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สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2558
ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

PROCESS SIMULATION OF CONTINUOUS BIODIESEL PRODUCTION
IN A REACTIVE DISTILLATION VIA TRANSESTERIFICATION
AND ESTERIFICATION OF WASTE COOKING OIL

Mr. Nattawat Petchsoongsakul



A Thesis Submitted in Partial Fulfillment of the Requirements
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Department of Chemical Engineering

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By	Mr. Nattawat Petchsoongsakul
Field of Study	Chemical Engineering
Thesis Advisor	Professor Suttichai Assabumrungrat, Ph.D.
Thesis Co-Advisor	Assistant Professor Kanokwan Ngaosuwan, Ph.D.

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

.....Dean of the Faculty of Engineering
(Associate Professor Supot Teachavorasinskun, D.Eng.)

THESIS COMMITTEE

.....Chairman
(Associate Professor Soorathep Kheawhom, Ph.D.)

.....Thesis Advisor
(Professor Suttichai Assabumrungrat, Ph.D.)

.....Thesis Co-Advisor
(Assistant Professor Kanokwan Ngaosuwan, Ph.D.)

.....Examiner
(Pimporn Ponpesh, Ph.D.)

.....External Examiner
(Assistant Professor Worapon Kiatkittipong, Ph.D.)

ณัฐวัตร เพชรสูงสกุล : การจำลองกระบวนการผลิตไบโอดีเซลแบบต่อเนื่องในหอกลั่นที่มี
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สาขาวิชา	วิศวกรรมเคมี	ลายมือชื่อ อ.ที่ปรึกษาหลัก
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This research focuses on biodiesel production in a reactive distillation via transesterification and esterification of waste cooking oil. Process simulations were performed by using Aspen Plus. Three different continuous processes for biodiesel production from waste cooking oil were developed to compare with a based case (conventional process). The first process employed a reactive distillation in biodiesel synthesis using homogeneous catalyst (NaOH). This process still required many process equipment to separate homogeneous catalyst from biodiesel product. The second process used heterogeneous catalyst instead of homogeneous catalyst for biodiesel synthesis. The number of process equipment was decreased but this process still need separation unit in the pretreatment step. The third process combining the pretreatment and biodiesel synthesis steps in a reactive distillation and using heterogeneous catalyst system (Amberlyst-15 and $\text{CaO}/\text{Al}_2\text{O}_3$) was proposed. This process required fewer number of process equipment and offered good performance compared to the other processes. Then, the effects of various operating parameters of the third process were investigated to find suitable condition. The efficient process can produce biodiesel yield of 99.50% under column pressure of 3 bar, methanol to oil ratio of 4:1 and reflux ratio 0.1.

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Chapter 1

Introduction

1.1 Introduction

Energy consumption is inevitable for human existence. There are many reasons that people are trying to find alternative energy fuel, or whether it is. This is because of the environmental concern, economic competition and locally available. First reason is the demand to use fossil fuel energy in all sectors of human life such as transportation, electricity production in each process for industry or residential consumption [1]. The present demand is steadily increasing, which affects the environment such as CO₂ emissions from energy usage causing of global warming. Energy consumption from statistics have been expected increasing by the rate of 53% per year until year 2030 For instance, petroleum consumption will rise from 84.4 to 116 million barrels per day in USA until year 2030 [2, 3]. Second reason is energy from fossil-fuel resources are non-renewable and they are going to run out in the future [4]. Finally reason is the volatility of fuel prices such as the price of crude oil, which affects countries with limited resources or lack [5]. For these reasons, thus resulting in the discovery and development of alternative energy or renewable energy. At present, there are many types of renewable energy such as wind solar, hydro nuclear, biofuel and biodiesel but all this is still in the research and development stage.

Biodiesel is a mono alkyl ester of a fatty acid that is produced from vegetable oils or animal fats [6, 7]. In other words when vegetable oils or animal fats react with alcohol, it can produce to fatty acid methyl ester (FAME), vegetable oil contains hydrocarbon saturated (triglycerides), which consists of glycerol moiety and ester of fatty acid chains. Fatty acid chain have different numbers of bonds and carbon chain lengths. There are different kinds of modification methods such as dilution, thermal cracking (pyrolysis), transesterification, and microemulsification to produce biodiesel from vegetable oils. However, transesterification is the best method for producing higher quality biodiesel [8-11]. All fatty acid sources such as animal fats or vegetable

oils (over 300 species) that can be used to produce biodiesel [12-16]. Taking advantage of these type of sources is causing some concern in the food chain materials [17, 18]. In other words, the production of biofuels from human nutrition sources that can cause a food crisis. Consequently, most research focuses on non-edible oil or waste cooking oil as feedstock for biodiesel production such as algae oil [19-21], microalgae [22-26], jatropha oil [27] and grease oil [28]. Moreover, the use of waste edible oil as feedstocks can reduce biodiesel production costs by 60-90% [29-33]. People around the world use edible oils for cooking, after that the oil is discarded. However, the water and free fatty acid (FFA) content in waste cooking oil have a negative influence on the transesterification [34, 35]. Hydrolysis of triglyceride will also take place in the presence of heat and water resulting to increase the percent of FFA in the oil [36]. Therefore, in order to produce biodiesel, well maintained, the amount of FFA and water must be eliminated or reduced before transesterification. There are various methods for biodiesel production from waste cooking oil which can be divided into three main groups: (a) homogeneous, (b) heterogeneous and (c) non-catalytic transesterification. Many types of design can be produced using batch reactor, membrane reactor, ultrasonic reactor, microwave reactor, reactive adsorption and reactive distillation unit etc. [37].

Reactive distillation is a process that included the chemical reaction and distillation column process for biodiesel production occur simultaneously in a single equipment. This is useful function for certain effects for one reaction or more reactants, (1) the reaction that needs to remove some of the products for completion (2) the recovery process of co-product recycling or product is complicated and (3) the mixture in process has the possibility for azeotrope formation. A variety of reactions with homogeneous catalyst and heterogeneous catalyst and without-catalyst can be carried out in the reactive distillation process, in which the operating condition such as pressure and temperature should be concerned as well as in the distillation unit to obtain a high product yield with high purity [38] The application of reactive distillation process has some advantages such as: continuous removal of product from reaction zone can eliminate the equilibrium conversion limitation and it can also decrease capital cost because both reaction and separation processes are carried out using the

same equipment. In addition, this integration unit requires the lower costs in piping and instrumentation, heat integration and pumps. There are many reactive distillation design for biodiesel production [39] However, the design process using reactive distillation can be carried out only one reaction in the column such as reactive distillation system as designed for transesterification of refined oil only to produce biodiesel [39, 40] etc. The aim of this work is concentrated on the biodiesel production using waste cooking oil as feedstock and designed process by the combination of individual pretreatment unit and reactive distillation for transesterification to produce biodiesel and designed simultaneous two reactions in a single column. Conceptual of this reactive distillation design consists of the top section for pretreatment waste cooking oil reaction to eliminate FFA and the bottom section for converting of triglyceride (main composition) to biodiesel. However, this concept should be noted that have to separate the main biodiesel product form other components.

1.2 Research Objectives

To propose the continuous process for biodiesel production from waste cooking oil (high FFA content) via simultaneous transesterification and esterification in a single reactive distillation column.

1.3 Scope of work

1. Design biodiesel production process using a single reactive distillation unit. Esterification of FFA and transesterification of triglyceride with methanol are considered. The simulation results are performed by Aspen Plus program. The purity of biodiesel, biodiesel yield and energy consumption are main consideration.

2. Compare the performances of a single reactive distillation with conventional process with proposed process (process I: pretreatment and reactive distillation unit and process II: 2 reactions on 2 reactive distillation units) regarding to purity of biodiesel and biodiesel yield.

3. Find suitable operating conditions of simultaneous esterification and transesterification in a single reactive distillation using heterogeneous catalyst. The

effects of important operating parameters (methanol to triglyceride feed molar ratio, feed temperature, reboiler duty and molar reflux ratio) and design parameters (number of reaction stage, number of rectifying stage and stripping stage, methanol and oil feed location) are optimized.

1.4 Expected Outputs

An efficient process for biodiesel production via simultaneous esterification and transesterification in a single reactive distillation column is expected.



Chapter 2

Theory

2.1 Biodiesel

2.1.1 What is biodiesel?

Biodiesel is an alternative fuel that can replace fossil energy. Biodiesel is a component of mono alkyl ester (methyl or ethyl ester) of long chain fatty acid such as methyl palmitate, methyl linoleate, methyl oleate, methyl stearate etc. Biodiesel can be used for diesel engines through 4 methods: blending with petro-diesel, pyrolysis, microemulsification (co-solvent blending), and transesterification [41]. In general, biodiesel will be produced from vegetable oil and alcohol using homogeneous catalyst or heterogeneous catalyst via transesterification. Properties of the mono alkyl ester of long chain fatty acid is shown in the Table 2.1 [42]. Moreover, the standard of biodiesel in a commercial provided for two types which are American Society for Testing and Materials (ASTM) D6751 or the European EN 14214 as shown in Table 2.2

Table 2.1 Properties of fatty acid alkyl esters [42]

Fatty acid alkyl ester	Formula*	Molecular weight [g/mol]	Higher heating value [MJ/kg]	Oxidation stability [h]	Kinematic viscosities [cSt]
Methyl palmitate	C _{16:0}	256.42	39.18	22.13	4.41
Methyl stearate	C _{18:0}	284.48	40.21	17.93	5.82
Methyl oleate	C _{18:1}	282.46	40.13	6.61	4.55
Methyl linoleate	C _{18:2}	280.45	40.06	4.37	3.69
Methyl linolenic	C _{18:3}	278.43	39.98	3.87	3.22
Ethyl palmitate	C _{16:0}	284.48	40.64	23.76	4.62
Ethyl stearate	C _{18:0}	312.53	41.98	21.77	5.92
Ethyl oleate	C _{18:1}	310.51	41.63	6.68	4.81
Ethyl linoleate	C _{18:2}	308.5	40.86	5.02	4.28
Ethyl linolenic	C _{18:3}	306.5	40.69	4.23	3.46

* Note: C_{a,b} describes a fatty acid with a carbon atoms and b double bonds

Table 2.2 Specification of biodiesel following ASTM and EN standards

Property/units	ASTM test method	ASTM limits	EN test method	EN limits
Oxidation stability at 110°C (h)	EN 14112	Min 3 h	EN-ISO 14112	Min 6 h
Cloud point (°C)	D-2500	-	EN-ISO 23015	-
Pour point (°C)	D-97	-	EN-ISO 3016	-
Cold filter plugging point (°C)	D-6371	-	EN 116	Variable
Cold soak (filterability/s (max))	D-7501	360	-	-
Viscosity at 40 °C (cSt)	D-445	1.9-6.0	EN-ISO 3104	3.5-5.0
Sulfated ash (% mass)	D-874	0.02 (max)	EN-ISO 3987	0.02 (max)
Sulfur (% mass)	D-5453 / D-4294	0.0015 (S15, max) 0.05 (S500, max)	EN-ISO 20846/ 20884	0.0010 (max)
Sodium and potassium (mg kg ⁻¹)	-	-	EN 14108/ 14109	5 (max)
Calcium and magnesium (mg kg ⁻¹)	-	-	EN 14538	5 (max)
Flash point (°C)	D-93	130 (min)	EN-ISO 3679	120 (max)
Cetane number	D-613	47 (min)	EN-ISO 5156	51 (min)
Methanol or ethanol (% mass)	-	-	EN 14110	0.20

Property/units	ASTM test method	ASTM limits	EN test method	EN limits
Copper strip corrosion	D-130	3 (max)	EN-ISO 10370	1 (max)
Phosphorus (% mass)	D-4951	0.001 (max)	EN 14107	0.001 (max)
Conradson carbon residue (100%) (% mass)	D-4530	0.05 (max)	EN-ISO 10370	0.3 (max)
Ester content (% mass)	-	-	EN 14103	96.5 (max)
Distillation temperature (°C)	D-1160	90% at 360°C	-	-
Total contamination (mg kg ⁻¹)	-	-	EN-ISO 12662	24 (max)
Water and sediment (% vol.)	D-2709	0.05 (max)	-	-
Neutralization value (mg KOH per gram)	D-664	0.5 (max)	EN-ISO 14104	0.5 (max)
Free glycerin (% mass)	D-6584	0.02 (max)	EN-ISO 14105/ 14106	0.02 (max)
Total glycerin (% mass)	D-6584	0.24 (max)	EN-ISO 14105	0.25 (max)
Monoglyceride content (% mass)	-	-	EN-ISO 14105	0.8 (max)

Property/units	ASTM test method	ASTM limits	EN test method	EN limits
Diglyceride content (% mass)	-	-	EN-ISO 14105	0.2 (max)
Triglyceride content (% mass)	-	-	EN-ISO 14105	0.2 (max)
Density (kg/m ³)	-	-	EN 3675	860-900
Lubricity at 60 C (WSD/ μ m)	-	-	-	-

2.1.2 Biodiesel feedstocks

Feedstocks for biodiesel production mainly consists of two reactants, namely vegetable oil (or animal fat) and alcohol. Shad and Jamal [43] has reported that there are over 300 different types of feedstock used to produce biodiesel. Table 2.3 shows the feedstock is divided into two groups: conventional and non-conventional biodiesel production.

Table 2.3 Conventional and non-conventional feedstocks used for the biodiesel production [43]

Conventional feedstocks		Non-conventional feedstocks
Mahua	Soybeans	Lard
Piqui	Rapeseed	Tallow
Palm	Canola	Poultry fat
Karang	Babassu	Fish oil
Tobacco seed	Brassica carinata	Bacteria
Rubber plant	Brassica napus	Algae
Rice bran	Copra	Fungi
Sesame	Groundnut	Micro algae
Sunflower	Cynaracardunculus	Terpenes
Cotton seed	Barley	Latexes
Coconut	Jatropha nana	Microalgae
Laurel	Jojoba oil	
Used cooking oil	Pangamiaglabra	

Palm oil, soy bean and sunflower oil are generally used as feedstocks for produce biodiesel. However, the composition of fatty acid each type of feedstocks as shown in Table 2.4 is related to alkyl ester composition in biodiesel such as molecular weight and physics properties of biodiesel.

Alcohol is another reactant for biodiesel production, methanol is a common choice for use in the reactions. This is due to methanol is also provided high activity than other long-chain alcohol. It also has a low boiling point, which makes separation by distillation and it is easier than alcohol with the higher molecular weight.

Table 2.4 Composition of fatty acid in each type of feedstock [44]

Source	Structure	Molecular weight (MW)		Typical composition, wt%				
		Fatty acid	Triglyceride	Jatropha	Palm	Canola	Soy bean	Sun flower
Capric	C _{10:0}	172.3	554.8	0.0	0.0	0.6	0.0	0.0
Lauric	C _{12:0}	200.3	639.0	0.0	0.0	0.0	0.0	0.0
Myristic	C _{14:0}	228.4	723.2	0.0	2.5	0.1	0.0	0.0
Palmitic	C _{16:0}	256.4	807.3	15.9	40.8	5.1	11.5	6.5
Palmitoleic	C _{16:1}	254.4	801.3	0.9	0.0	0.0	0.0	0.2
Stearic	C _{18:0}	284.5	891.5	6.9	3.6	2.1	4.0	5.8
Oleic	C _{18:1}	282.5	885.4	41.1	45.2	57.9	24.5	27.0
Linoleic	C _{18:2}	280.4	879.4	34.7	7.9	24.7	53.0	60.0
Linolenic	C _{18:3}	278.4	873.3	0.3	0.0	7.9	7.0	0.2
Arachidic	C _{20:0}	312.5	975.6	0.0	0.0	0.2	0.0	0.3
Eicosenoic	C _{20:1}	310.5	969.6	0.2	0.0	1.0	0.0	0.0
Behenic	C _{22:0}	340.6	1059.8	0.0	0.0	0.2	0.0	0.0
Erucic	C _{22:1}	338.6	1053.8	0.0	0.0	0.2	0.0	0.0
Estimated MW:				869.7	847.0	876.9	871.9	876.7

2.1.3 Catalyst for biodiesel production

The general biodiesel forming reaction can use homogeneous catalyst or heterogeneous catalyst. Common homogeneous catalyst for biodiesel production is alkali catalyst because these catalysts are cheap, readily available and can produce biodiesel at mild conditions with high yield in a short reaction time. However, alkali catalyst is very sensitive to water and high FFA content. If the feedstocks have high FFA content, it will cause a saponification reaction, which will decrease biodiesel yield. Similarly, as homogeneous catalyst in acid catalyst type. This catalyst can be used in biodiesel production, which can have the reaction as simultaneous esterification and transesterification. However, that catalyst has a very slow reaction rate resulting in the increase of reaction time. In addition, the main problem of the homogeneous catalyst is then difficult to separate from product which leads to many problems in downstream purification and biodiesel recovery process.

Heterogeneous catalyst that is interesting in that it could be replaced the conventional homogeneous catalyst. Heterogeneous catalyst gains more advantages in many aspects such as it is improved selectivity, avoiding the washing step of biodiesel, easy to separate the catalyst from the biodiesel product, reduced waste water problem, low product contamination and easy regeneration. However, it has some limitations including of more mass transfer resistance, slow reaction rate and possible obtained undesirable side reactions. Table 2.5 summarized the different technologies to produce biodiesel.

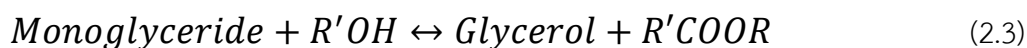
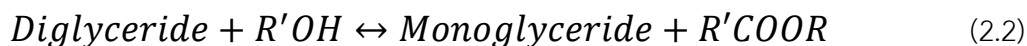
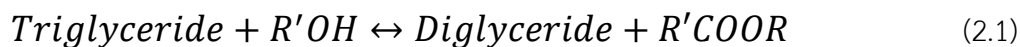
Table 2.5 Comparison of the different technologies to produce biodiesel [45]

Variable	Base Catalyst	Acid catalyst	Lipase catalyst	Supercritical alcohol	Heterogeneous catalyst
Reaction temperature (°C)	60 - 70	55 -80	30 - 40	239 - 385	180 - 220
Free fatty acid in raw materials	Saponified products	Ester	Methyl esters	Esters	Not sensitive
Water in raw materials	Interfere with reaction	Interfere with reaction	No influence	-	Not sensitive
Yield of methyl esters	Normal	Normal	Higher	Good	Normal
Recovery of glycerol	Difficult	Difficult	Easy	-	Easy
Purification of methyl esters	Repeated washing	Repeated washing	None	-	Easy
Production cost of catalyst	Cheap	Cheap	Relatively expensive	Medium	Potentially cheaper

2.2 Reaction forming in biodiesel production

2.2.1 Transesterification

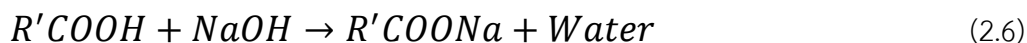
Transesterification considered to be composed of three small reversible reactions. Triglycerides (TGs) are converted to diglycerides (DGs) then, diglycerides are converted to monoglycerides (MGs) followed by conversion of monoglycerides to glycerol (Equation 2.1-2.3). Biodiesel may be produced in each of the converted, so the overall reaction for one molecule TGs will be able to produce 3 molecules of fatty acid alky-ester ($R'COOR$, biodiesel) as shown in Equation 2.4

Consecutive reactionsOverall reaction**2.2.2 Esterification**

Esterification is a reaction between alcohols and carboxylic acid to produce ester and water shown in Equation 2.5. Esterification will be take place when using oil with a high free fatty acid content in the reactant such as waste cooking oil. This condition can produce water as a by-product of esterification. This can cause other reaction (side reaction) called hydrolysis of triglyceride.

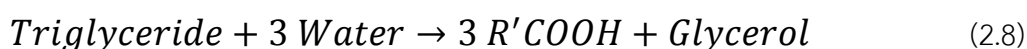
**2.2.3 Saponification**

Saponification is a reaction between carboxylic acids and strong base reactant such as sodium hydroxide (NaOH) or potassium hydroxide (KOH) to produce sodium soap (R'COONa) or potassium soap (R'COOK) respectively (shown in Equation 2.6 and 2.7).



2.2.4 Hydrolysis

Hydrolysis is a reaction involving the breaking of a bond in a molecule using water, the water molecules break bonds. Large molecules will be break down into smaller molecules such as the water can break the bonds of triglycerides into glycerol and FFAs ($R'COOH$) as seen in Equation 2.8. It will be seen that water molecules can also react to triglycerides. Therefore, if we have lots of water in the system or a taking place of esterification, biodiesel yield might be decreased.



2.4 Biodiesel production process

There are many techniques for biodiesel production. Conventional process it can be divided into two systems including of batch and continuous process. Batch process is a good process that flexibility to adapt or various types of feedstocks. The mainly reactions in this process will be transesterification. It is used as an acid or base catalyst, which also operate in this manner, it will make high operating cost but the equipment cost are low.

On the other side, continuous processes are preferred over batch processes in large-capacity commercial production scale because these processes result in the consistent product quality and low capital and operating costs per unit of product. However, these processes have disadvantages for using homogeneous catalyst. It requires the additional separation steps and processes generate waste streams into processes.

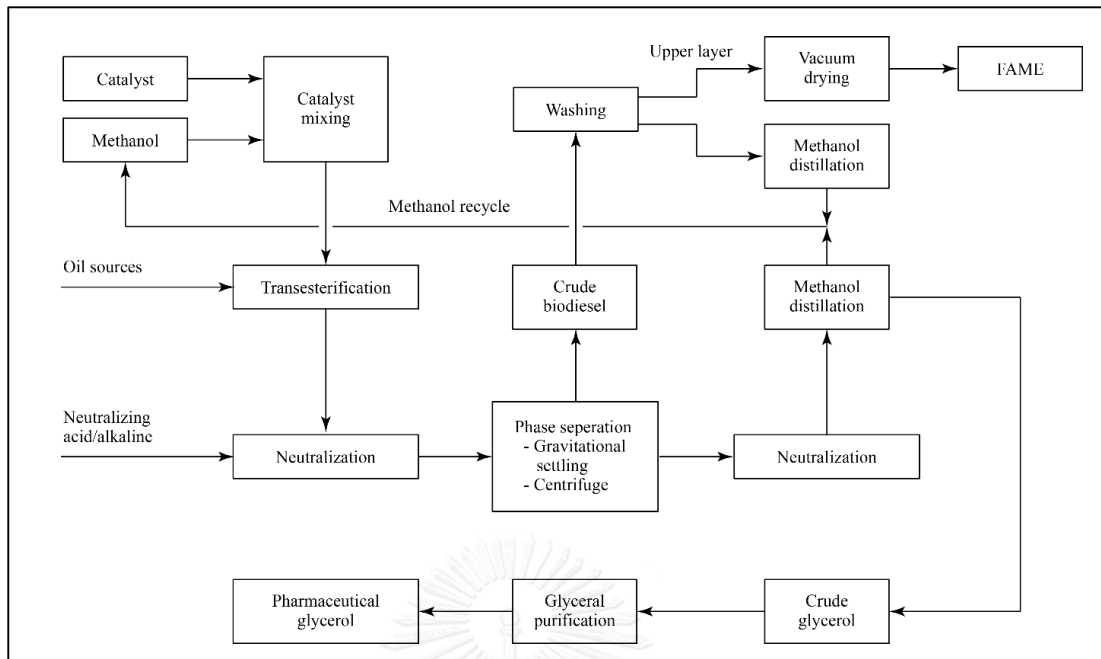


Figure 2.1 Process flow diagram of conventional homogeneous acid/alkaline catalyzed transesterification reaction [8]

Figure 2.1 shows process flow diagram of conventional homogeneous acid/alkaline catalyzed transesterification. Homogeneous catalyst is mixed with methanol to prepare alkali-methoxy to send it to react with oil via transesterification. The resulting product was enter to the catalyst neutralizing step to sorting out the product. It then passed into the decanting unit to separate polar and non-polar compounds from each other. The non-polar compound (crude biodiesel) and some methanol part will be purified through a process to make biodiesel purity and conform the standard. The polar compound containing methanol and glycerol are used for neutralizing any residual water and catalyst out. After that, the glycerol (by-product) will purified to valuable subtract for other process.

However, major quality related problems were encountered and it was main hindrance for large scale industrial production of biodiesel by homogeneously catalyzed transesterification. Production costs were rather high as the process involved number of washing and purification steps in order to meet the stipulated quality [46]. It was quite difficult to remove the traces catalyst remaining in the product and separation of glycerol also posed technical challenges. The higher amount of water

used in washing and consequent treatment of the resulting effluent added to the overall process cost. Therefore, heterogeneous catalyst is a good alternative to solve this problem for biodiesel production. This catalyst was easy to remove the traces remaining in the product but one disadvantage with use of solid catalyst is the formation of three phases together with oil and alcohol, which leads to diffusion limitations thus decreasing the rate of the reaction.

2.5 Reactive distillation

Reactive distillation column as a unit operation that caused the reaction and separation processes combined in a single unit. Considering reactive distillation column can be divided into three sections consist of rectifying, stripping section and reactive section as shown in Figure 2.2.

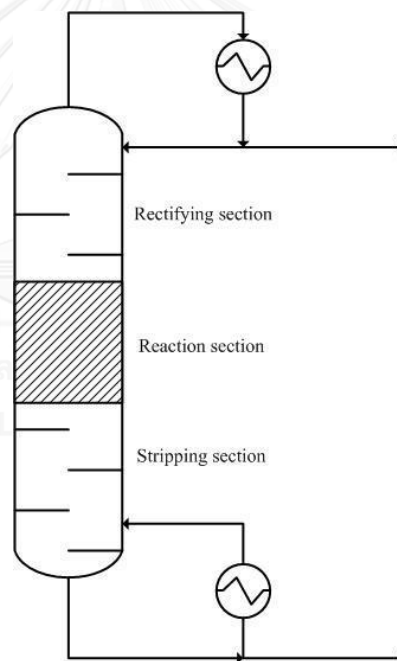


Figure 2.2 The general configuration of reactive distillation

The purpose of it is a reactive distillation column continuous removal of product from reactive zone to improve the conversion. Because it was shift equilibrium restrictions [40]. Apart from increased conversion the following benefits can be obtained:

- Reduced capital investment cost because it combines two process as a single process, thus reducing costs such as pump, piping and equipment.
- Reduce the use of catalysts for the reaction (compared to the same degree of conversion).
- Product selectivity can be improved by removing product from the reactive zone will cause the lead to reduction of side reactions.
- If a reaction occurs within reactive distillation column, the reaction is exothermic heat of reaction can be performed vaporization of liquid, the volume reboiler duty reduction (lower operation cost).

Reactive distillation column is limited by chemical equilibrium reactions such as etherification, dehydration, transesterification and esterification reactions. The nature of the chemical equation is shown in Equation 2.9 which A and B are reactants and C and D are products [47-49].

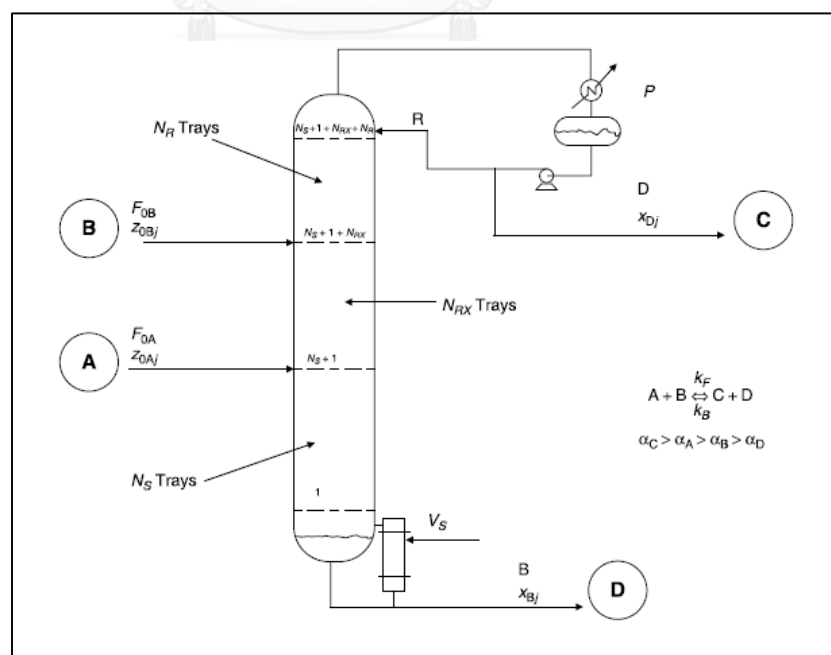


Figure 2.3 Ideal reactive distillation column [48]

Designed for reactive distillation column (ideal case), product C is light component when D is the heaviest component. The relative volatilities value of reactant and product are in a relationship together shown in Figure 2.3. In general design, a precursor to heavier (B) enter the stage at higher stage compared to substrate lighter (A) as seen in Figure 2.3. At that stage of the reaction (N_{RX} trays) are located between rectifying (N_R trays) and stripping (N_S trays) with product C, resulting in a system that is the lightest product to evaporate up into the top of the tower. In turn, the product D is the heaviest product is removed from the bottom of the tower in the form of a liquid phase. Rectifying section that will help to separate the product C from the heavier component. Similarly, stripping section to help isolate the product D from light components. For the above reasons make a production out of the column with high purity.

Temperature along the column is an important parameter for reactive distillation design because it affects the phase equilibrium and chemical kinetics. At the low temperature will slow the reaction rate which can be designed to increase liquid holdup (or increase amount of catalyst) in order to obtain a higher conversion. On the other hand, if high temperature operation will cause high reaction rate, which will result in the separation is done so rarely. For the above reasons, reactive distillation column should be considered in designing the appropriate operated with optimum temperature. Furthermore, there are other operating and design parameter should be considered including of pressure, reactive tray holdup, number of stage (stripping, reactive, rectifying), feed locations, reflux ratio and reboiler heat duty.

Chapter 3

Literature review

3.1 Conventional process and development for biodiesel production

The most common way to produce biodiesel is by transesterification, which refers to a catalyzed chemical reaction involving vegetable oil and an alcohol to yield fatty acid alkyl esters (i.e., biodiesel) and glycerol. Triacylglycerols (triglycerides), as the main component of vegetable oil, consist of three long chain fatty acids esterified to a glycerol backbone. When triglycerides react with an alcohol (e.g., methanol), the three fatty acid chains are released from the glycerol skeleton and combine with the alcohol to yield fatty acid alkyl esters (e.g., fatty acid methyl esters or FAME). Glycerol is produced as a by-product. Biodiesel production process via transesterification from vegetable oil was designed by Duffy and Patrick in 1853 [50]. In that work aims to produce glycerol for soap production and obtained biodiesel as by-product. After that in 1987, biodiesel can developed using sunflower oil as a feedstock. The obtained biodiesel offers same properties as those of petro-diesel. Biodiesel production has developed to improve process until present day.

Zhang and Dube [51], developed four different continuous process flowsheets for biodiesel production from virgin vegetable oil or waste cooking oil using alkaline or acidic conditions on a commercial scale. Four different continuous processes were designed and simulated. Two of them were alkali-catalyzed processes, one using virgin oil (process I) and the other using waste cooking oil (process II). The remaining two processes (process III and IV) were acid-catalyzed processes using waste cooking oil as a raw material. (Process flowsheet is shown in Figure 3.1 – 3.4). All of these processes proved to be feasible for producing a high quality biodiesel product. However, each process had its limitations. First process I, alkali-catalyzed process using virgin oil (Figure 3.1) was the simplest process using the least amount of process equipment but it required the higher raw material cost than other processes Next, process II is an alkali-catalyzed process using waste cooking oil (Figure 3.2). The aim of this process is to lower the cost of biodiesel by replacing virgin oil with waste cooking oil. It used from

waste cooking oil in a continuous alkali catalyzed process as same as process I (base case) and added a pretreatment unit as esterification of FFAs, glycerol washing and methanol recovery unit before transesterification unit. It was found in this process have the most complex process with the largest number of equipment unit because of the addition of a pretreatment unit for FFAs removal. Acid-catalyzed process using waste cooking oil or process III (Figure 3.3) is insensitive to any FFAs content in the oil. Consequently, process III was an acid catalyzed continuous process from waste cooking oil. In this process required less number of equipment than that of process II, but the large methanol was required resulting in more and larger transesterification reactor size, as well as a larger methanol distillation column. Finally, process IV was acid-catalyzed process using hexane extraction (Figure 3.4). In this process try to avoid the formation of emulsions due to water washing (change to hexane or petroleum ether as a solvent). This process needs to increase the number of process equipment and sizes of some separation units. In brief, for process simplicity, the alkali-catalyzed process using virgin vegetable oil (process I) is recommended. However, if raw material cost was also noticed, the acid-catalyzed process using waste cooking oil (process III) is a relatively simple process and proved to be a competitive alternative to processes I and II.

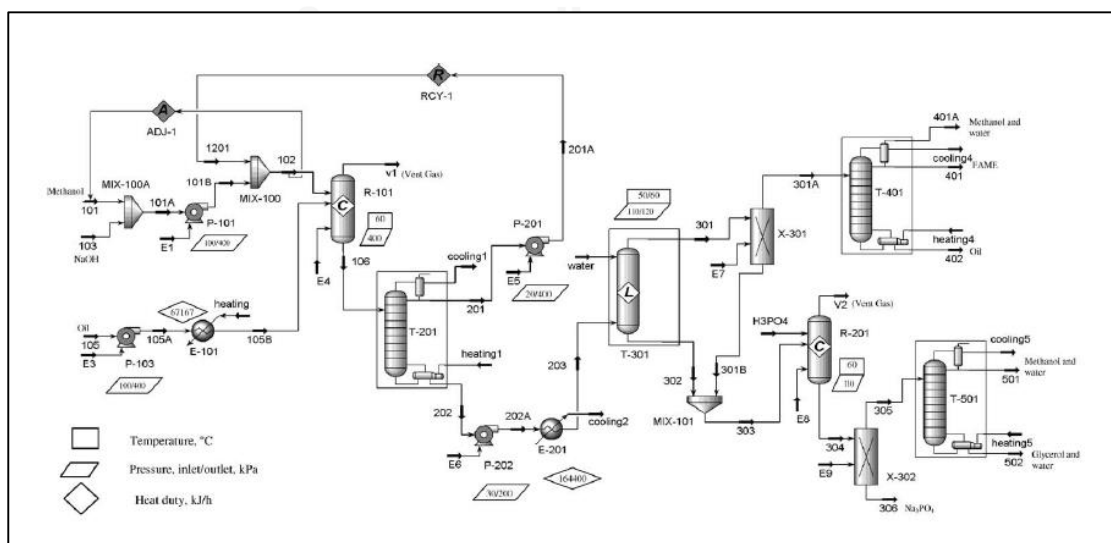


Figure 3.1 Alkali-catalyzed process to produce biodiesel from virgin oils.

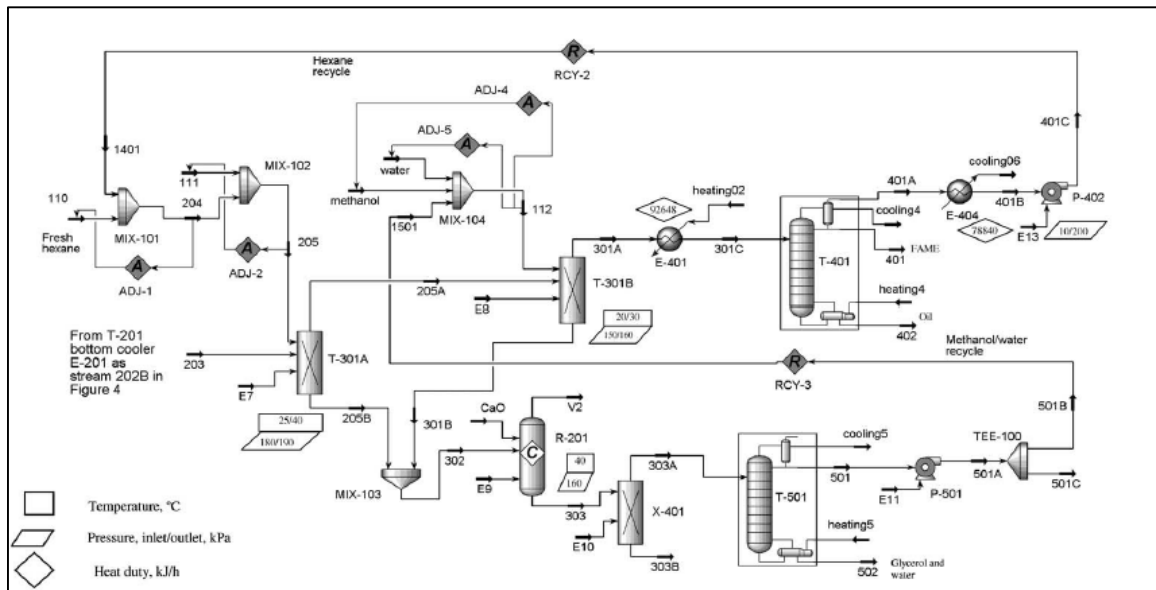


Figure 3.4 Alternative acid-catalyzed process to produce biodiesel from waste oils using hexane extraction.

3.2 Reactive distillation technologies for biodiesel production

Process intensification (PI) technologies play an important role on chemical processes. It improves the processes by reducing equipment volume, energy consumption, or waste formation, and ultimately leading to cheaper, safer, sustainable technologies. Reactive separation, which is combination of separation and reaction, offers new process alternatives that decrease energy consumption, improve the productivity and selectivity and reduce investment cost. According to the problems of conventional process of biodiesel production, multi-functional reactors were proposed to solve these problems such as membrane reactor, reactive distillation, reactive absorption and reactive extraction as demonstrate in Table 3.1.

Table 3.1 Overview of reactive separation process for biodiesel production

Process	Reaction type	Catalyst/solvent type	References
Reactive distillation	Transesterification	- Homogeneous (NaOH, KOH) - Heterogeneous (calcium oxide, sodium methoxide, tungstated zirconia, heteropolyacid)	[39, 52-54]
	Esterification	- Homogeneous (H ₂ SO ₄) - Heterogeneous (ion exchange resins, mixed metal oxides, sulfated zirconia)	[55-57]
Reactive absorption	Esterification	- Heterogeneous (mixed metal oxides, or sulfated zirconia)	[58]
Reactive extraction	Transesterification	- Homogeneous (H ₂ SO ₄ , NaOH with/out supported lipase)	[59]
Membrane reactors	Transesterification	- Homogeneous + Membrane (carbon, ceramic, zeolite)	[60]
	Esterification	- Hetero/Homogeneous + Membrane (PVA/PES)	[61]

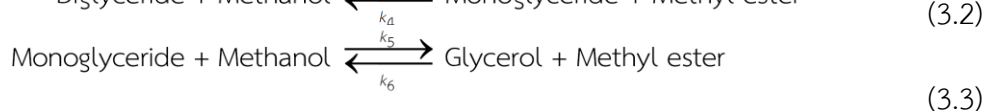
Lida Simasatitkul et al [62], proposed the use of a reactive distillation for transesterification of soybean oil and methanol catalyzed by sodium hydroxide to produce biodiesel. The aim of this work is to propose a reactive distillation using pure soybean oil to its low content of free fatty acid (less than 0.3%). Furthermore, the effect of various operating and design parameters on the performance of the reactive distillation for biodiesel production was also investigated including of effect of feed ratio of methanol and oil, effect of feed temperature, effect of reboiler heat duty, effect of a number of reactive stages and effect of feed location of methanol. The simulation results showed that a suitable configuration of the reactive distillation

column consists of three reactive stages. The optimal conditions for the reactive distillation operation are at the molar feed ratio of methanol and oil at 4.5:1, reflux ratio of 3, and reboiler duty of $1.6 \times 10^7 \text{ kJ h}^{-1}$. Methanol and soybean oil should be fed into the column at the first stage.

Mauro Banchero et al [63], proposed the process intensification through reactive distillation applied esterification of FFAs (long-chain fatty acid), which is a crucial step in the biodiesel synthesis (in a pretreatment step). The application of the reactive distillation technology has been analyzed by means of process simulation for the esterification of oleic acid with methanol. Simulations with a long-chain fatty acid and a pseudo-homogeneous second-order equilibrium kinetics are reported for the first time. Several different reactive distillation units were simulated and compared (top external recycle, top and bottom recycle and plug-flow reactor with methanol recycle). The reactive distillation column with a top external recycle allowed us to obtain a 90% of reactant conversion and proved to be the best solution among those examined because in these condition the reaction occurs under a large methanol excess even though the column.

3.3 Kinetic and mechanism of biodiesel forming reaction

Kinetic expressions and rate constants for each reaction are necessary information for process simulations. In transesterification reaction consists of three-step reactions in series are shown in Equations 3.1-3.3



Noureddini and Zhu [64] studied on biodiesel production from transesterification of soybean with methanol with three step reactions using sodium hydroxide catalyst (0.20 wt% based on soybean oil) on 1500 mL of reactor equipped with a mechanical stirrer. The effect of temperature in the range of 30 to 70°C on the

rate of reaction was studied while the molar ratio of alcohol to triglyceride was fixed at 6. The composition of triglyceride is similar to soybean oil. Methyl palmitate, methyl oleate and methyl linoleate (biodiesel) were taken as the product of transesterification, whereas glycerol was considered to be the by-product. The rate expressions are shown as following:

$$r_{TG} = -k_1[TG][A] + k_2[DG][E] \quad (3.4)$$

$$r_{DG} = k_1[TG][A] - k_2[DG][E] - k_3[DG][A] + k_4[MG][E] \quad (3.5)$$

$$r_{MG} = k_5[DG][A] - k_4[MG][E] - k_5[MG][A] + k_6[GL][E] \quad (3.6)$$

$$r_{GL} = k_5[MG][A] - k_6[GL][E] \quad (3.7)$$

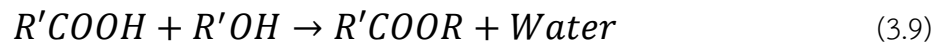
$$r_E = k_1[TG][A] - k_2[DG][E] + k_3[DG][A] - k_4[MG][E] + k_5[MG][A] - k_6[GL][E] \quad (3.8)$$

Where k_i is the rate constant of reaction i , and $[TG]$, $[DG]$, $[MG]$, $[GL]$, $[A]$ and $[E]$ are molar concentration of triglyceride, diglyceride, monoglyceride, glycerol, methanol, and methyl ester (biodiesel), respectively. The activation energy and reaction rate constant shown in the Table 3.2 were estimated by Arrhenius equation.

Table 3.2 Kinetic constants for transesterification when using sodium hydroxide as catalyst

Rate constant	k_i (L/mol/s)	E_a (J/mol)
k_1	3.90×10^7	54998.62
k_2	5.78×10^5	41555.44
k_3	5.91×10^{12}	83094.15
k_4	9.89×10^9	61249.51
k_5	5.34×10^3	26865.43
k_6	2.10×10^4	40116.15

Ming Chai et al. [65] investigated the kinetic of FFA pretreatment reaction using the used vegetable oil with 5 ± 0.5 % of FFA content and acid catalyst such as sulfuric acid. Acid catalyzed esterification is a reversible reaction as shown in Equation 3.9. However, for using of the significantly excessive methanol can assumed that the reverse reaction could be neglected. [66]



Hence, the activation energy can be determined by Arrhenius shown in Equation 3.10 where: k is the reaction rate constant (min^{-1}), A is the pre-exponential factor (min^{-1}) and E_a denotes the activation energy (J/mol) R and T stand for ideal gas constant (8.314 J/mol.K) and temperature (K), respectively. The results are listed in Table 3.3.

$$k = Ae^{\frac{-E_a}{RT}} \quad (3.10)$$

Table 3.3 The kinetic constants for esterification when using sulfuric acid as catalyst

Methanol-to- FFA molar ratio	Sulfuric acid (wt%) based on FFA	E_a (J/mol)	A	R^2
40	10	24440.67	207.41	0.96
50	10	23132.04	128.32	0.97
60	10	29235.35	1241.90	0.96

3.4 Biodiesel production by using heterogeneous catalyst

Kinetic expressions and rate constants for transesterification are indispensable information for process simulation. Heterogeneous catalyzed biodiesel forming reaction is more promising process to produce biodiesel from the transesterification of oil and alcohol. According to Nagaraju Pasupulety. et al. work [67], the kinetic of the transesterification with soybean oil and methanol using $\text{CaO}/\text{Al}_2\text{O}_3$ as solid base catalyst was studied. Transesterification is a reversible process as represented in Equation 3.11. Use of excessive alcohol can shift the chemical equilibrium toward the product mixture [68, 69]. The activation energy and the pre-exponential factor were calculated using linear regression of the experimental data reported and shown in Table 3.4.

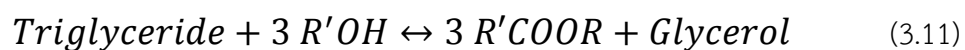


Table 3.4 Kinetic constants for transesterification when using CaO/Al₂O₃ as catalyst

Pre-exponential factor (A) (1/s)	0.5574
Activation energy (E _a) (J/mol)	30700

Besides transesterification, also the esterification of free fatty acid with alcohols (e.g. methanol) has been investigated. In contrast to these systems, information about the esterification of long chain carboxylic acids such as fatty acids by reactive distillation can hardly be found in Sven Steinigeweg and Jurgen Gmehling work [70]. Esterification of fatty acids is a common practice in the chemical industry. Fatty acid esters are important intermediates, surfactants, lubricants, or detergent. Heterogeneously catalyzed reactive distillation offers advantages over the homogeneously catalyzed process alternative (e.g., sulfuric acid). Size and location of the reactive section can be chosen regardless of thermodynamic constraints and at the same time corrosion problems will be minimized. The strongly acidic ion exchange resin Amberlyst-15 was used in this work. Furthermore, the values of kinetic constants and activation energy are given in Table 3.5 including of Langmuir-Hinshelwood-Hougen-Watson (LHHW) model and pseudo-homogeneous model.

Table 3.5 Kinetic constants for esterification when using Amberlyst-15 as catalyst

	Reaction	<i>i</i>	k_i^0 (mol/g.s)	$E_{A,i}$ (kJ/mol)
Pseudo-homogeneous model	esterification	1	9.1164×10^5	68.71
	hydrolysis	-1	1.4998×10^4	64.66
LHHW model	esterification	1	3.1819×10^6	72.23
	hydrolysis	-1	3.5505×10^5	71.90

Chapter 4

Process design and simulation

Process design is performed when developing new technologies, creating new facilities, or retrofitting of the existing production process. Therefore, data gathering information or details of the process synthesis, is important for the design and optimization technical process with increasing demands for sustainable growth.

In this section, the design flowsheet for sustainable process synthesis and design presented together with its implemented computer-aided methods and simulation software. The flowsheet allows the designer to assess the sustainability potential of a specified production process. The computer-aided methods and simulation software are also required to generate and more sustainable processing alternatives to meet the process product specifications. In this chapter, to assess the commercial feasibilities of the proposed processes, complete process simulations were first carried out. Despite some expected differences between process simulation results and actual process operation, most current simulation software can provide reliable information on process operation because of their comprehensive thermodynamic packages, vast component libraries and advanced calculation techniques. Aspen Plus program is used as process simulation software. The overview of framework proposed by Zhang and Dube [51] consists of four steps involving a pretreatment, an acid catalyst separation, a biodiesel synthesis and purification step, respectively. That are briefly discussed in Figure 4.1.

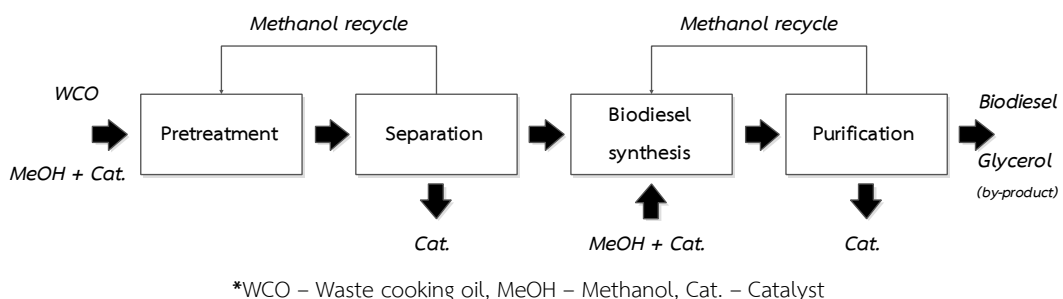


Figure 4.1 The overall design flowsheet for biodiesel production process by using waste cooking oil

Step-I: Pretreatment

The objective here is to pretreat waste cooking oil via esterification. Esterification of free fatty acid was carried out using 6:1 molar ratio of methanol to crude oil. Fresh methanol, recycled methanol stream and H_2SO_4 (acid homogeneous catalyst) stream were mixed together before pumping into esterification reactor. The waste cooking oil stream containing of 6 wt% free fatty acids was heated in the heat exchanger before entering reactor, all of free fatty acid was converted to fatty acid methyl ester (FAME). Then, it was cooled to prepare for feeding to the next step.

Step-II: Acid catalyst separation

The objective here is to completely remove water and acid catalyst (H_2SO_4) from pretreatment step before transport to biodiesel synthesis step (transesterification) by adding glycerol at ambient temperature. All resulting waste was removed from oil stream before sending to biodiesel synthesis step. For the other streams (unreacted methanol, glycerol, sulfuric acid (H_2SO_4), water and traces of esters) were flow into the recovery process to recover methanol back into pretreatment step.

Step-III: Biodiesel synthesis

The objective here is to produce biodiesel in a transesterification reactor using base catalyst (NaOH). Transesterification was carried out with a 6:1 molar ratio of methanol to oil (from step-II), 1 wt% of NaOH (based on oil). Fresh methanol, recycled methanol and anhydrous NaOH were mixed prior to pumping into reactor. 95% of triglyceride was converted to FAME and glycerol as a by-product.

Step-IV: Biodiesel purification

The objective here is to separate FAME from reaction mixture (glycerol, methanol and catalyst). Although FAME can separate by using a gravity settler, a complete separation could not be achieved under the operating condition based on Zhang and Dube [51] simulation results. Consequently, a water washing column was also used. FAME in outlet stream was separated from the glycerol, methanol and catalyst by adding water. In order to obtain a final biodiesel product following to ASTM specifications (greater than 99.6%), FAME distillation unit was also used. Methanol and water were removed in this column as overhead product (vent gas). FAME product was

obtained in liquid distillate (99.65%). Unconverted oil was remained at the bottom stage and only a small amount of unconverted oil was found. Moreover, glycerol, methanol and catalyst were fed to neutralization in reactor to remove NaOH (catalyst) by adding phosphoric acid (100% purity) after purification of FAME. The resulting Na_3PO_4 was removed in gravity separator. When potassium hydroxide is used as an alkali catalyst, the resulting potassium phosphate may be used as a valuable by-product (e.g., fertilizer). 85% of glycerol was found in stream after removing of the catalyst. If a glycerol as a by-product was required with the higher purity (e.g., 92%), this stream might be sent to distillation column for further removal of water and methanol. Water and methanol were removed in distillate unit at the bottom stage. 92% of glycerol was obtained as a high quality of by-product.

4.1 Process design

Zhang and Dube [51] were proposed the continuous biodiesel production process as a based case of this research. Similarly, this process can be divided unit operation equipment in two types, namely reactive or reaction equipment and separation equipment. Reactive distillation can improve production rate and decrease capital cost investment. As a result, this work aims to modify a continuous biodiesel production process by using waste cooking oil as biodiesel feedstock in a reactive distillation. Three different continuous flowsheet configuration were designed and simulated.

4.1.1 Process I - Based case (Zhang and Dube work [51])

The low cost biodiesel production process might be obtained by using waste cooking oil. Usually, free fatty acids content in waste cooking oil is about 6 wt% [51]. A pretreatment step can reduce the free fatty acid content via an esterification with methanol in the presence of sulfuric acid catalyst. Kinetic model of acid-catalyzed esterification with methanol was also investigated by Ming Chai et al. [65]. Due to the presence of the highly polar components including of methanol and glycerol, both the non-random two liquid (NRTL) and universal quasi-chemical (UNIQUAC)

thermodynamic/activity models were recommended to predict the activity coefficients of these components in a liquid phase.



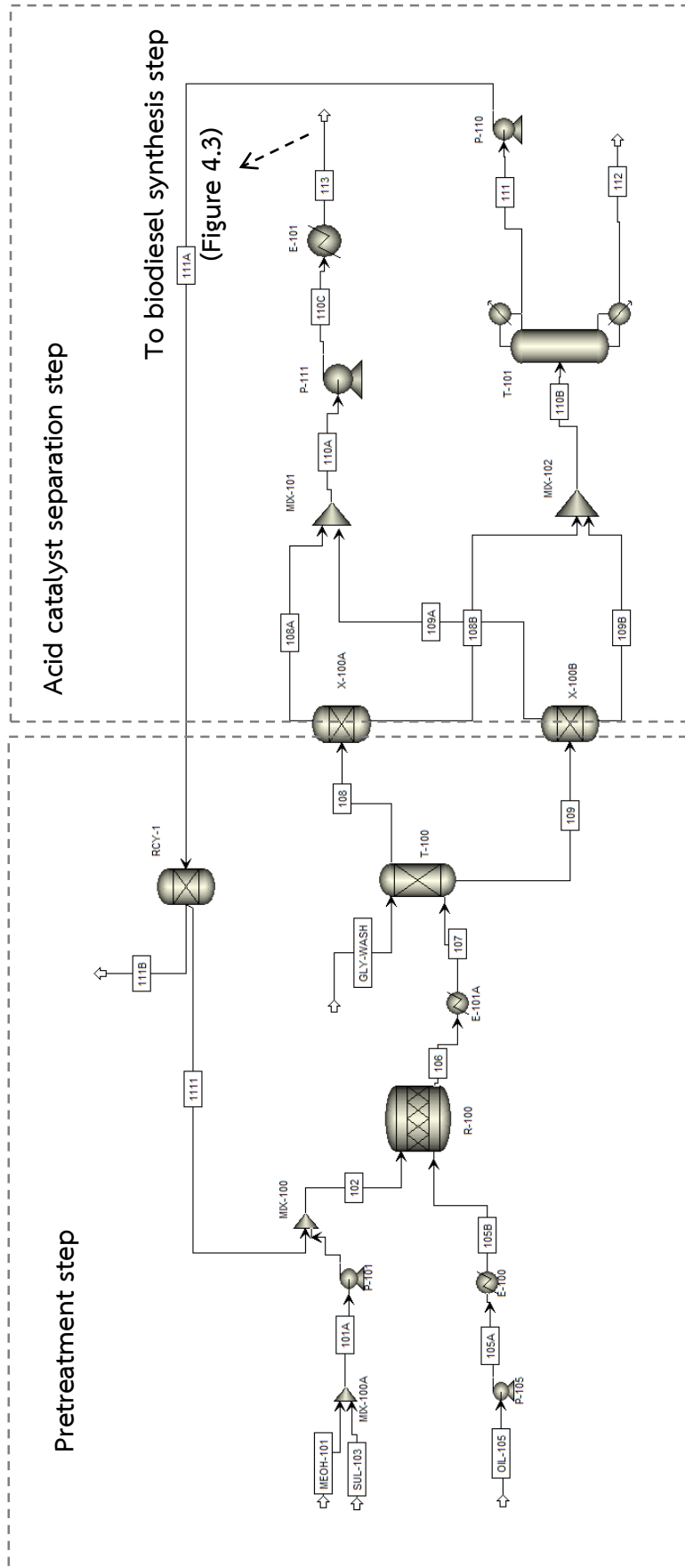


Figure 4.2 Process flow diagram of biodiesel production – pretreatment step and acid catalyst separation step

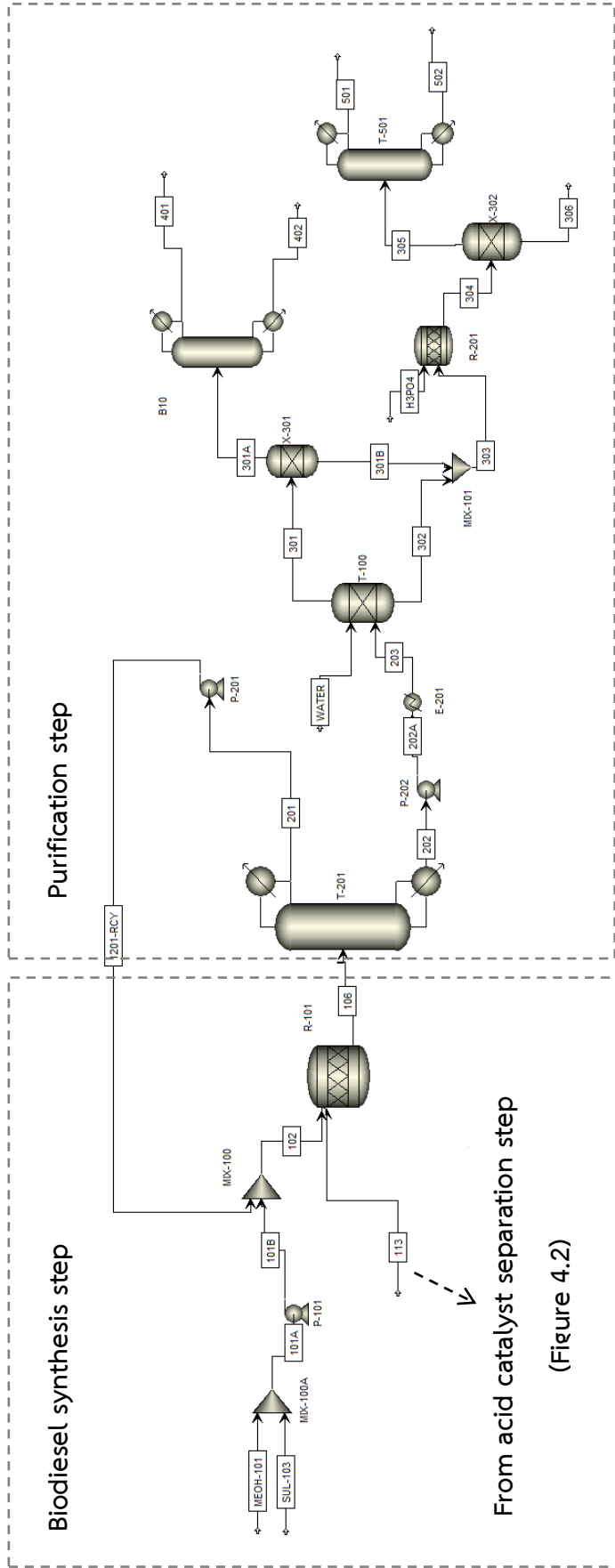


Figure 4.3 Process flow diagram of biodiesel production – biodiesel synthesis step and purification step

From acid catalyst separation step
(Figure 4.2)

The process flow diagram of process I – based case is illustrated in Figure 4.2-4.3 and units and methods applied for this simulation are shown as following:

Pretreatment step

- Pretreatment reactor (R-100): RStoic

Acid catalyst separation step

- Distillation to recover unconverted methanol (T-101): RadFrac
- Liquid extraction to wash triglyceride (T-100): Extract

Biodiesel synthesis step

- Transesterification reactor or synthesis reactor (R-200): RCSTR
- Distillation to recover unconverted methanol (T-201): RadFrac

Purification step

- Water washing to separate FAME from the glycerol, methanol and catalyst (T-301): Extract
- Purification distillation column (T-401, T-501): RadFrac
- Catalyst removal reactor (R-201): Rstoic

4.1.2 Process II - Modified by using reactive distillation system in biodiesel synthesis step.

From process I – based case, it was found that many equipment in purification stage were required after biodiesel synthesis step. On the other hand, it was complicate to purified product through compliance process I. Many equipment (distillation and extraction) were used leading to obtain high capital cost investment. For this drawback, reactive distillation can decrease the capital cost of purification equipment. Hence, process II was modified by using reactive distillation column in biodiesel synthesis step (Figure 4.4). On the other side, in process II still used same pretreatment unit and acid separation unit as well as process I (Figure 4.1).

Due to the modification with installation of reactive distillation column which is different form process I for biodiesel production using waste cooking oil as a feedstock. In biodiesel synthesis step, transesterification was carried out in reactive

distillation only meanwhile methanol with the lowest boiling point component was vaporized into top of column and recycled to mix with fresh methanol and catalyst (NaOH) for preparation to feed into column again. Furthermore, FAME, glycerol and some NaOH with higher boiling point components than that of methanol was flowing down to bottom of column. Then, the bottom stream was sent into purification step. Water was used to wash to FAME separating from the other components in the purification step. Glycerol distillation unit is require to increase glycerol purity.

The units and methods applied for this simulation are shown as following:

Pretreatment step and acid catalyst separation step: same process I

Biodiesel synthesis step

- Reactive distillation to produce biodiesel (RD-201): RadFrac

Purification step

- Water washing to separate FAME from the glycerol, methanol and catalyst (T-301): Extract
- Purification distillation column (T-401, T-501): RadFrac
- Catalyst removal reactor (R-201): Rstoisic

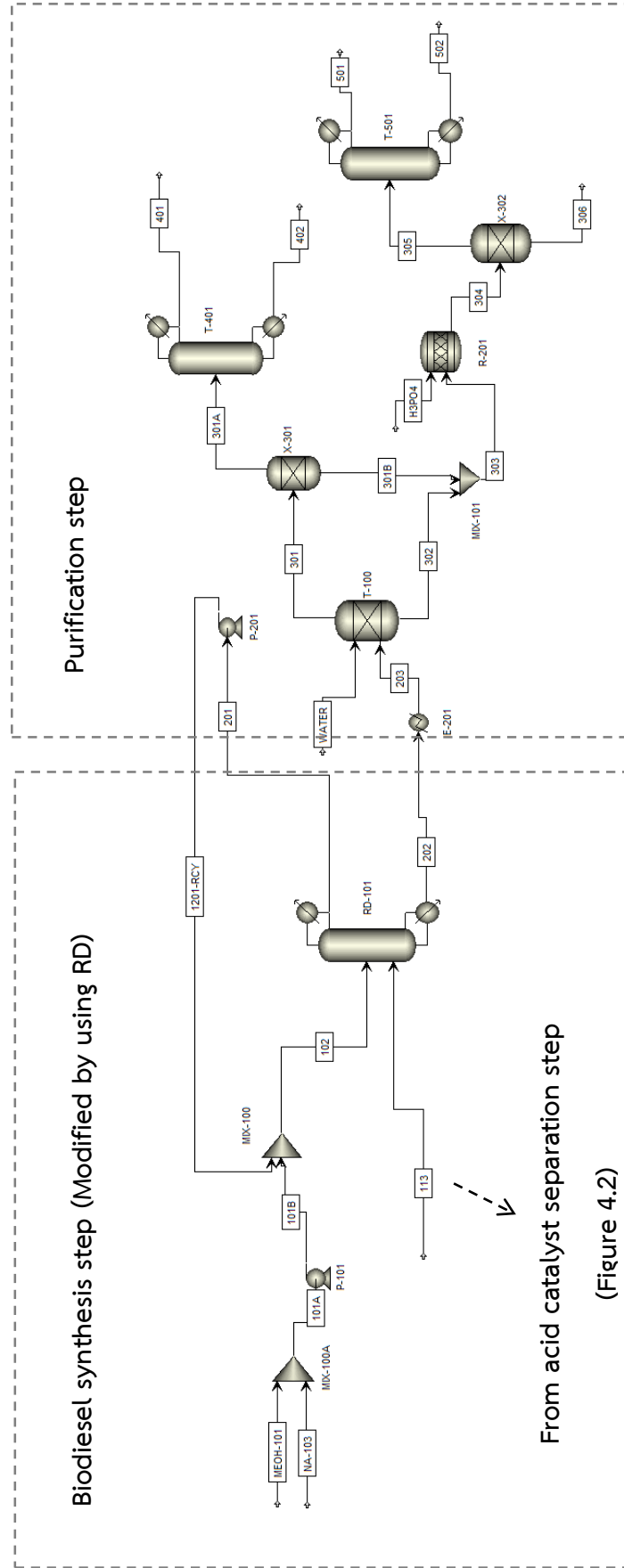


Figure 4.4 Process flow diagram of biodiesel production – modified biodiesel synthesis step by using reactive distillation and purification step

From acid catalyst separation step
(Figure 4.2)

4.1.3 Process III - Modified by using of reactive distillation with heterogeneous system in biodiesel synthesis step.

Due to the results from process II – modified by using of reactive distillation system in biodiesel synthesis step with homogeneous catalyst system (Figure 4.4) showed the complicated equipment for biodiesel production and purification as well as found in part of separation of NaOH catalyst from product and by-product. In order to design the feasible process, heterogeneous catalyst should be used in this process. Hence, calcium oxide on alumina catalyst ($\text{CaO}/\text{Al}_2\text{O}_3$) was used instead of NaOH catalyst for biodiesel synthesis step (Figure 4.5).

As a result, using $\text{CaO}/\text{Al}_2\text{O}_3$ as catalyst in biodiesel synthesis process and modified by using reactive distillation to produce biodiesel, can reduce distillation or separation unit in purification step because this process does not need equipment to separate homogeneous catalyst (NaOH) where solute in the reaction mixture.

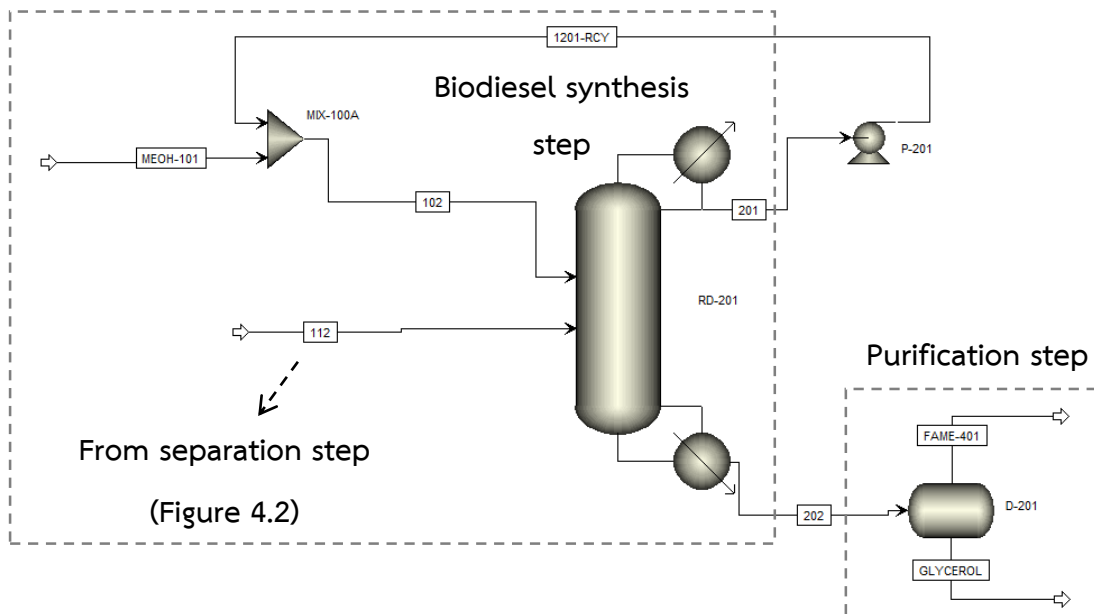


Figure 4.5 Process flow diagram of biodiesel production in heterogeneous catalyst system –modified by using of reactive distillation with heterogeneous system in biodiesel synthesis step

The units and methods applied for this simulation are shown as following:

Pretreatment step and acid catalyst separation step: same process I

Biodiesel synthesis step

- Reactive distillation to produce biodiesel (RD-201): RadFrac

Purification step

- Decanter to separate biodiesel and glycerol (D-201): Decanter

4.1.4 Process IV - Modified by combination of pretreatment and biodiesel step in a reactive distillation column

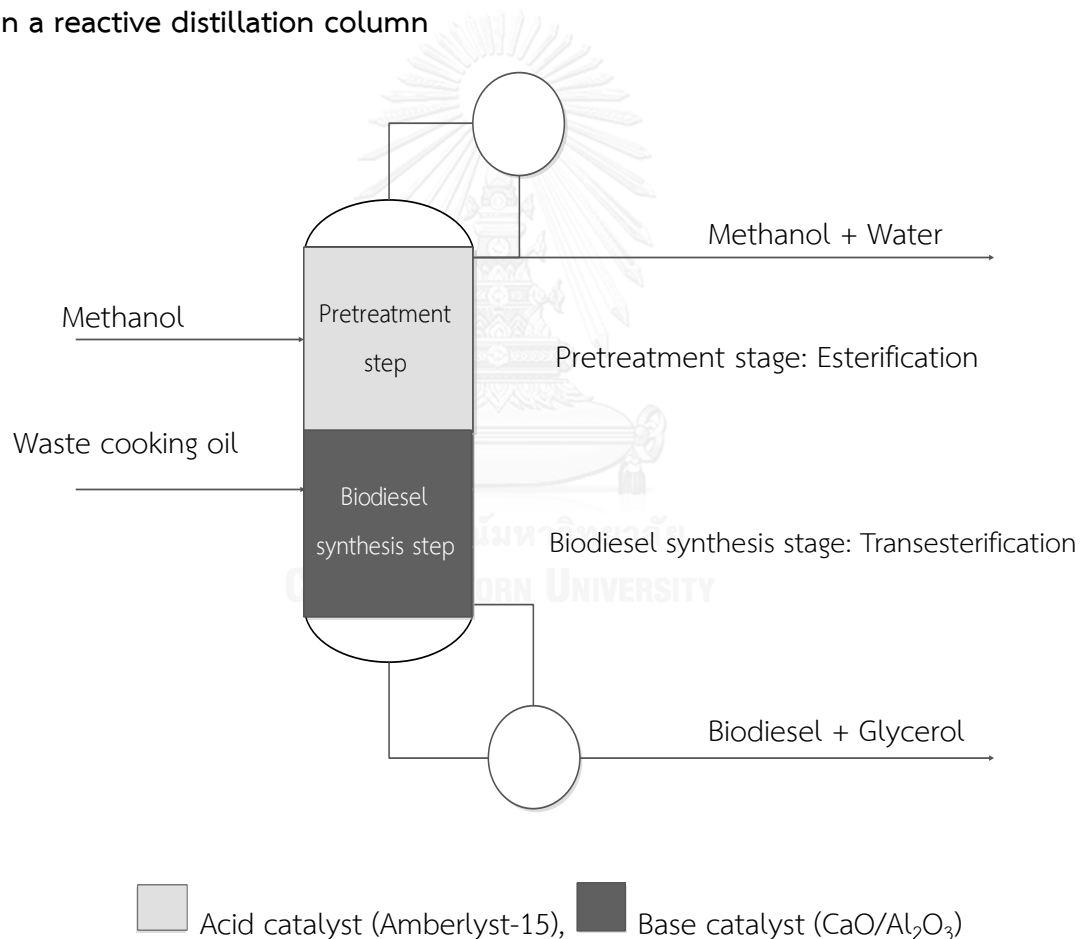


Figure 4.6 Process flow diagram of biodiesel production using heterogeneous catalyst system – modified pretreatment and biodiesel synthesis step in a reactive distillation

Process IV is a process that is particularly interesting because this process used only one reactive distillation unit for biodiesel production (Figure 4.5). Heterogeneous catalyst was used in pretreatment step (Amberlyst-15 was used instead of sulfuric acid) and biodiesel synthesis step (CaO/Al₂O₃ was used instead of NaOH catalyst). Therefore, this process do not need acid catalyst separation in the pretreatment step and also in biodiesel synthesis step. Moreover, the difference in heterogeneous catalyst type is leading to obtained different reaction taking place. The pretreatment step can reduce free fatty acid content via esterification while biodiesel synthesis can produce biodiesel via transesterification in a reactive distillation column. Likewise, acid catalyst can catalyze esterification while base catalyst gives higher catalytic activity for transesterification. As a result, this can design using different catalysts type can control the reaction type. Besides, both reactions required the similar reactant as methanol. The modification of reactive distillation to produce biodiesel gives more advantage as making lower amount of methanol in column. After completely reaction in reactive distillation, product downstream (FAME and glycerol) was fed into purification step using only decanter to separate biodiesel from glycerol.

4.2 Definition

This research aims to find the suitable operating condition of biodiesel production processes to obtain high process performance and reduce the unit operation. The performance of process are defined by:

Production yield

- Biodiesel produce via esterification (pretreatment step)

$$ESTER Yield (\%) = \frac{F_{FAME}}{F_{FFA,0}} \times 100\%$$

- Biodiesel produce via transesterification (biodiesel synthesis step)

$$FAME Yield (\%) = \frac{F_{FAME}}{3 \times F_{TG,0}} \times 100\%$$

- However, process IV could not define the actual biodiesel yield obtained from which step (pretreatment or biodiesel synthesis step) because the biodiesel product have same component. Thus, this process should be defined FAME yield as:

$$FAME \text{ Overall Yield (\%)} = \frac{F_{FAME}}{(3 \times F_{TG,0}) + F_{FFA,0}} \times 100\%$$



CHAPTER 5

RESULTS AND DISCUSSION

This chapter presents results and discussion of simulation studies of biodiesel production processes. The processes were simulated by using Aspen plus program. The results of interest are including of pretreatment efficiency, biodiesel production, biodiesel purity and energy requirement at various operating conditions of the process.

5.1 Validation of biodiesel production process

Since this work studied the simulation process for several biodiesel production processes (using homogeneous catalyst or using heterogeneous catalyst), the validation part of these process is necessary to confirm the feasibility of the simulation model. Therefore, this section is evidently presented the validation of these catalyst kinetic data and process I (based case) with previously published papers as shown in section 5.1.1 – 5.1.2.

5.1.1 Kinetic data validation

(1) Kinetic data for transesterification using sodium hydroxide validation

For homogeneous catalyst process, the simulation result in biodiesel synthesis step were validated with the results from Nouredini and Zhu [64]. This published kinetic data was obtained by using NaOH as a homogeneous catalyst to produce biodiesel via transesterification reported experiment and simulation data for model validation. Hence, the simulation result for this kinetic data compared with the experimental data [64] is exhibited in Figure 5.1.

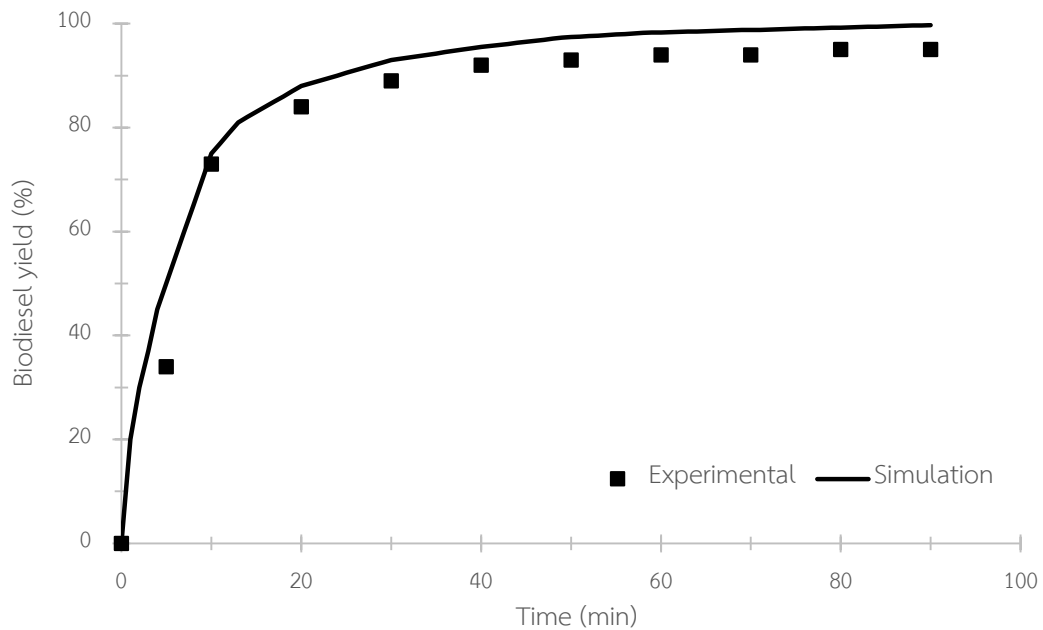


Figure 5.1 Model validations of kinetic model catalyzed by sodium hydroxide using temperature of 50 °C and methanol to oil ratio of 6:1.

Figure 5.1 showed that the result from this work was in good agreement with those data reported by Nouredini and Zhu. [64]. Therefore, this kinetic data was acceptable for further investigation for transesterification using homogeneous catalyst in biodiesel synthesis step.

(2) Kinetic data for esterification using Amberlyst-15 validation

The kinetic data for pretreatment step by using heterogeneous catalyst was also validated using Amberlyst 15 as a solid acid catalyst to catalyze esterification in pretreatment step. There is the published report by Sven Steinigeweg and Jurgen Gmehling [70], providing the necessary data. That research studied the Katapak-S of Amberlyst-15 in a reactive distillation experiment. The validation results in terms of conversion and reflux ratio are provided in Figure 5.2.

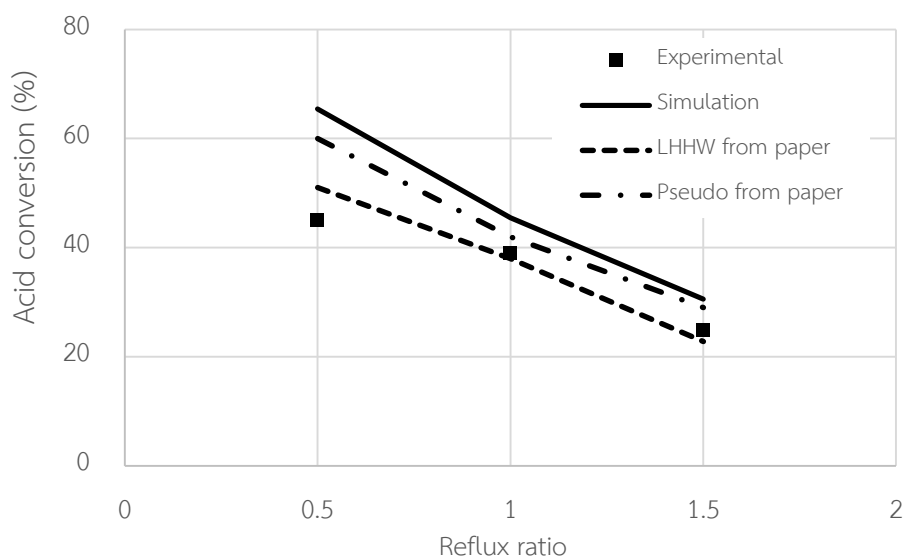


Figure 5.2 Model validations of kinetic data using Amberlyst-15
(Conversion as a function of reflux ratio using packing of Katapak-SP)

From the results reported by Sven Steinigeweg and Jürgen Gmehling [70], the validation results was a bit different from experiment data due to the limit of kinetic model used for reactive distillation. They found that Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic model was more fitted to the experiment result than that of pseudo-homogeneous kinetic model. However, pseudo-homogeneous kinetic model was used to simulate heterogeneous catalyzed esterification in reactive distillation as a pretreatment step due to the limitation of software.

(3) Kinetic data for transesterification using calcium oxide supported on Al_2O_3 validation

Kinetic expressions and rate constant for transesterification are indispensable information for process simulation. In this work, heterogeneous base catalyst is considered to produce biodiesel from biodiesel synthesis via transesterification of triglyceride and alcohol. The kinetic data was obtained by using $\text{CaO}/\text{Al}_2\text{O}_3$ as a catalyst according to Nagaraju Pasupulety et al. work [67]. The simulation result for this kinetic data was comparable to the experimental data [67] as exhibited in Figure 5.3.

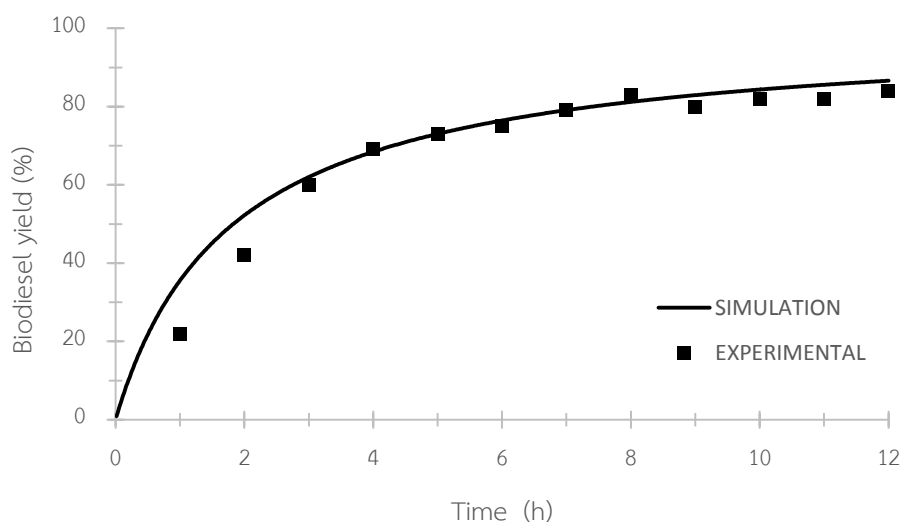


Figure 5.3 Model validations of kinetic model catalyzed by $\text{CaO}/\text{Al}_2\text{O}_3$

(Reaction conditions: temperature 150 °C, methanol/oil mole ratio 9:1 and catalyst concentration of 3 wt%)

Figure 5.3 confirmed that the simulation results of biodiesel yield was in good agreement with the previous results Nagaraju Pasupulety et al. [67]. Thus, this simulation kinetic data was reasonable to use to study the variable parameter affected on transesterification in biodiesel synthesis.

5.1.2 Process I – validation

In addition, the validation of kinetic data, the process validation is important thing for comparison with other cases. Zhang and Dube work [51] was used as a based case of this research. This process was designed for biodiesel production using raw material as a waste cooking oil through a similar process where discussed in Chapter 4. In Zhang work, the homogeneous catalyst system for biodiesel production (catalyst: sulfuric acid for pretreatment step and sodium hydroxide for biodiesel synthesis step) was proposed. These two-steps required a catalyst separation unit to remove homogeneous catalyst. The validation data was shown in Table 5.1 below.

Stream name	301A		305		306		401	
	[51]	This work	[51]	This work	[51]	This work	[51]	This work
Temperature	59.0	60.0	60.0	60.0	60.0	60.0	217.8	241.2
Pressure	120	120	120	110	120	110	20	20
Molar flow	3.48	3.27	3.97	2.31	0.09	0.10	3.38	3.38
Mass flow	1048.19	1050.23	152.61	125.75	15.03	15.30	997.29	1001.60
Liquid volume flow	1.194	1.328	0.134	0.108	0.006	0.007	1.137	2.950
Component mass fraction								
Methanol	0.001	0.001	0.037	0.118	0.000	0.000	0.000	0.000
Triglyceride	0.047	0.047	0.000	0.000	0.000	0.000	0.001	0.002
FAME (biodiesel)	0.952	0.951	0.006	0.000	0.000	0.000	0.997	0.997
Glycerol	0.000	0.000	0.633	0.768	0.000	0.000	0.000	0.000
H ₂ SO ₄	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
NaOH	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
H ₂ O	0.001	0.001	0.324	0.115	0.000	0.000	0.002	0.001
Oleic acid (Free fatty acid)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
H ₃ PO ₄	0.000	0.000	0.000	0.000	0.000	0.107	0.000	0.000
Na ₃ PO ₄	0.000	0.000	0.000	0.000	1.000	0.893	0.000	0.000

Stream name	402		501		502	
	[51]	This work	[51]	This work	[51]	This work
Temperature	434.2	451.7	64.7	65.7	107.6	109.1
Pressure	30	30	40	40	50	50
Molar flow	0.05	0.05	2.02	2.02	1.95	1.92
Mass flow	48.62	48.62	38.87	38.91	113.74	113.84
Liquid volume flow	0.054	0.036	0.040	0.043	0.094	0.097
Component mass fraction						
Methanol	0.000	0.000	0.146	0.146	0.000	0.000
Triglyceride	1.000	1.000	0.000	0.000	0.000	0.000
FAME (biodiesel)	0.000	0.000	0.000	0.000	0.008	0.007
Glycerol	0.000	0.000	0.000	0.000	0.850	0.850
H ₂ SO ₄	0.000	0.000	0.000	0.000	0.000	0.000
NaOH	0.000	0.000	0.000	0.000	0.000	0.000
H ₂ O	0.000	0.000	0.854	0.854	0.142	0.143
Oleic acid (Free fatty acid)	0.000	0.000	0.000	0.000	0.000	0.000
H ₃ PO ₄	0.000	0.000	0.000	0.000	0.000	0.000
Na ₃ PO ₄	0.000	0.000	0.000	0.000	0.000	0.000

Table 5.1, shows the comparison of the results of between previous work and our simulation. The results from this work were in good agreement with those data reported by Zhang [51].

5.2 Process II - Modified by using reactive distillation system in biodiesel synthesis step.

As mentioned above, in Chapter 4 on improving processes from Process I. Process II are applied reactive distillation to help in the biodiesel synthesis step. A simple flow diagram is shown below.

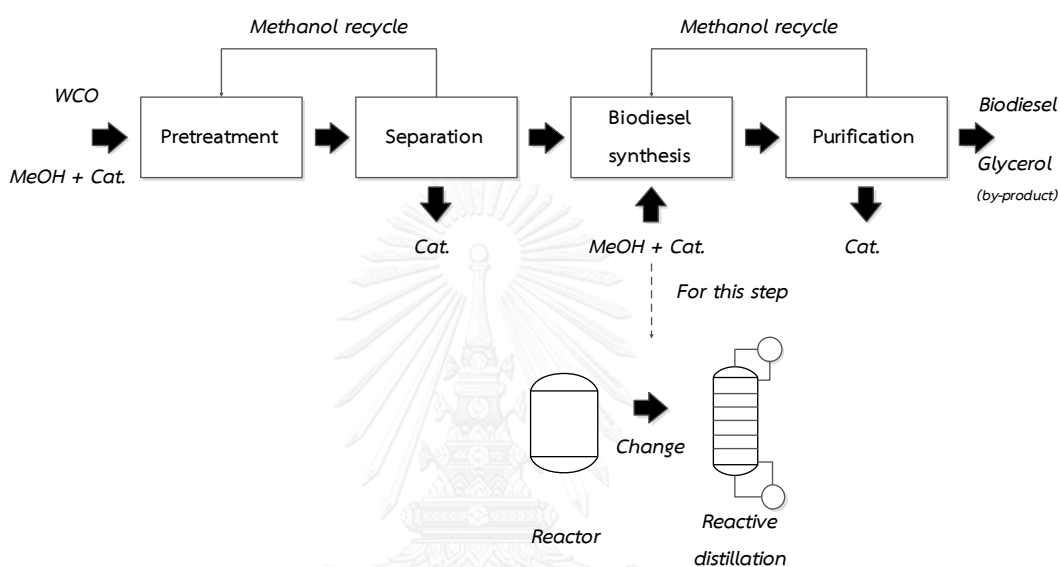


Figure 5.4 Process II flow diagram and improve reactive distillation concept

The pretreatment process where used process from the based case or process I. After pretreatment step and acid catalyst separation step, triglyceride was feed into the reactive distillation to react with methanol and NaOH (co-reactant and the catalyst) in this column. Using 22 actual stages (20 reactive stages), methanol to oil ratio of 4:1, and reflux ratio of 1, triglyceride, methanol and catalyst were fed into the 2nd stage. Biodiesel yield was obtained for 98.32 % and liquid composition, vapor composition and temperature profiles, are shown below. (Figure 5.5-5.7).

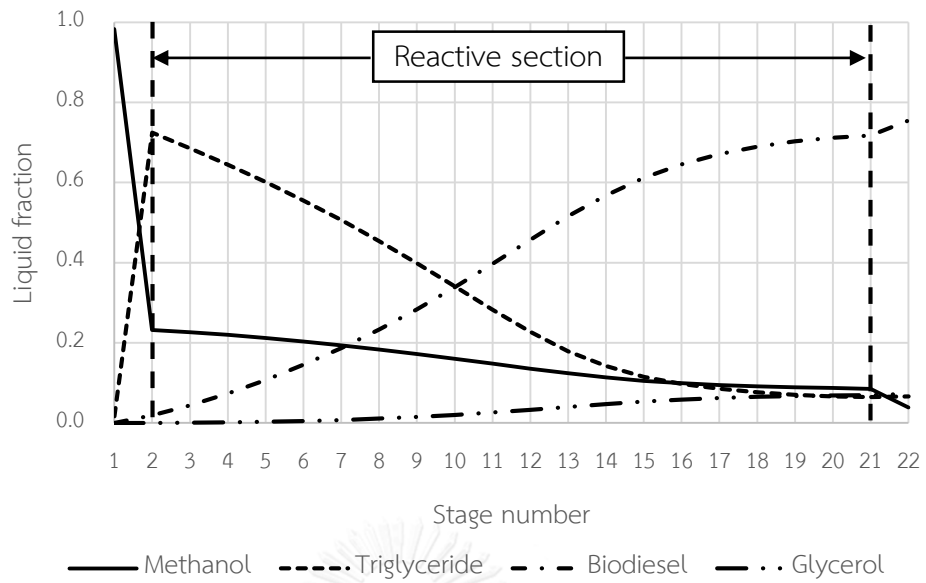


Figure 5.5 Process II Liquid composition profiles within the reactive distillation column using NaOH as catalyst

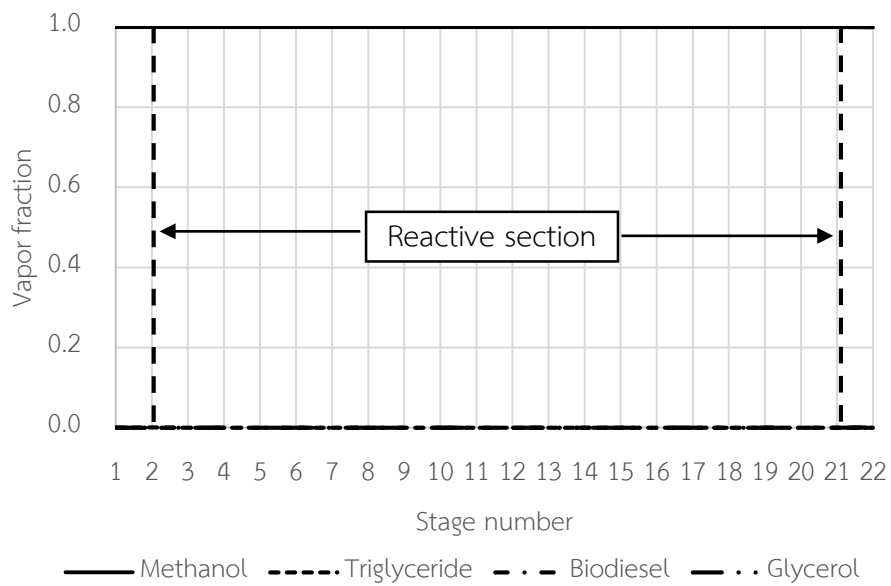


Figure 5.6 Process II Vapor composition profiles within the reactive distillation column using NaOH as catalyst

Figure 5.5 and 5.6 show the liquid and vapor composition profiles within the reactive distillation column, respectively. For liquid composition profiles, large amount of methanol was found at the top of the column, whereas no triglyceride, biodiesel and glycerol are presented here. At bottom of the column, high amount of biodiesel and glycerol were obtained. Therefore, the top product of the reactive distillation column is methanol and bottom stream is biodiesel and glycerol. For vapor composition profile is also corresponding to liquid fraction profiles of methanol in vapor phase was equal to 1.

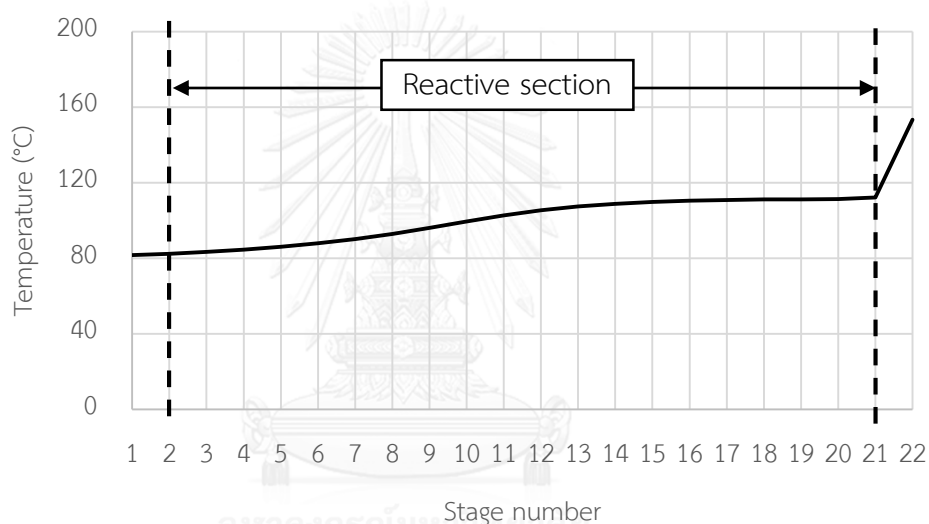


Figure 5.7 Process II temperature composition profiles within the reactive distillation column using NaOH as catalyst

Figure 5.7 illustrated the temperature profiles in the reactive distillation column. The reactive distillation column is operated in the temperature range of 80-153°C at the ambient pressure. The results of the simulation is similar to the previous work [71].

Table 5.2 Description of operating conditions of main equipment in process II
Reactive distillation (RD-101)

Parameter	Values
Total stages	22
Reactive stages	2-21
Reflux ratio, mole	0.1
Oil feed location	2
Methanol feed location	2
Methanol to oil ratio	4:1
Free fatty acid content	0 %

The purity of the biodiesel was 99.59 wt% and glycerol was 92.39 wt% when purification by distillation column under this operation condition following diagrams in Figure 5.4. Process II was modified equipment in biodiesel synthesis and purification step resulting to reduce the capital cost investment compared to process I. This is because the number of unit operation was decrease by using reactive distillation. However, this process still used many equipment in purification step. The operating condition for this process are shown in Table 5.2. This design provides consistency results as well as previous design by Natja-nan Boon-anuwat [71].

5.3 Process III – Modified by using reactive distillation with heterogeneous system in biodiesel synthesis step.

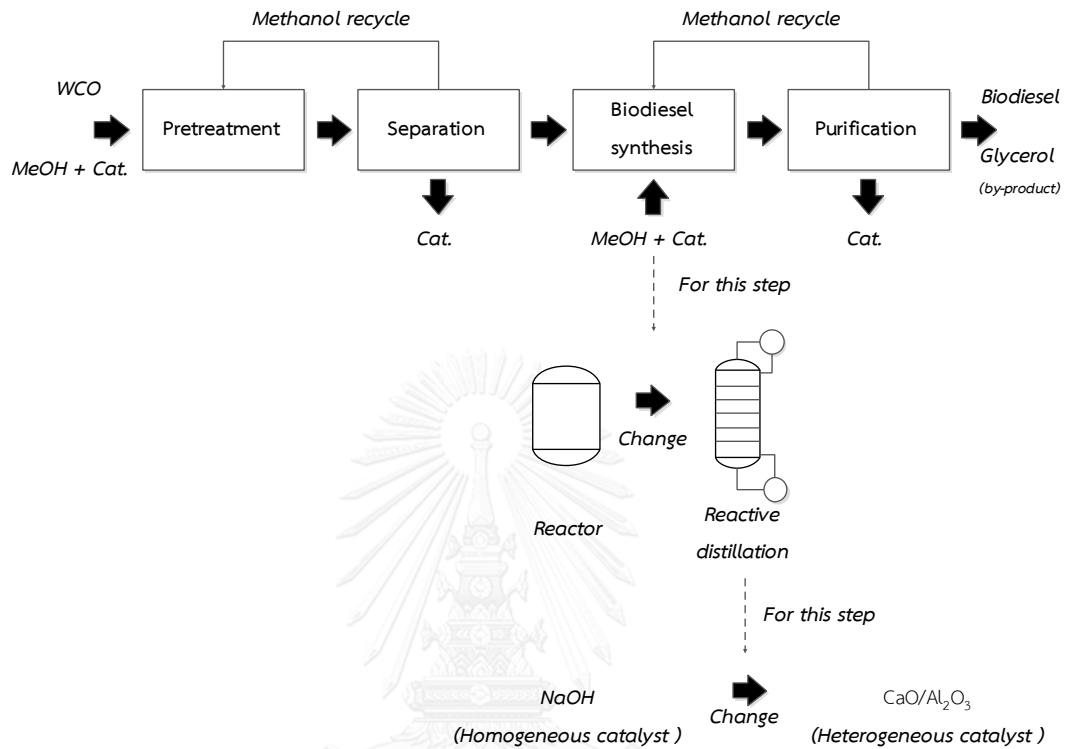


Figure 5.8 Process III flow diagram and improve reactive distillation concept

Process III is being developed further from process II by changing the catalyst type in the biodiesel synthesis step from a homogeneous to heterogeneous catalyst system by using solid base catalyst as $\text{CaO}/\text{Al}_2\text{O}_3$. The distillation column or liquid extraction column was not required for this process therefore the number of unit operation was decreased. This process only used the distillation unit to recover methanol back to reactive distillation and used decanter to purified biodiesel to obtain high quantity product. Therefore process III is an interesting process, although the performance of the selection heterogeneous catalyst was lower than using a homogeneous catalyst in term of reaction rate. This process can be produced equivalent biodiesel yield as using homogeneous catalyst.

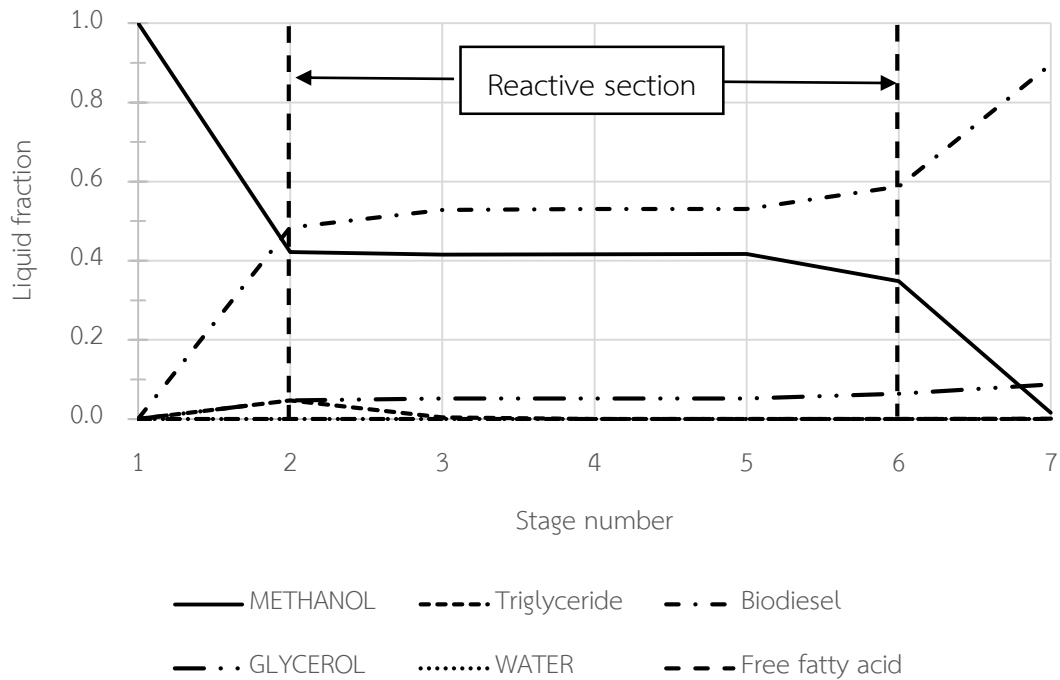


Figure 5.9 Process III Liquid composition profiles within the reactive distillation column using $\text{CaO}/\text{Al}_2\text{O}_3$ as a catalyst

Figure 5.9 shows the liquid composition profiles within the reactive distillation column. It was found that triglyceride was introduced at top column can produce to biodiesel, whereas biodiesel and glycerol are found at bottom of column due to its high boiling point component. However, large amount of methanol with the lowest boiling point component will vaporized to the top of column. Similar vapor composition profile in this process was found as process II (Figure 5.6).

Figure 5.10 shows the temperature profile in the reactive distillation column. The reactive distillation column is operated in the temperature range of 95-240°C under pressure of 3 bar. This simulation results is corresponding to results proposed by Chin-Chia Liu [72].

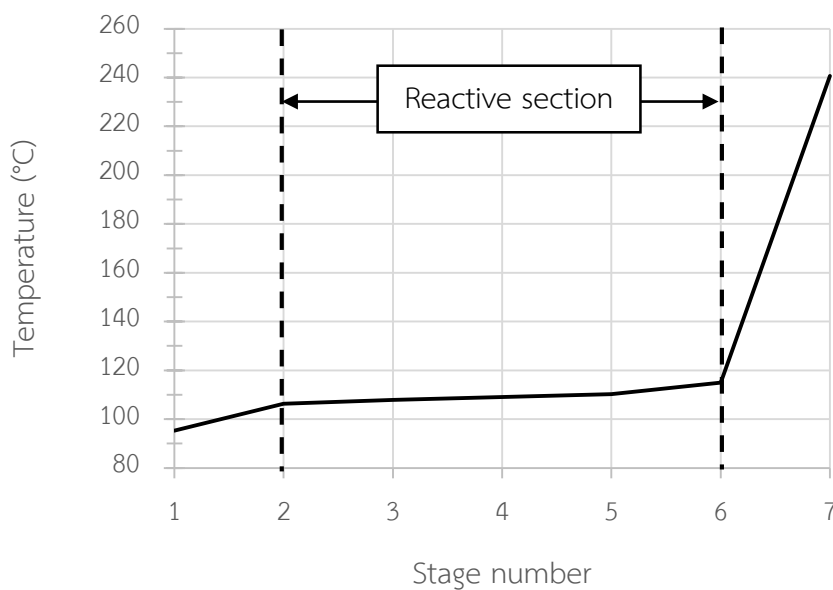


Figure 5.10 Process III temperature composition profiles within the reactive distillation column using $\text{CaO}/\text{Al}_2\text{O}_3$ as catalyst

Table 5.3 Description of operating conditions of main equipment in process III reactive distillation (RD-101)

Parameter	Values
Total stages	7
Reactive stages	2-6
Reflux ratio, mole	0.6
Oil feed location	2
Methanol feed location	2
Methanol to oil ratio	4:1
Free fatty acid content	-

This biodiesel production process design configuration could reduce the capital cost investment as compared to process II. Moreover, high purity of biodiesel product was also achieved to 98.25 % and biodiesel yield was 99 %. The obtained results are in good agreement with other studies and the designed parameter and condition is also similar to the previous work (used different heterogeneous catalyst namely magnesium methoxide).

5.4 Process IV - Modified by combination of pretreatment step and biodiesel step in a reactive distillation column

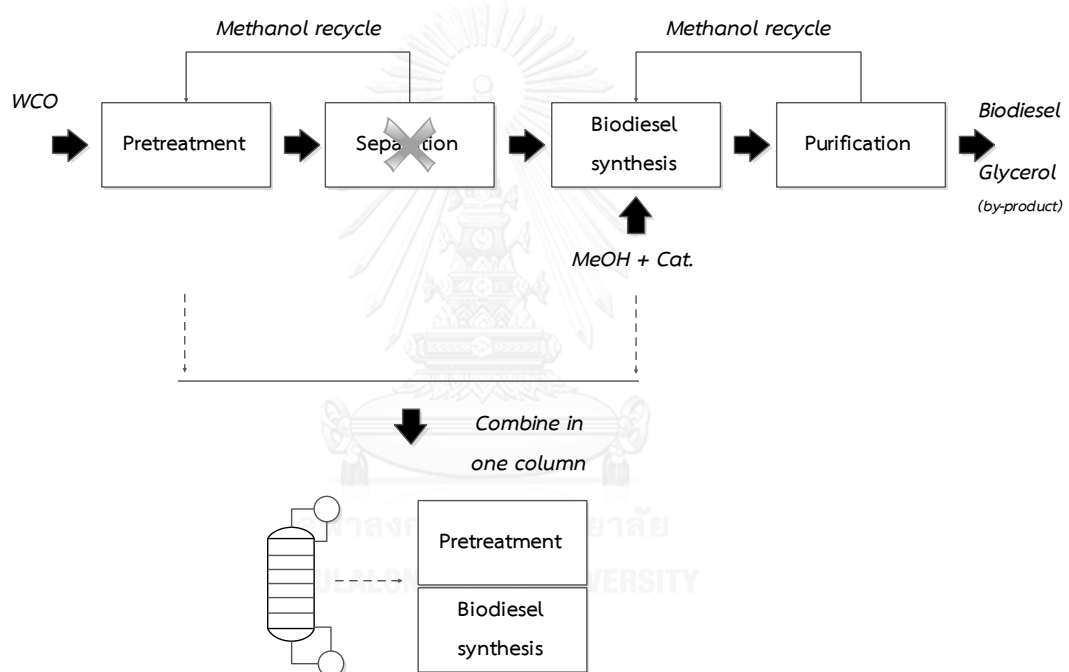


Figure 5.11 Process IV flow diagram and improve reactive distillation concept with two reactions in one column

The conceptual design of the biodiesel production process by using waste cooking oil is based on a reactive distillation column where combined the reaction and separation in a single unit. However, the pretreatment step via esterification is also concerned to reduce free fatty acid content in feed before sending to biodiesel synthesis by transesterification. Therefore, this process design proposed a reactive distillation column where two reactions are taking place. The top section or top of

column was packed solid acid catalyst (Amberlyst-15) for esterification. After reducing free fatty acid content, the liquid reactants will flow down into next section. In this section was packed solid base catalyst ($\text{CaO}/\text{Al}_2\text{O}_3$) for transesterification. So, from above conceptual design of pretreatment step, Amberlyst-15 was packed for three reactive stages (to reduce 6 wt% of free fatty acid content) and biodiesel synthesis step, $\text{CaO}/\text{Al}_2\text{O}_3$ was packed for five reactive stages. As shown in Table 5.4.

Table 5.4 Description of operating conditions of main equipment in process III reactive distillation (RD-101)

Parameter	Values
Total stages	10
Reactive stages	Pretreatment: 2-4 Biodiesel synthesis: 5-9
Reflux ratio, mole	0.1
Oil feed location	2
Methanol feed location	2
Methanol to oil ratio	4:1
Free fatty acid content	6 wt%

The operating condition was provided under this designed concept in Table 5.4. This can produce biodiesel yield and biodiesel purity of 99.50 % and 97.88 %, respectively. This process can also recover unreacted methanol in biodiesel synthesis step by using one reactive distillation, the purity of methanol was 99.42 % in recovery methanol in the column.

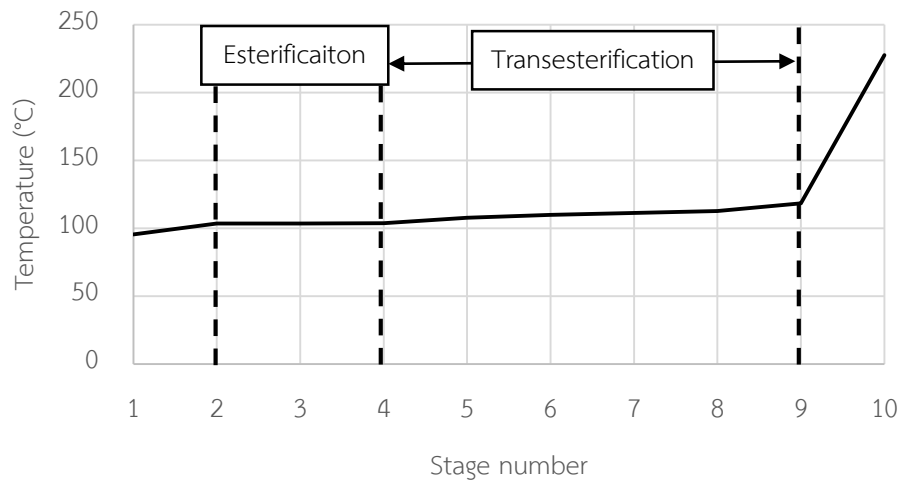


Figure 5.12 Process IV temperature composition profiles within the reactive distillation column using $\text{CaO}/\text{Al}_2\text{O}_3$ as a catalyst

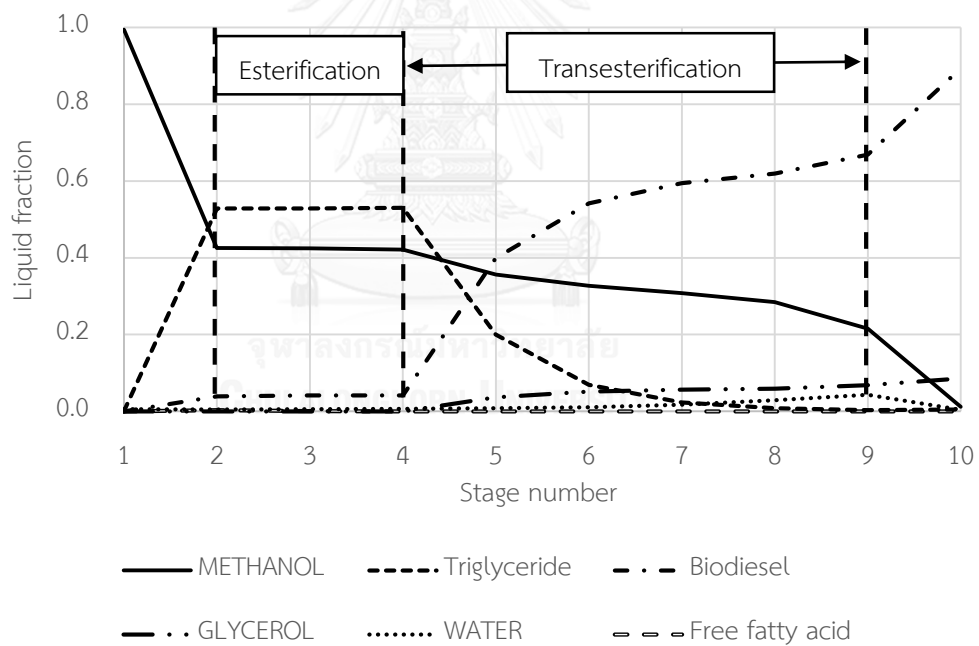


Figure 5.13 Process IV liquid composition profiles within the reactive distillation column using $\text{CaO}/\text{Al}_2\text{O}_3$ as a catalyst

Figure 5.12 shows the temperature profiles in the temperatures range of 95-227°C under pressure of 3 bar in this column. Figure 5.13 shows the liquid composition profiles obtained from this reactive distillation column. This was divided into 2 parts of reaction zones: the first part is esterification to eliminate all free fatty acid (6 wt%) in only one stage and the second part is transesterification to produce biodiesel yield of 99.50 %. Biodiesel, glycerol (by-product) and some trace of triglyceride with the highest normal boiling point (triolein b.p. of 554.2°C, glycerol b.p. of 287.85°C, and methyl oleate b.p. of 343.85°C) were flown down into the bottom of the column, the boiling point of methanol and water (methanol b.p. of 64.7°C and water b.p. of 100°C) which is lower than the temperature inside the column resulting to these two components were vaporized to the top of the column.

5.5 Process performance comparison

Table 5.5 Number of main processing units required for each process

Number of unit operation	Process I	Process II	Process III	Process IV
Reactor	3	2	1	-
Reactive column	1	1	1	1
Distillation column	4	3	1	-
Decanter	-	-	1	1
Extraction column	2	2	1	-
Total unit operation	9	7	5	2

Table 5.6 Energy consumption and methanol net flow for each process

	Process I	Process II	Process III	Process IV
Energy requirement (kW)	749.56	696.52	647.78	160.84
Methanol net flow (kmol/hr)	8.20	8.00	8.00	4.00

A technical comparison of the four different processes is summarized in Tables 5.5. However, the energy requirement presented in Table 5.6 did not include the energy for pressurized column at 3 bar of process III and process IV. It was found that when applied by reactive distillation the number of unit will be decrease as well as the capital investment cost will also decrease process IV was found that the number of unit operation was minimal. This process also requires less energy consumption and total amount methanol to produce biodiesel (Table 5.6). Hence, the conceptual design of process IV is the best choice for biodiesel production from waste cooking oil. Therefore, the effect of designed parameter to find operating window or designed sustainable process for flexible biodiesel production by using waste cooking oil will be provided in the next section.

5.6 Effect of operation and design parameter on performance of process IV

5.6.1 Pressure column

Aashish Gaurav [54] revealed that the process design for biodiesel production via transesterification using reactive distillation column under high pressure column of 3 bar. The higher biodiesel yield was obtained under this condition (better than operated at normal pressure of 1 bar). Therefore, pressure of column should be one variable parameter to concern for biodiesel production in the reactive distillation as seen in Figure 5.14. It was found that the highest biodiesel yield was produced under pressure of 3 bar because the higher temperature profile is resulting to the higher reaction rate than that of the normal pressure. Aashish Gaurav [54] also reported that under the column pressure of 3 bar, transesterification can take place in five reactive stages. Due to in this case considered only transesterification because main composition in waste cooking oil is triglyceride (94 wt%) leading to consider only transesterification.

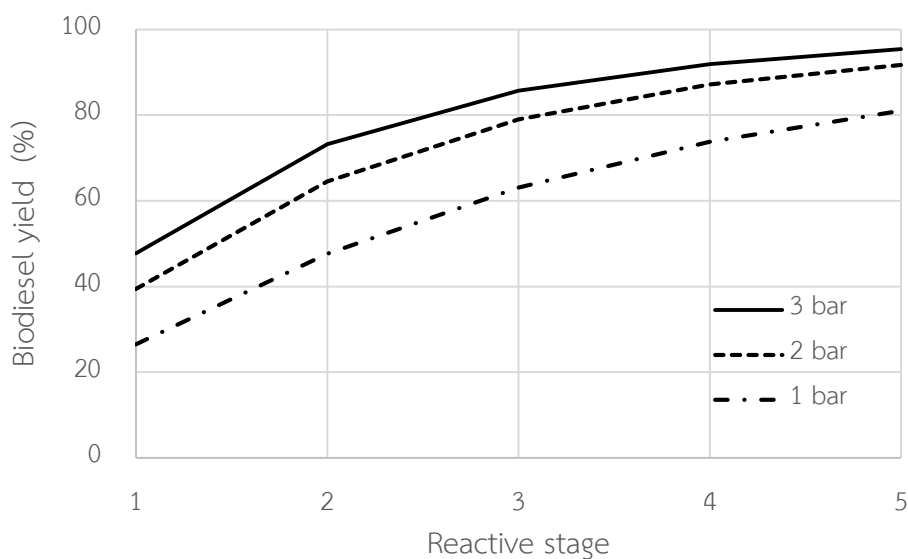


Figure 5.14 Effect of pressure column using methanol to oil ratio 4:1 and reflux ratio 0.1 for only transesterification)

5.6.2 Number of reaction stage

Process IV combines two reactions in one column including of the first reaction via esterification as a pretreatment step and the second via transesterification for biodiesel synthesis step. As can be seen in Figure 5.14, transesterification can provided 99.50 % of biodiesel yield in five reactive stages. Thus, the five transesterification stages will be fixed in this part and then the investigation of the optimum number of stage for esterification to eliminate free fatty acid content (6 wt%) was shown in Figure 5.15.

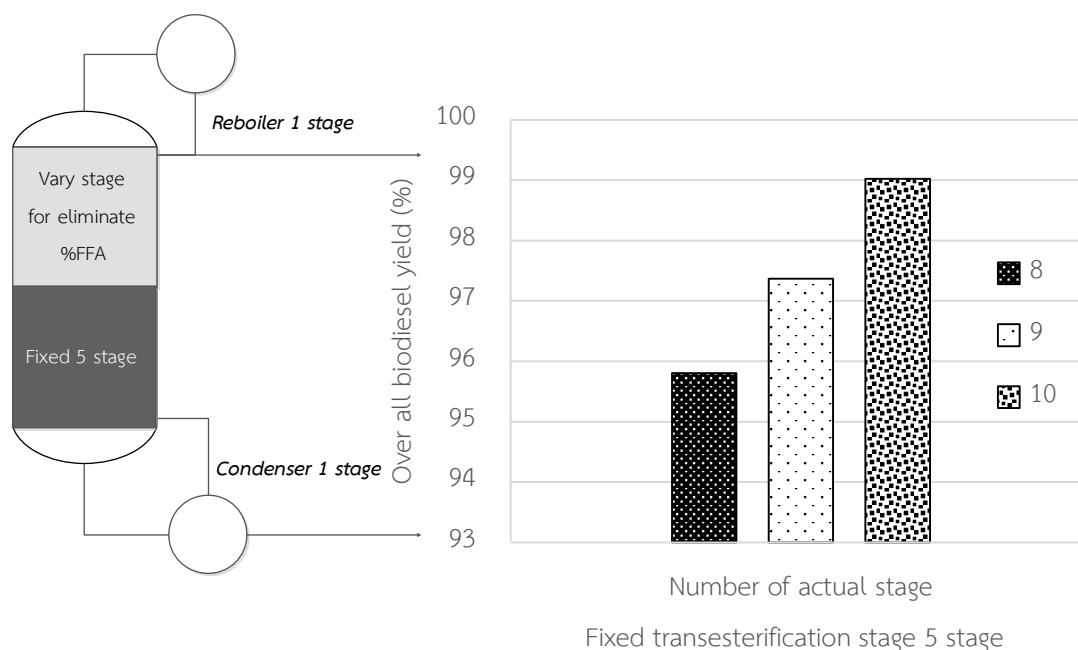


Figure 5.15 Effect of reactive stage using methanol to oil ratio 4:1 with reflux ratio 0.1 under pressure of 3 bar

From the simulation results, this showed that if it needs to eliminate 6 wt% of free fatty acid content, esterification stage will require at least three stages. This means that the total number of this reactive distillation will be ten stages including of one reboiler stage, one condenser stage, five transesterification stages and three esterification stages). Under this design, all free fatty acid can be eliminated (FFA conversion of 99.9%).

5.6.3 Methanol to triglyceride feed molar ratio

The molar feed ratio of methanol to oil is one of the key parameters which indicated the performance of the reactive distillation. Waste cooking oil feed flow rate was fixed with various amount of methanol to increase the methanol to oil molar ratio. Figure 5.16 shows the effect of molar feed ratio of methanol to oil on biodiesel yield, reboiler duty and bottom temperature.

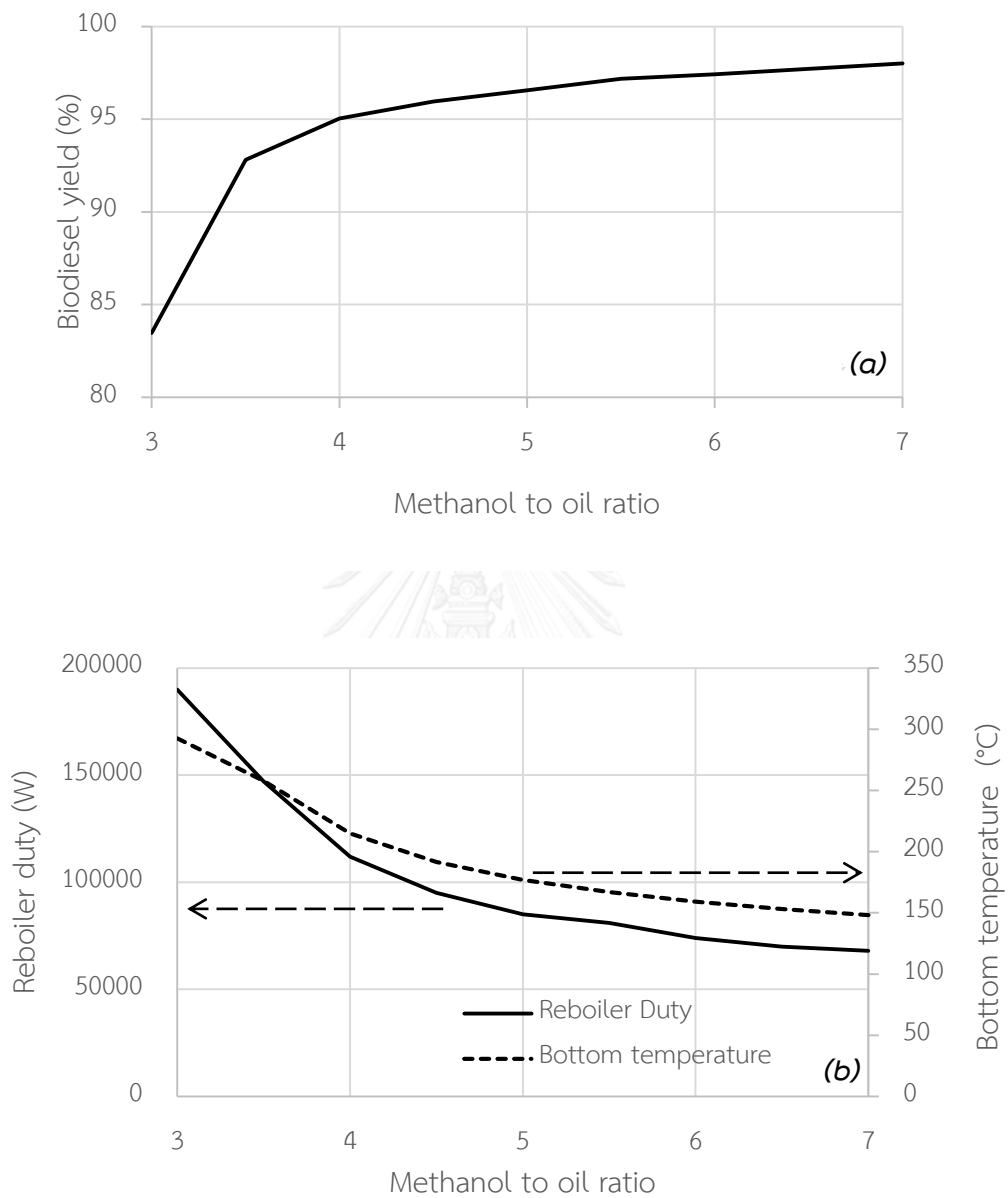


Figure 5.16 Effect of molar feed ratio of methanol and oil on (a) biodiesel yield and (b) reboiler duty and bottom temperature with reflux ratio of 0.1 and 8 reactive stages

Figure 5.16 (a) shows the effect of methanol to oil ratio on biodiesel yield, it was found that biodiesel yield was increased when increase the methanol to oil molar ratio due to the higher methanol concentration can drive this reversible reaction to produce more biodiesel product. On the other side, when methanol to oil ratio

increase, the reboiler duty will require more energy to vaporize unreacted methanol back into top column. Moreover, temperature at bottom stage will be increase when increase reboiler duty. The simulation was shown in Figure 5.16 (b), the energy used for the reboiler duty was reduced when increase methanol to oil ratio. This simulation results was in beyond the expectation. The energy consumption should be increased with increase the methanol to oil molar ratio. The effect of extend of reaction with increase methanol to oil ratio was simulated to support the hypothesis as shown in Figure 5.17. The reaction rate along the column was increased with the higher methanol. More amount of methanol was consumed with the higher reaction rate resulting to lower amount un-reacted methanol in liquid phase. This is leading to lower amount of energy used to vaporize methanol. Besides that, when reboiler duty required less energy resulting to decrease in bottom temperature to vaporize methanol back to top column. To confirm this simulation result, the excess methanol to oil ratio (30:1) was used to determine to effect of reboiler duty and bottom temperature. It was found that the excess of methanol to oil ratio of 30 is leading to increase reboiler duty and bottom column temperature due to its required more energy to vaporize the excess methanol.

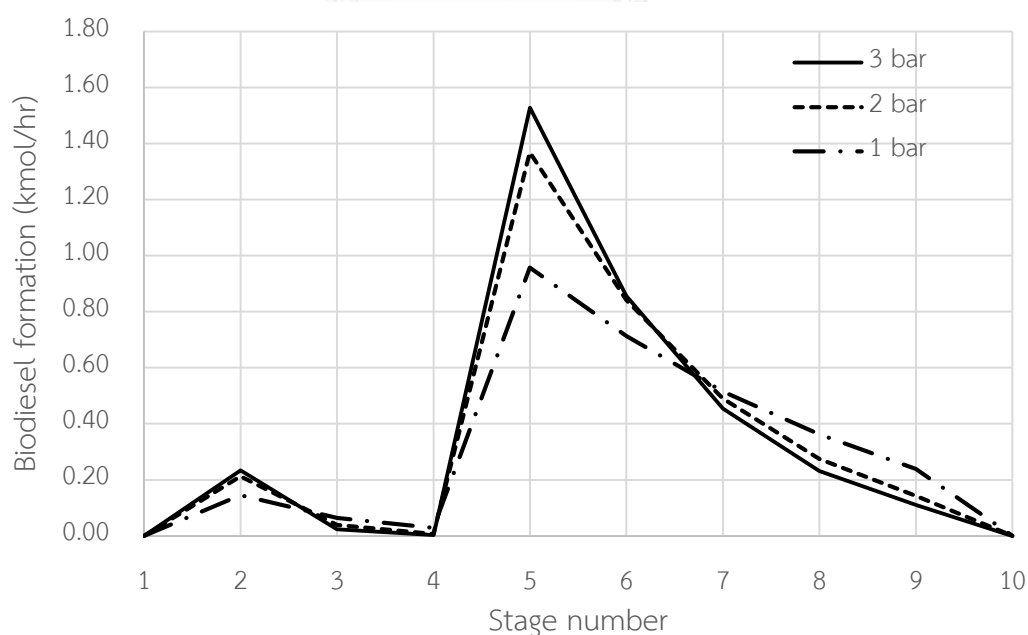


Figure 5.17 Reaction rate profiles with in the reactive distillation column using methanol to oil ratio 4:1, reflux ratio 0.1 and 8 reactive stages

5.6.4 Feed temperature

Feed temperature is another parameter which effects on biodiesel yield. Both reactions (esterification and transesterification) were taking place in the liquid phase. Total feed flow rate, methanol to oil molar ratio, reboiler duty and reflux ratio were fixed while methanol feed temperature was varied from 30 to 300°C. Figure 5.18 shows the effect of methanol feed temperature on biodiesel yield with fixed the position of methanol feed at two stage. If feed temperature was lower than methanol boiling point temperature, biodiesel yield was better than the high temperature feed (more than boiling point of methanol of 94.95°C at 3 bar). This is because methanol in vapor phase cannot react to oil as presented in liquid phase in the reactive distillation.

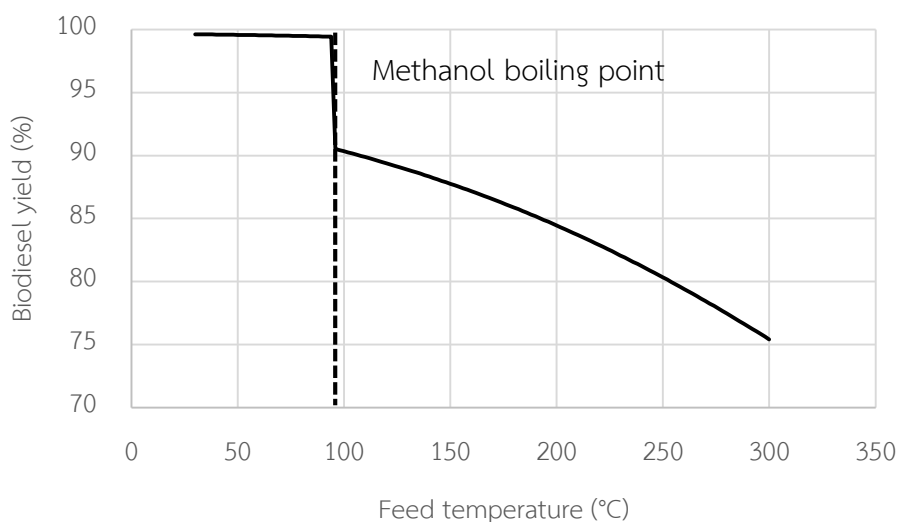


Figure 5.18 Effect of feed temperature using methanol to oil ratio 4:1, reflux ratio 0.1 and 8 reactive stages

5.6.5 Reboiler duty

The effect of reboiler heat duty on the performance of reactive distillation is shown in Figure 5.19. The simulation results was used at methanol to oil feed molar ratio of 4 and reflux ratio of 0.1. Total feed flow rate, methanol to oil molar ratio, and specification of methanol purity at top column (99%) were fixed while reboiler duty in reactive distillation was varied from 140 to 250 kW. Biodiesel yield is slightly improved by increasing reboiler heat duty as seen in Figure 5.19. Increase reboiler duty is leading

to increase column temperature. Therefore, the reaction rate was also increase when increase the reboiler duty.

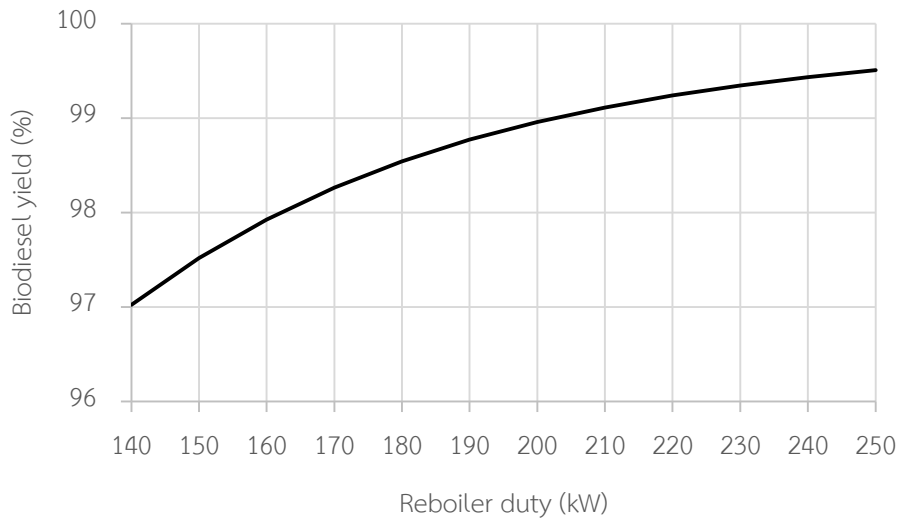


Figure 5.19 Effect of reboiler duty using methanol to oil ratio 4:1, reflux ratio 0.1 and 8 reactive stage

5.6.6 Molar reflux ratio

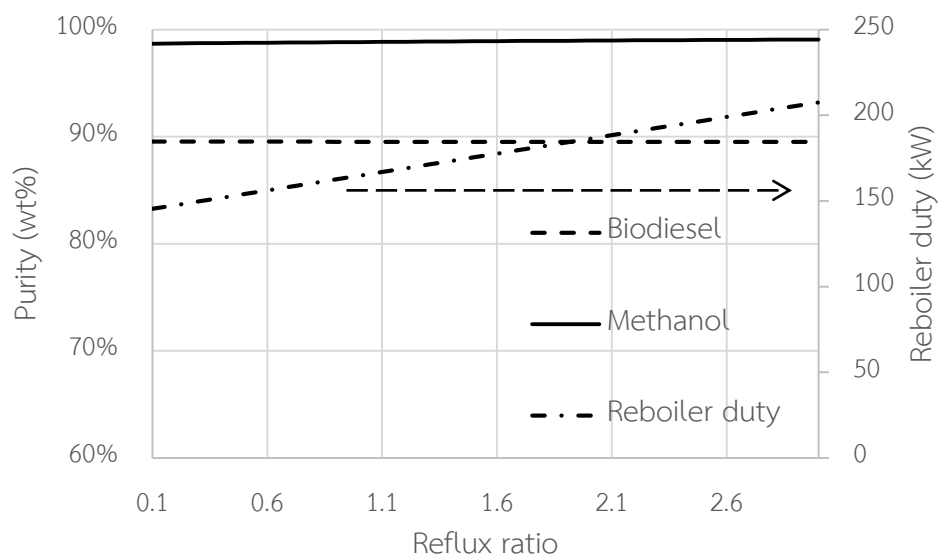


Figure 5.20 Effect of reflux ratio using methanol to oil ratio 4:1, reflux ratio 0.1 and 8 reactive stages

The reflux ratio is defined as the ratio of the liquid returned to the column divided by the amount of removed liquid as product, in the other meaning reflux ratio is a design parameter that affects the purity in the system. The reflux ratio was varied from 0.1 to 3. Total feed flow rate, methanol to oil molar ratio and specification of biodiesel yield (97 %) were fixed while reflux ratio was varied 0.1 to 3. The simulation results indicate the purity of biodiesel (dash line) and methanol (line) were not change when increase reflux ratio 0.1 to 3 at methanol to oil feed ratio 4:1. However, increase the reflux ratio is leading to increase the energy consumption due to more amount of methanol was refluxed back into the column which required more condenser and reboiler duty to condense and vaporize. It was found that the reflux ratio of 0.1 is enough to produce biodiesel because this reflux ratio can provide the purity of biodiesel conformed the standard.

5.6.7 Number of rectifying stage and stripping stage

Rectifying stage and stripping stage is a stage that allows to separate each component in the distillation. Reactive distillation column has rectifying stage at top part and stripping stage in bottom part. Total feed flow rate, methanol to oil molar ratio and reflux ratio were fixed while the number of stage in rectifying and stripping section was varied to find suitable condition. It was found that the difference in boiling point temperature between each component are greatly significant. Thus, this reactive distillation do not need rectifying and stripping stage to provide more separation of each component from the main product.

5.7.8 Methanol and oil feed location

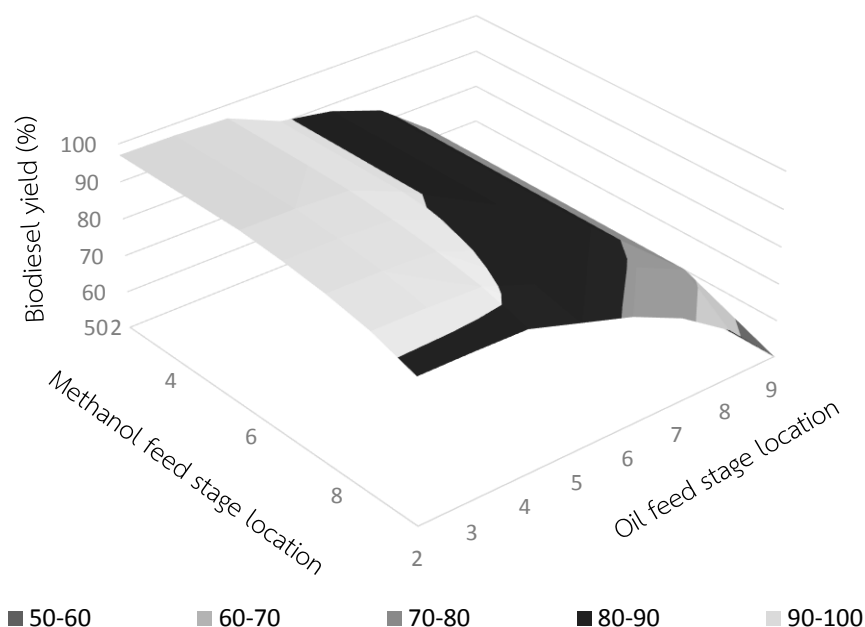


Figure 5.21 Effect of feed location of methanol on biodiesel yield using methanol to oil ratio 4:1, reflux ratio 0.1 and 8 reactive stages

The location of a feed stream is an important design parameter having an effect on a reactive distillation performance. In general, a lighter reactant should be fed on the bottom stage of the reactive zone, whereas a heavier reactant is fed on the top stage of the reactive zone. However, for simultaneous esterification and transesterification of oil and methanol, both reactants are introduced to the column at the first reactive stage as corresponding to the previous work. Total feed flow rate, methanol to oil molar ratio and reflux ratio were fixed while oil and methanol feed location were varied from top of reactive stage to end of reactive stage (2nd -9th stage). Figure 5.21 shows the different feed location of methanol and oil. High biodiesel yield zone (90-100 % yield) was found with oil feed location stage of 2-5 because oil has more residence time to contact with methanol mostly presented in the top of column. Moreover, methanol should be also feed in higher stage because the upper stage has lower temperature than the bottom stage resulting to the higher methanol in liquid

phase than in the vapor phase. Therefore the methanol must feed into the top of the reactive distillation.

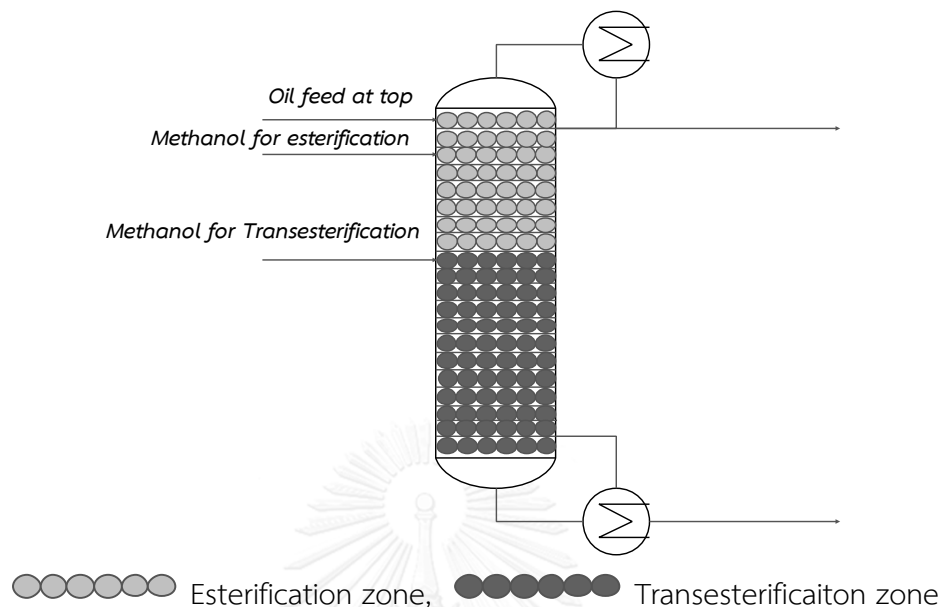


Figure 5.22 Designed reactive distillation for methanol splitting stream using methanol to oil ratio 4:1, reflux ratio 0.1 and 8 reactive stages

Figure 5.22 shown this reactive distillation designed is divided into two sections for esterification and transesterification. From theoretical stoichiometry, transesterification required more molar ratio of methanol to oil than that of esterification. Therefore, it should be useful to investigate the splitting fraction of methanol stream to reactive distillation on biodiesel yield. The methanol feed stream was change by splitting fraction in two streams for esterification on the top section (stage 2) and for transesterification on below section (stage 5) using the optimum methanol to oil molar ratio of 4:1, reflux ratio 0.1 and 8 reactive stages. From Figure 5.23, it was found that the split fraction of methanol does not affect the performance of biodiesel production or biodiesel yield. Because temperature profile in a 2nd stage (1st stage in esterification zone) and temperature in 5th stage (1st in transesterification zone) have not significant difference. Therefore, unreacted methanol from esterification zone was flown down in transesterification zone with the similar temperature (shown in Figure 5.12).

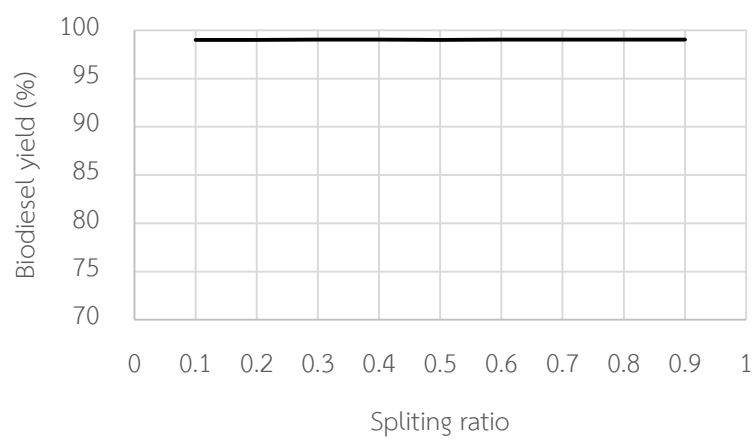
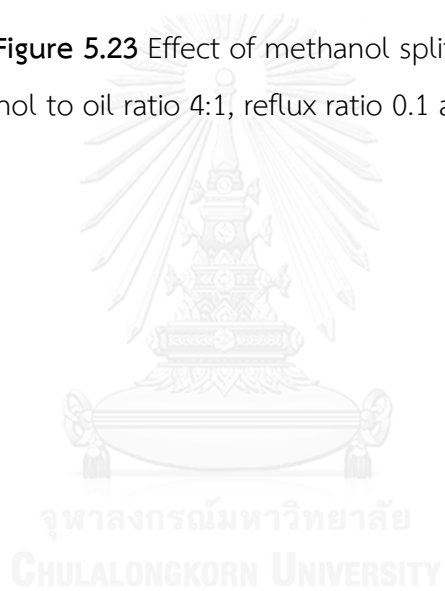


Figure 5.23 Effect of methanol splitting ratio using methanol to oil ratio 4:1, reflux ratio 0.1 and 8 reactive stages



5.7.9 Free fatty acid content

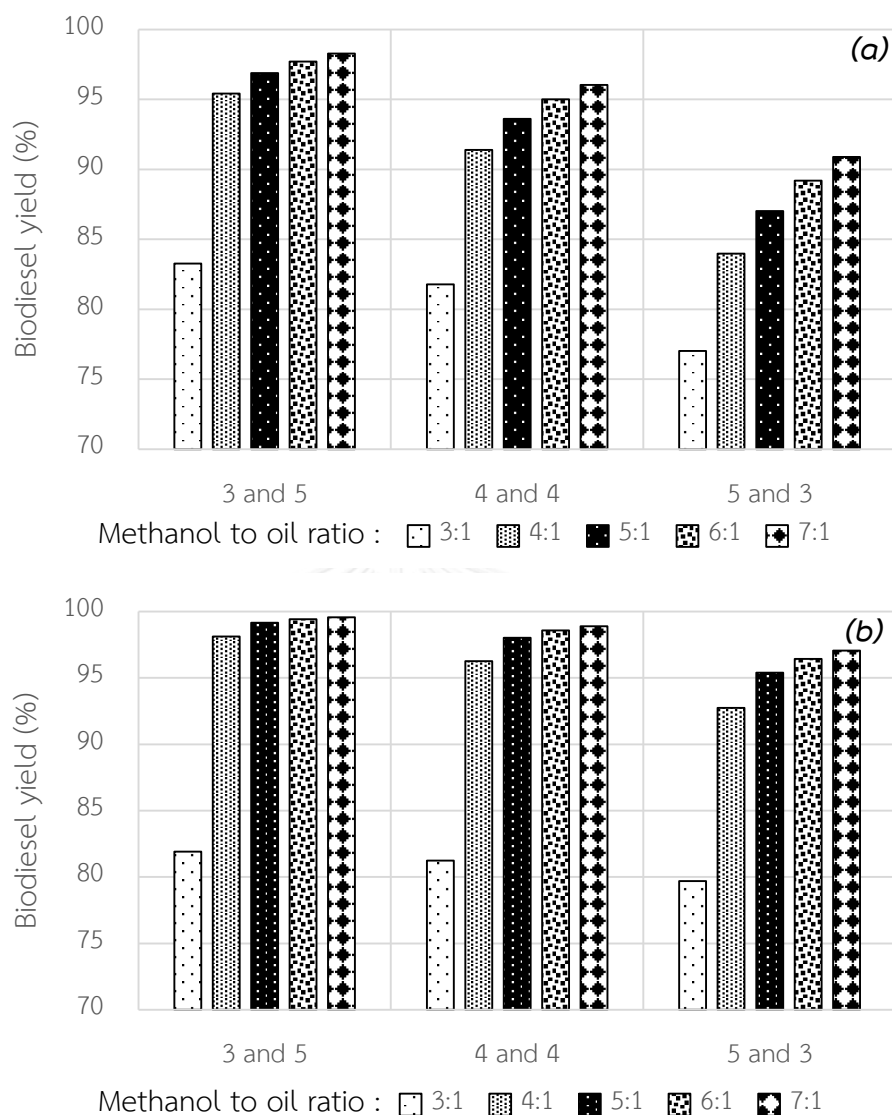


Figure 5.24 Effect of free fatty acid content and reactive stage for each methanol to oil ratio (a) 6 wt% free fatty acid content and (b) 50 wt% free fatty acid content using reflux ratio 0.1 and 8 reactive stages

Remark: For each number of group was referred to number of esterification stage and transesterification stage

The amount of free fatty acid content is depended on the type or source of feedstocks. Therefore, the effect of free fatty acid content must be concerned to determine the suitable operating condition for this reactive distillation. If the number of stage for esterification was not sufficient to eliminate all free fatty acid content,

biodiesel production rate will be decreased from side reaction (saponification). Reboiler duty and reflux ratio were fixed while free fatty acid content, methanol to oil molar ratio, esterification and transesterification stage were varied. Figure 5.24 shows a comparison of biodiesel yield obtained from 6 wt% free fatty content (from based case) and 50 wt% free fatty acid content with various methanol to oil ratio and difference reactive stage ratio via esterification and transesterification (fixed total reactive stage eight stages). It was found that if feedstock contains high free fatty acid content, it was require more esterification stage to eliminate, which make biodiesel yield is higher than increasing amount of methanol to oil ratio. For 6 wt% free fatty acid content (triglyceride 94 wt%). The number of transesterification stage has more important that esterification stage in term of biodiesel yield because main component in waste cooking oil is triglyceride. It is required optimum stage which can be convert triglyceride to biodiesel via transesterification. Thus, the reactive distillation design for free fatty acid content (of less free fatty acid content) was required more transesterification stage and enough esterification stage to eliminate free fatty acid. On the other side, high free fatty acid content (50 wt%) was shown in Figure 5.24 (b), the number of transesterification stage has less effect on the biodiesel yield. Because the amount of triglyceride in waste cooking oil was decrease (triglyceride 50 wt%). This case required less transesterification stage and require more esterification stage for eliminate free fatty acid content.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

6.1.1 Biodiesel production process by using homogeneous catalyst

From the simulation study biodiesel production process by using sulfuric acid and NaOH as homogeneous catalyst, the following conclusions can be drawn below;

1). This process requires more equipment for separating the catalyst from the liquid product before transferring it to the next step, thus resulting in higher capital cost investment.

2). Process II was modified using reactive distillation (instead of conventional reactor) to reduce the number of unit operation. However, process II also required equipment to separate the catalyst in the pretreatment step from the liquid product because the reactive distillation only performed transesterification and recovery of unreacted methanol.

6.1.2 Biodiesel production process by using heterogeneous catalyst

From the simulation study biodiesel production process by using Amberlyst-15 and $\text{CaO}/\text{Al}_2\text{O}_3$ as heterogeneous catalyst, the following conclusions can be drawn below;

1). The problem of using homogeneous catalyst is to need of equipment to separate the catalyst from biodiesel product. Heterogeneous catalyst can overcome this drawback. High energy consumption of catalyst separation equipment is also reduced. This process can use a decanter to separate solid catalyst from biodiesel product.

2). Process III was developed from the process II by replacing homogeneous catalyst with heterogeneous catalyst. In this process, the number of equipment is fewer than the previous process, but still able to operate under similar condition and provide reactive distillation performance as same as using homogeneous catalyst.

3). When using heterogeneous catalyst presented in process IV for two reactions (esterification and transesterification), the number of unit was reduced. Only two equipment including of reactive distillation and decanter were used in this process.

6.1.3 Operating of window for simultaneous esterification and transesterification in a reactive distillation in process IV can be concluded below;

- For pressure and methanol to oil ratio, the simulation results show the optimum values of 3 bar and 4:1, respectively.

- Considering the specification of reactive distillation, it was found that the optimum reflux ratio was 0.1 because all components in this system can be easily separated. It does not require high reflux ratio (high reflux ratio requires high energy consumption). A suitable feed stage location is on the top of reactive stage because methanol and oil can achieve more residence time to contact and provided higher biodiesel yield.

- Under this design configuration, it was found that the total ten stages including esterification of three stages, transesterification of five stages and reboiler-condenser of two stages (without stripping and rectifying stage) can produce biodiesel from waste cooking oil with high free fatty acid content.

6.1.4 An efficient process for biodiesel production by using waste cooking oil as feedstock

The four continuous biodiesel production processes using waste cooking oil as feedstock were designed and simulated. From the technical assessment, all of these processes proved feasible for producing high quality biodiesel product and high purity glycerol. Process I and process II using homogeneous catalyst were the simplest process but these processes require many process equipment. Process III used fewer equipment units than those of process I and process II because of the change of homogeneous catalyst to heterogeneous in the biodiesel synthesis step. However, the pretreatment step still used same process equipment to recover methanol and remove acid catalyst. Process IV can reduce the overall equipment because process

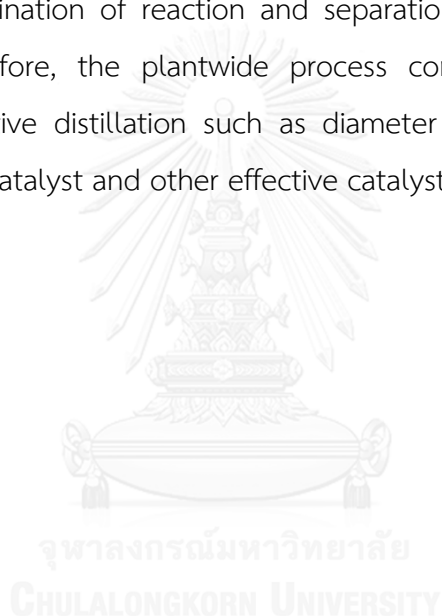
IV was modified two steps (pretreatment and biodiesel synthesis step) in one reactive distillation by using heterogeneous catalyst.

6.2 Recommendation

The following recommendations are provided for further studies on developing the biodiesel production process.

1). In this work, the scope of work only focuses on the number of process equipment, and the yield and purity of biodiesel. However, other considerations such as capital investment and operation cost should be included.

2). The combination of reaction and separation results in more difficult in controllability. Therefore, the plantwide process control should determine the specification of reactive distillation such as diameter of column, type of packed catalyst, life time of catalyst and other effective catalyst.



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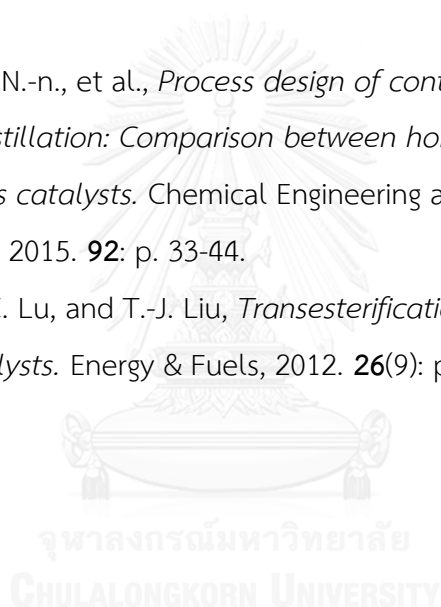
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VITA

Mr.Nattawat Petchsoongsakul was born on 16 March 1992 in Chancheungsao, Thailand. He received his bachelor degree of Chemical Engineering from Silpakorn University, Thailand in 2014. He continued his master's study at department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University in July 2014.

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