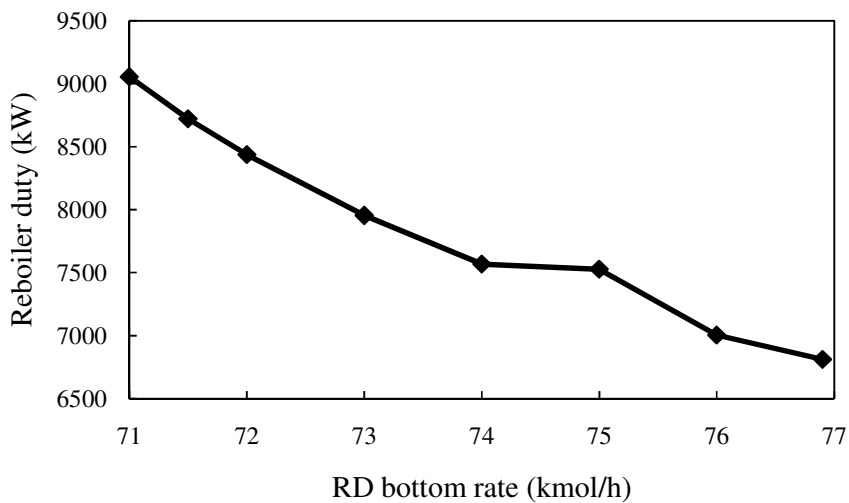
Fig. 6-11 Effect of bottom rate on reboiler duty in reactive distillation column for HIRD process.

6.1.1.4 Effect of reactive stages for HIRD process

The effect of reactive stage at the different stripping stages for HIRD process on the performance of reactive distillation in term of oleic acid conversion and biodiesel purity is investigated as shown in Figs. 6-12 to 6-14. It is demonstrated that the decreased conversion of oleic acid and purity of biodiesel with the decreased reactive stages less than 15 at the different stripping stages because the relatively constant temperature in reactive section results the amount of biodiesel product in reactive zone is generated with constant reaction rate, like the r-TCRD. When the specified reactive stage, it is shown that increase in the stripping stage no affecting to improvement of system performance. However, the reboiler duty is increased because heat from reboiler is difficulty reached in reactive zone; the external energy is more supplied to system. Therefore, in study of this effect has illustrated that the reactive stage is 15 where no stripping stage.

Fig. 6-12 Effect of reactive stages on conversion of oleic acid in reactive distillation column for HIRD process.

Fig. 6-13 Effect of reactive stages on purity of methyl oleate in reactive distillation column for HIRD process.
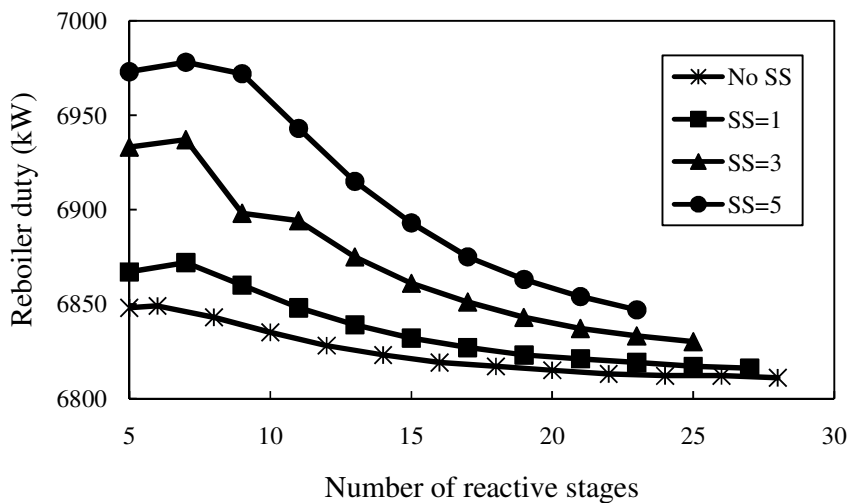

**Fig. 6-14** Effect of reactive stages on reboiler duty in reactive distillation column for HIRD process.

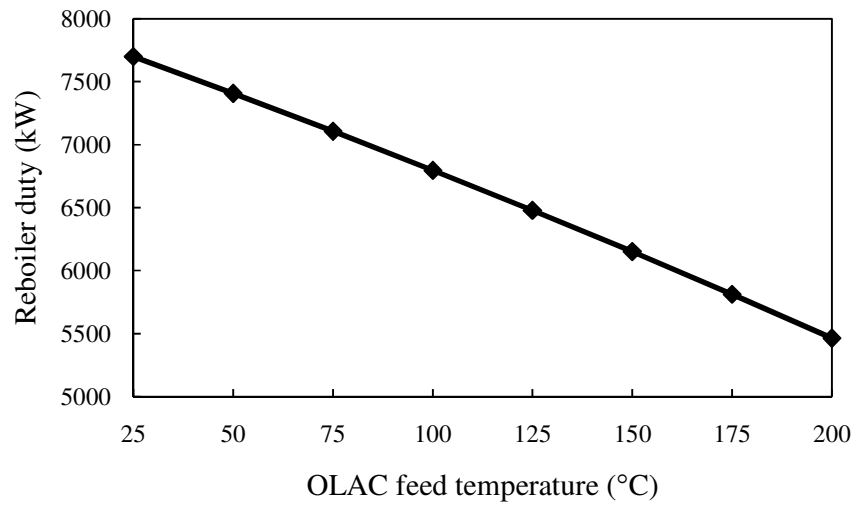*6.1.1.5 Effect of feed locations for HIRD process*

Like the previous chapters, the effect of feed locations of oleic acid and methanol for HIRD configuration on the performance of reactive distillation in term of the oleic acid conversion and biodiesel purity are investigated as shown in Figs. 6-15 to 6-20. In the previous section, the HIRD process is illustrated with the reactive stage is 15 where no stripping stage. Similar as the past, the oleic acid feed, it is fed from the top to bottom trays of the column when specified stage of methanol feed at tray 28 for standard condition. While methanol feed is fed from the bottom to top tray of the column after obtaining the optimum location of oleic acid feed. The simulation results have been shown that change in feed location of oleic acid affects to the performance of reactive distillation that is decrease in oleic acid conversion and biodiesel purity when location of oleic acid feed is changed from top to bottom tray as shown in Figs. 6-15 and 6-16. Considering the reboiler duty with oleic acid feed location in Fig. 6-17, it is shown that the optimum tray of oleic acid feed as tray 2 because the reboiler requires the minimum heat energy and obtaining the maximum conversion and purity. For methanol feed, changing the feed location from bottom to top trays when oleic acid is fed at tray 2 is resulted that the oleic acid conversion and biodiesel purity are decreased as shown in Figs. 6-18 and 6-19. Considering the reboiler duty with methanol feed location as shown in Fig. 6-20, it is demonstrated that feeding methanol from the bottom to the top trays cause increase in reboiler duty because immediately vaporized methanol to the top of column, decreased an amount of methanol in reactive section, and the shorter reaction time between oleic acid and methanol. By the reasons is similar in the previous chapter for this effect. However, the previous parameter of reactive stage has reported the number of reactive stage of 15 and no stripping stage then the reactive distillation column has total stage of 17 (include reboiler stages). Therefore, the feed locations of oleic acid and methanol are shifted to follow on column stage where oleic acid and methanol are fed at tray of 2 and 16, respectively.

Fig. 6-15 Effect of oleic acid feed tray on conversion of oleic acid in reactive distillation column for HIRD process.
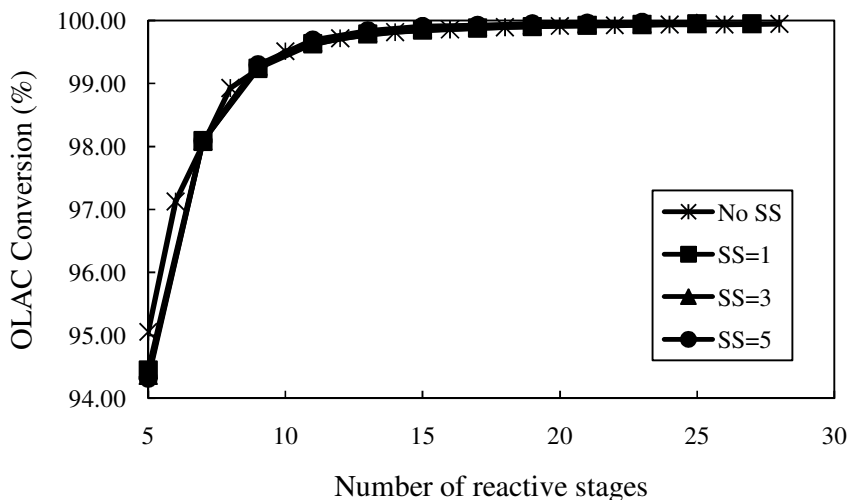

Fig. 6-16 Effect of oleic acid feed tray on purity of methyl oleate in reactive distillation column for HIRD process.
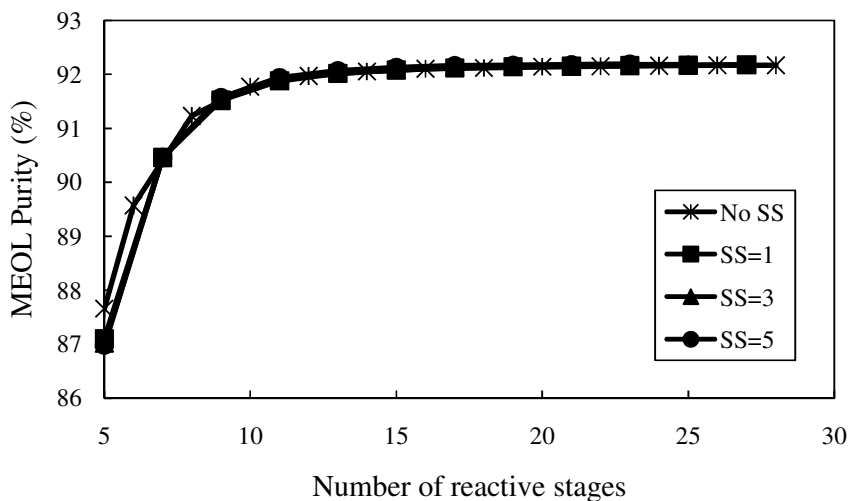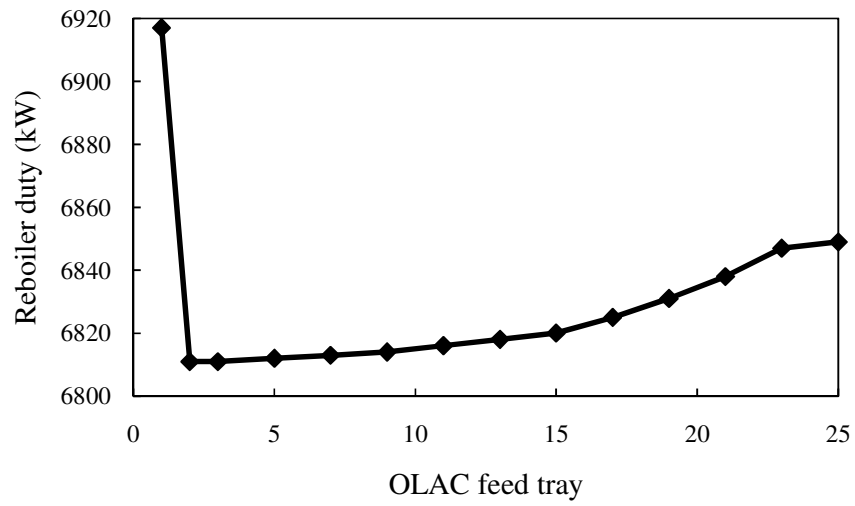
Fig. 6-17 Effect of oleic acid feed tray on reboiler duty in reactive distillation column for HIRD process.
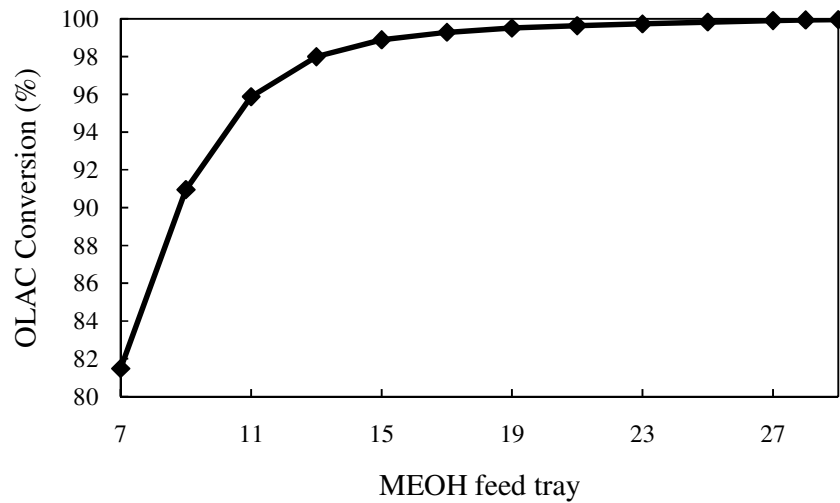
Fig. 6-18 Effect of methanol feed tray on conversion of oleic acid in reactive distillation column for HIRD process.
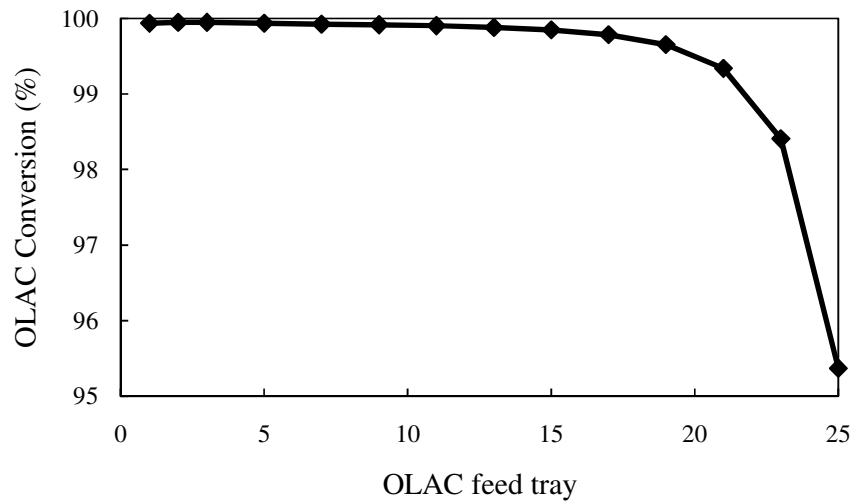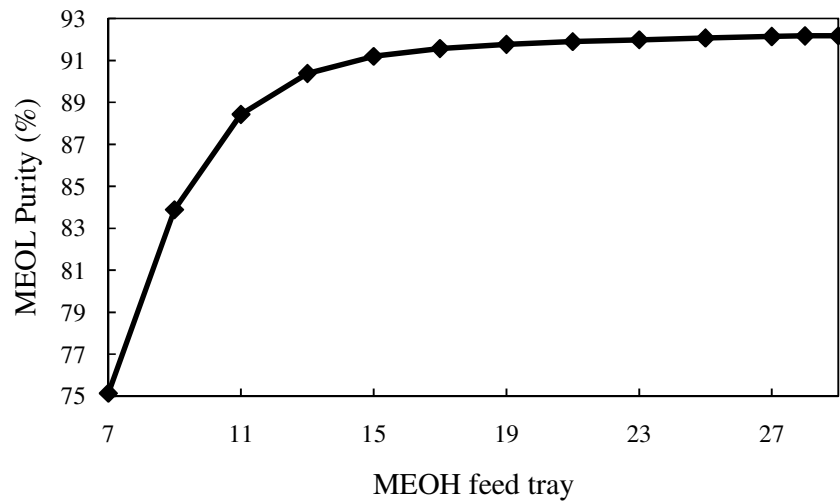
Fig. 6-19 Effect of methanol feed tray on purity of methyl oleate in reactive distillation column for HIRD process.
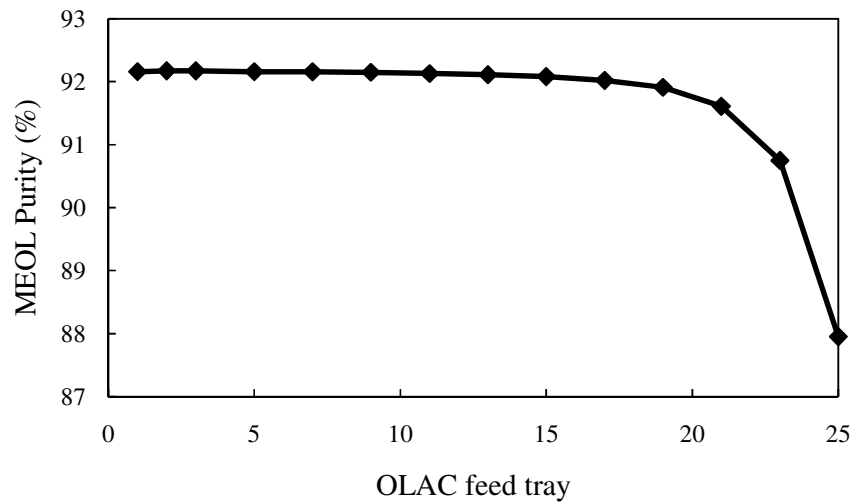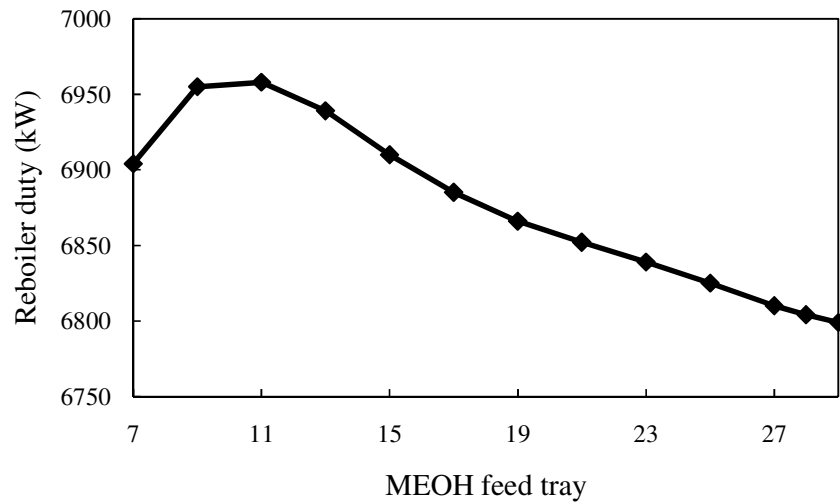

Fig. 6-20 Effect of methanol feed tray on reboiler duty in reactive distillation column for HIRD process.

6.1.1.6 The best conditions for HIRD process

The best conditions for heat integrated reactive distillation are obtained including the column pressure of 3.5-4 bar, oleic acid feed temperature of 175°C, bottom rate of 71.5 kmol/h, the number of reactive stage of 15 and no stripping stage with the total column stage of 17 (include reboiler stage), and feed stages of oleic acid and methanol at tray of 2 and 16, respectively. The profiles of temperature and composition in reactive distillation column T-100 are shown in Fig. 6-21 and 6-22, respectively. It can be seen that in the reactive zone, temperature remains almost constant and increasing at the final stage of reactive zone. Likely, the biodiesel product and unreacted methanol are continuously separated from the top of reactive zone unless the low purity until at the bottom of reactive zone that methyl oleate is purified and methanol is vaporized to the top with the same reason to r-TCRD. Moreover, the advantage of HIRD is the lower water concentration in reactive zone avoiding deactivation of solid catalyst.
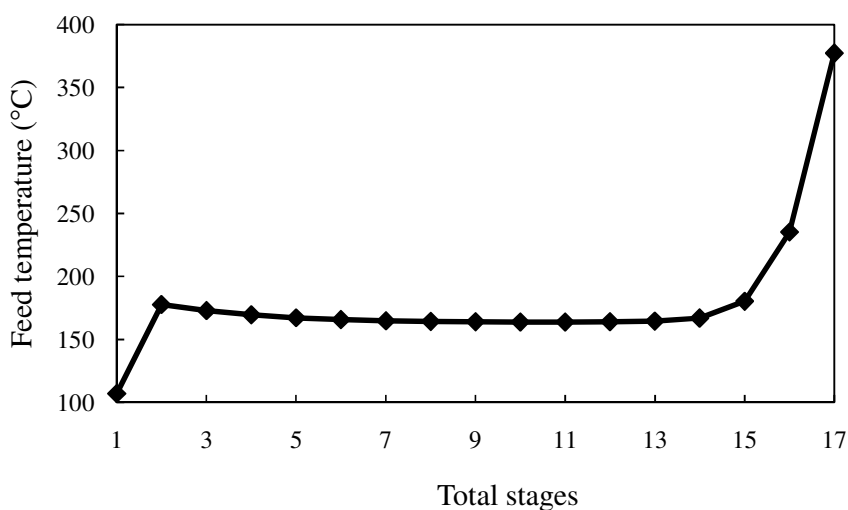
Fig. 6-21 Temperature profile in reactive distillation column for HIRD process.
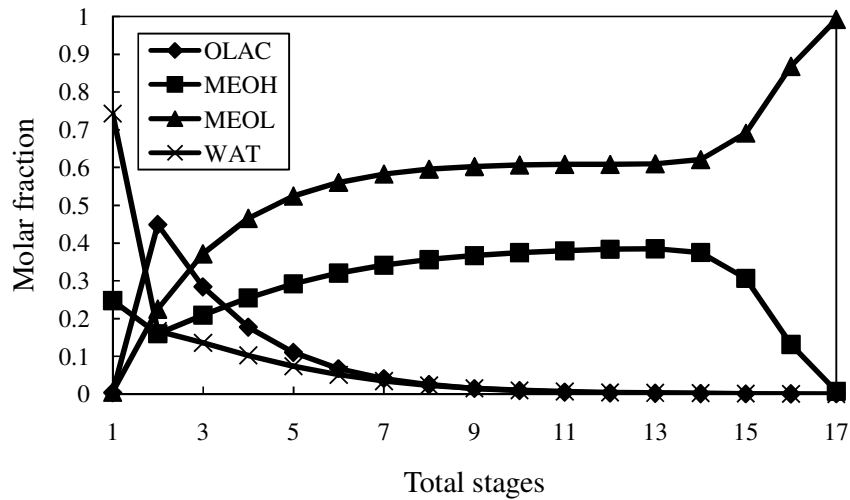
Fig. 6-22 Composition profile in reactive distillation column for HIRD process.

6.1.2 Methodol distillation column for HIRD process

From Fig. 6-2, the stream SIDECON2 is fed to final stage of methanol separation column T-101. The methanol distillation column can be design from chapter 3 in section 3.4. The finished design has demonstrated that the column is specified by the total trays of 25 where the forced feed to final tray and the fixed reflux ratio of 1.55 with the obtained rates of distillate and bottom as 84.16 and 28.98 kmol/h, and also stream SIDE (drawn from stage 15) of 104.6 kgmol/h, respectively, The molar purities of methanol in distillate and water in stream SIDE are obtained as 99.84 and 67.7%, respectively. The temperature and composition profiles of methanol distillation column T-101 are presented in Fig. 6-22 and 6-23, respectively. They is shown the profiles at the minimum number of trays which is equal to 16 trays because no causing to the product purity in the top and bottom of column. However, the water concentration in the bottom cannot purify due to ability of rectifier column usage, the optimum feed tray is fixed at bottom of column, and the sidedrawn stream of distillation column design for HIDC is not carried out.
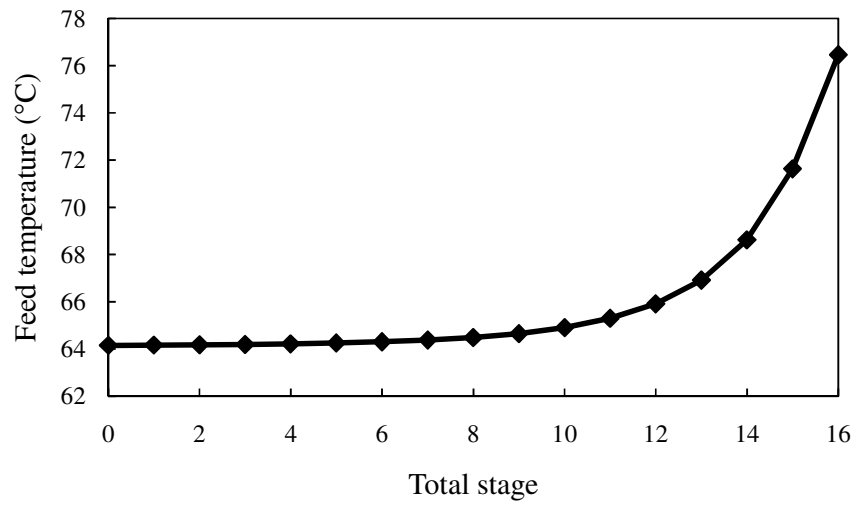
Fig. 6-23 Temperature profile in methanol distillation column for HIRD process.
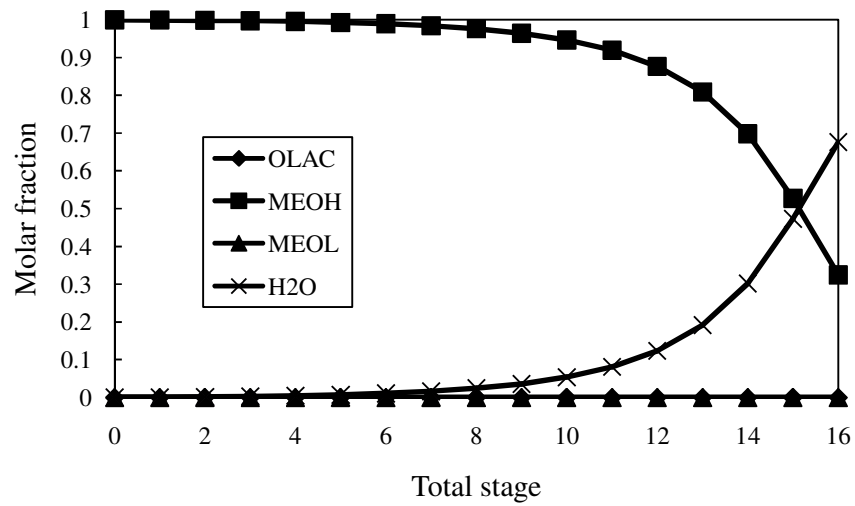
Fig. 6-24 Composition profile in methanol distillation column for HIRD process.

CHAPTER VII

COMPARISON OF THE REACTIVE DISTILLATION PROCESSES FOR BIODIESEL PRODUCTION

In this chapter, the simulation results of biodiesel processes using reactive distillation from the chapter iv, v, and, vi are compared on the performance of reactive distillation column, the design of methanol distillation column, and the total energy consumption for biodiesel production as followed in subsections.

7.1 Reactive distillation T-100

Table 7-1 compares the operating conditions and configurations for reactive distillation column T-100 in conventional, stripper and rectifier-thermally coupled, and heat integrated reactive distillation processes to achieve a high-purity biodiesel product are considered. All of the processes achieve the purity up to 99% due to higher reboiler temperature, as well as the completely esterification of oleic acid and methanol with the oleic acid conversion up to 99% by removing continuously the reaction products.

Table 7-1 Operating conditions and configurations of reactive distillation column (T-100) for CRD, s-TCRD, r-TCRD and HIRD processes.

Condition & configurations	Reactive distillation column			
	CRD	s-TCRD	r-TCRD	HIRD
Number of stages	17	22	21	17
Feed stage				
OLAC1	2	2	2	2
MEOH2	15	20	19	16
SIDE2	-	1	-	1
MEOHRE3	-	-	-	16
SIDEREB3	-	-	15	15
Feed temperature, ^{o}C				
OLAC1	175	150	175	175
MEOH2	110	110	110	110
MEOHRE3	-	-	-	130
Molar reflux ratio	0.1	-	0.1	-
SIDEREB flow rate, kgmol/h	-	-	194	-
Reaction stage	2-15	2-13	2-19	2-16
Distillate rate, kgmol/h	191.9	179.7	104.6	219
Condenser duty, kW	-2096	-	-1208	-
Condenser/top temperature, ^{o}C	106.2	152.5	113.6	-
Condenser/top pressure, bar	3.5	2.5	3.5	3.5
SIDEREB stage	-	-	19	-
Reboiler duty	4543	4164	4198	3969
Bottom rate, kgmol/h	71.5	71	71.5	71.5
Reboiler temperature, ^{o}C	395.3	395	395.1	395
Reboiler pressure, bar	4	3	4	4
Total conversion, mol%	99.94	99.84	99.99	99.97
Biodiesel purity (%)	99.13	99.70	99.18	99.16

7.2 Methanol distillation column T-101

Table 7-2 compares the operating conditions and configurations for methanol distillation column T-101 in conventional, stripper and rectifier-thermally coupled, and heat integrated reactive distillation processes to achieve a high-purity either methanol or water products are considered. All of the processes, the methanol is purified up to 99% while the water is not obtained. However, the rather purified water is obtained in the CRD and s-TCRD processes. For r-TCRD process, the feed stream from T-100 to enter T-101 contains the almost composition of methanol and methyl oleate, so separated methyl oleate as purity about 96.58% which it is heat transfer to T-100. The last process, it is known that the bottom temperature is too lower for boiling of the water when compare to the first of 2 processes causing the unpurified water.

Table 7-2 Operating conditions and configurations of methanol distillation column (T-101) for CRD, s-TCRD, r-TCRD and HIRD processes.

Condition & configurations	Distillation column			
	CRD	s-TCRD	r-TCRD	HIRD
Number of stages	17	18	4	17
MEOH+H2O feed stage	14	11	-	-
SIDEREB feed stage	-	-	3	-
SIDECON2	-	-	-	16
Molar reflux ratio	0.911	1.55	0.3	1.55
SIDE flow rate, kgmol/h	-	7	-	104.4
Distillate rate, kgmol/h	120	97.78	18.77	85.44
Condenser duty, kW	-2256	-2450	-277	-2145
Condenser temperature, ^{o}C	64.51	64.28	64.21	64.17
Condenser/top pressure, bar	1	1	1	1
SIDE stage	-	1	-	16
Reboiler duty	2072	400.1	-	-
Bottom rate, kgmol/h	72.1	74.91	175.2	28.98
Reboiler/bottom temperature, ^{o}C	96.63	91.86	252	76.56
Reboiler pressure, bar	1	1	1	1
%Purity of MEOH	97.39	99.06	99.78	99.88
%Putity of Water	98.2	94.53	96.58*	67.93

*methyl oleate

7.3 Total energy requirement in reactive distillation process for biodiesel production

Table 7-3 compares the total energy consumption for biodiesel production. It can be seen that the TCRD and HIRD process requires lower total energy than the CRD process for production of biodiesel and methanol (recycle) to achieve a high purity. In CRD process, all of the equipments are required the energy supply to operate the biodiesel process which ineffective usage of energy is seen in each unit. While the s-TCRD is eliminated the condenser in T-100 due to side condenser of T-101 where T-101 is lower consumed energy in CRD process for methanol separation because temperature in T-100 is enough high to support the T-101. For r-TCRD, it is demonstrated that the energy in units of T-100 and T-101 are reduced from the CRD and s-TCRD process due to elimination the reboiler from T-101 and supplying the boil-up from T-100 where the reactive section has been moved and lumped with T-101 column and heat transfer between two columns is transferred streams contain almost methyl oleate is high boiling point then the high temperature. The last, in units of T-100 and T-101 for HIRD are required the minimum energy. The two columns are configured in a particular way so that the energy of the hot rectifying column can be used to heat the stripping column. The T-101 is like as side condenser to T-100 while T-101 is compare as side reboiler to T-100, as well as the cooled power of biodiesel product is lower due to directly feeding the heated methanol with stream of biodiesel product causing load of cooling the product is reduced. Therefore, it is shown that the HIRD process utilizes the minimum total energy consumption for biodiesel product followed by r-TCRD and s-TCRD, respectively; comparing to CRD process. However, the energy for heating and cooling is known that there are the different costs. Fig. 7-1 shows to compare the required heating and cooling energy for processes of biodiesel production. It can be seen that the heating energy is used a lot with a lot cooling energy. The processes applying the technologies of thermal coupling and heat integration can be compared the energy saving as shown in Fig. 7-2.

Table 7-3 Comparison of energy requirement for different biodiesel processes

Equipment description/parameter	Process			
	CRD	s-TCRD	r-TCRD	HIRD
RD column, T-100				
QR1	4543	4164	4198	3969
QC1	-2096	-	-1208	-
MEOH distillation column, T-101				
QR2	2072	400.1	-	-
QC2	-2256	-2450	-277	-2145
Cooler				
E-102	-1982	-1833	-2318	-1254
E-103	-110	-109.1	-233.2	-134
Compressor, K-100	-	-	-	265
Pump				
P-100	0.5706	0.0166	0.0917	0.4102
P-101	-	0.3131	8.250	0.68
Total	13059.6	8956.5	8234.2	7768.1

Unit in kW
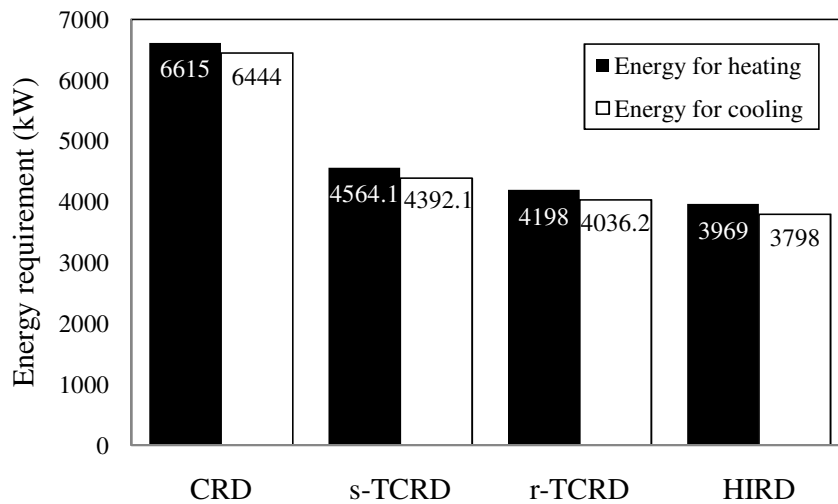
Fig. 7-1 Comparison of energy for heating and cooling in CRD, s-TCRD, r-TCRD, and HIRD.
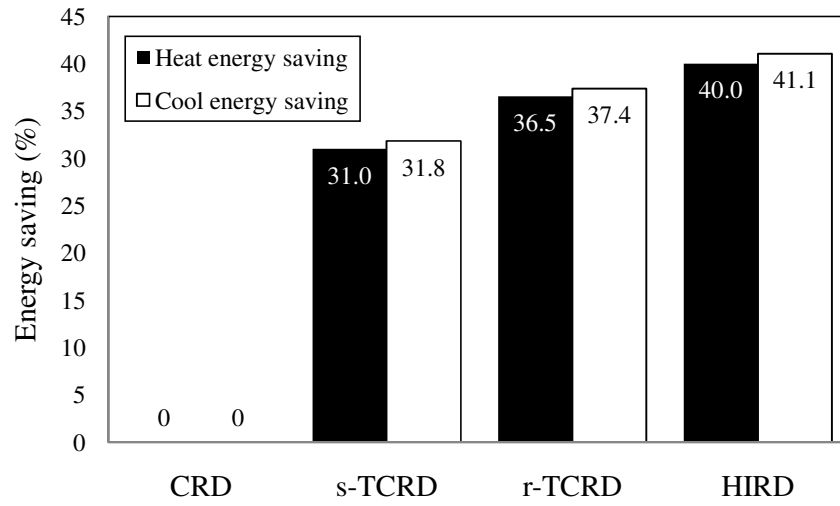
Fig. 7-2 Comparison of energy saving for heating and cooling in CRD, s-TCRD, r-TCRD and HIRD.

CHAPTER VIII

CONCLUSIONS

8.1 Conclusions

In this study, the reactive distillation process for biodiesel production from the esterification of oleic acid and methanol is investigated. This work investigates the effect of parameters on the performance of reactive distillation for biodiesel production from oleic acid and determine the suitable reactive distillation condition and configuration based on total energy consumption. The comparison of the design of different configuration of reactive distillation by the applied concepts of thermal coupling and heat integration, i.e., conventional reactive distillation, stripper-thermally coupled reactive distillation, rectifier-thermally coupled reactive distillation, and heat integrated reactive distillation based on the same product specification methyl ester, and also recycled methanol.

8.1.1 Performance of reactive distillation for biodiesel production

The biodiesel production by using reactive distillation is investigated. Oleic acid is represented as triglyceride. Simulations of the reactive distillation using an equilibrium stage model in HYSYS are performed to study the effect of operating parameters such as column pressure, feed temperature, bottom raye, reactive stages and feed location of oleic acid and methanol on the reactive distillation performance. The CRD, the results show that increasing column pressure does not improve the performance of reactive distillation in term of the conversion oleic acid and purity of methyl oleate but feed temperature slightly enhance to be insignificant. Increasing the reboiler duty is not unimproved on the conversion of oleic acid whereas the purity of the biodiesel product gives an opposite trend. The reactive stages also improve the performance of the reactive distillation. The feed

location of oleic acid and methanol should be introduced at the ends of reaction stage of column. For s-TCRD is the same result in column pressure and feed temperature. Increasing reboiler duty enhance in purity but insignificant conversion. The reactive stage is in line with CRD by differing only in a range. In r-TCRD is attached with the analysis of interlinking stage effect. It is seen that connecting at bottom stage of reactive zone enhancing performance. Likewise, the tending of column pressure and reactive stage are the same in first of two processes whereas oleic acid feed temperature enhance both conversion and purity. Finally, HIRD is specified at the high column pressure. Other parameters are the same trend to CRD and s-TCRD differing on simulation result.

8.1.2 Total energy consumption for biodiesel production

Considering total energy consumption, an optimum condition configuration of the reactive distillation process for biodiesel production is determined to minimize total energy consumption. The comparison of CRD, s-TCRD, r-TCRD, and HIRD is concluded that reactive distillation with thermal coupling and heat integration is more attractive. The total energy consumption for biodiesel production using s-TCRD is lowers than CRD, while r-TCRD is lower than that and HIRD is lowest than of all because of less energy respectively. Processes of s-TCRD, r-TCRD, and HIRD is heat energy saving as 31, 36.5, and 40%, respectively; comparing to CRD process in while the biodiesel product and recycled methanol are achieve with high purity up to 99%, respectively, as well as the obtained conversion of oleic acid up to 99% in esterification step. In conclude, using the concept of energy reduction to reactive distillation can improve the biodiesel process so as to lower required energy, and the configuration of HIRD is alternative process that greatest consumes the energy effectively.

8.2 Recommendation

The performance of reactive distillation for biodiesel production should be analyzed the least simultaneous two parameters to study effect of variable interaction for better efficiency process.

REFERENCES

Babcock, R.E., Clausen, E.C., and Popp, M. Yield characteristics of biodiesel produced from chicken fat-tall oil blended feedstocks. <u>Department of Transportation, University Transportation Centers Program</u> (2005).

Baur, R. Modeling reactive distillation dynamics, <u>Clarkson University</u> (2000).

Barroso-Muñoz, F.O., Hernández, S., and Ogunnaike, B. Analysis of design and control of reactive thermally coupled distillation sequences. <u>European Symposium on Computer Aided Process Engineering</u> 17 (2007) : 877-882.

Chongkhong, S., Tongurai, C., Chetpattananondh, P., and Bunyakan, C. Biodiesel production by esterification of palm fatty acid distillate. (2007).

Freedman, B. and Bagby, M.O. Heats of combustion of fatty esters and triglycerides. <u>Journal of the American Oil Chemists' Society</u> 66 (1989) : 1601-1605.

Hiwale, R.S., Bhate, N.V., Mahajan, Y.S., and Mahajani. S.M. Industrial applications of reactive distillation: Recent trends. <u>International Journal of Chemical Reactor Engineering</u> 2 (2004) : Review R1.

Hung, S.B., Chen, J.H., Lin, Y.D., Huang, H.P., Lee, M.J., and Ward, J.D., Yu, C.C. Control of plantwide reactive distillation processes: Hydrolysis, transesterification and two-stage esterification. <u>Journal of the Taiwan Institute of Chemical Engineers</u> 41 (2010) : 382–402.

Jana, A.K. Heat integrated distillation operation. <u>Applied Energy</u> 87 (2010) : 1477–1494.

Gerpen, J.V. Biodiesel processing and production. <u>Fuel Processing Technology</u> 86 (2005) : 1097– 1107.

Gómez-Castro, F.I., Rico-Ramírez, V., Segovia-Hernández, J.G., and Hernández-Castro, S. Esterification of fatty acids in a thermally coupled reactive distillation column by the two-step supercritical methanol method. <u>Chemical engineering research and design</u> (2010).

Kansedo J.B. Synthesis of biodiesel from palm oil and sea mango oil using sulfated zirconia catalyst. <u>Universiti Sains Malaysia</u> (2009).

Kiss, A.A., Omota, F., Dimian, A.C., and Rothenberg, G. The heterogeneous advantage: biodiesel by catalytic reactive distillation. <u>Topics in Catalysis</u> 40 (2006) : 1–4.

Kiss, A.A. Separative reactors for integrated production of bioethanol and biodiesel. <u>Computers and Chemical Engineering</u> 34 (2010) : 812–820.

Kiss, A.A. Heat-integrated reactive distillation process for synthesis of fatty esters. <u>Fuel Processing Technology</u> (2011).

Knothe, G. Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. <u>Fuel Processing Technology</u> 86 (2005) : 1059-1070.

Mali, S.V., Jana, A.K. A partially heat integrated reactive distillation: Feasibility and analysis. <u>Separation and Purification Technology</u> 70 (2009) : 136-139.

Miranda-Galindo, E.Y., Segovia-Hernández, J.G., Hernandez, S., Álvarez, G. de la R., Gutiérrez-Antonio, C., and Briones-Ramírez, A. Design of reactive distillation with thermal coupling for the synthesis of biodiesel using genetic algorithms. <u>European Symposium on Computer Aided Process Engineering</u> 19 (2009).

Mueanmas, C, Prasertsit, K., and Tongurai, C. Transesterification of Triolein with Methanol in Reactive Distillation Column: Simulation Studies. <u>International Journal of Chemical Reactor Engineering</u> 10 (2010) : article A141.

Nguyen, N., and Demirel, Y. Using thermally coupled reactive distillation columns in biodiesel production. <u>Energy</u> (2011) : 1-10.

Omota F., Dimia A.C., and Bliek A. Fatty acid esterification by reactive distillation. Part 1: equilibrium-based design. Chemical Engineering Science 58 (2003) : 3159–3174.

Qiu, Z., Zhao, L., and Weatherley, L. Process intensification technologies in continuous biodiesel production. Chemical Engineering and Processing 49 (2010) : 323–330.

Thotla, S. and Mahajani, S. Reactive distillation with side draw. Chemical Engineering and Processing 48 (2009) : 927–937.

Santander, C.M.G., Rueda, S.M.G., Silva, N.D.L. da, Costa, A.C. da, Filho, R.M., and Wolf, M.R.M. Simulation of the reactive distillation process for biodiesel production. European Symposium on Computer Aided Process Engineering. 20 (2010).

Singh, A.P., Thompson, J.C., and He, B.B. A continuous-flow reactive distillation reactor for biodiesel preparation from seed oils. An ASAE/CSAE Meeting Presentation (2004) : 046071.

Sundram, K. Palm Oil: Chemistry and nutrition updates. Malaysian Palm Oil Board (MPOB).

Sundmacher, K., Qi, Z. Conceptual design aspects of reactive distillation processes for ideal binary mixtures. Chemical Engineering and Processing 42 (2003) : 191-200.

Tesser, R. Kinetics of oleic acid esterification with methanol in the presence of triglycerides. Ind. Eng. Chem. Res. 44 (2005) : 7978-7982.

Wang, S.J., Wong, D.S.H., and Yu, S.W. Design and control of transesterification reactive distillation with thermal coupling. Computers and Chemical Engineering 32 (2008) : 3030–3037.

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