CHAPTER 1 INTRODUCTION

1.1 Background

The demand of diesel has been increasing continuously since it is widely used in the industrial economy. Due to the increasing in crude oil prices, limitation resources of fossil oil and environmental concerns, the development of renewable alternative fuel has become a crucial issue. Biodiesel is the one that meets the requirement since it is, generally, derived from fats or oils; such as vegetable oils, animal fats, and microbial oil. Moreover, it produces less significant pollution gas.

For many decades, biodiesel production has been researched. There are many alternative methods to produce biodiesel: (1) direct use and blending of vegetable oil, (2) use of micro emulsions with short-chain alcohols, (3) thermal cracking or pyrolysis of vegetable oils, (4) transesterification of triglycerides catalyzed by bases, acid, or enzymes, and (5) esterification of fatty acids with alcohols, using acid catalyst (H_2SO_4) or solid acids. However, trans-esterification is the most selective method for the biodiesel production.

Transesterification is a catalyzed chemical reaction involving with triglycerides and alcohol to obtain a fatty acid ester mixture (main product) and glycerol (by-product). In general, there are various types of catalysts involved in the production: (1) alkaline-catalyst (NaOH, KOH, NaOMe), (2) acid-catalyst (Sulphuric acid, phosphoric acid, hydrochloric acid, sulfonic acid), (3) enzymatic-catalyst (lipases), and (4) inorganic heterogeneous catalyst (solid phase catalyst). The catalyst selection depends of free fatty acid contained in the feed stock. The oils with lower amount of free fatty acid are better catalyzed with the based catalyst while the ones with higher amount of free fatty acid is preferable to acid catalyzed esterification following by transesterification reaction. The homogeneous catalyzed reaction is introduced as the commercial production since it gives high yield, and rapid reaction. However, there are some disadvantages presented such as high energy consumption, saponification reaction, and high-priced separation of catalyst from reaction products, and high amount of waste water produced. On the other hand, heterogeneous catalyst provides more potential than the homogeneous one since its reusability results in economical production cost. Moreover, the heterogeneous catalyst can be easily separated from the reaction products therefore it requires lower production cost.

Currently, key success of the biodiesel manufacturing contains less time and cost spent in the production. Hence, process intensification is employed to make an alteration to the biodiesel production. Process intensification is defined as any chemical engineering development that leads to a substantially smaller, cleaner, safer, and more energy and production efficient technology. That can be accomplished through the reduction in capital cost by reducing size and inventory as well as the reduction in operating cost by reducing energy consumption and raw materials requirement. Among the various methods of performing process intensification, one of them that widespread employed in biodiesel production is reactive distillation.

Reactive distillation is a hybrid process which distillation separation and chemical reaction are combined into a single operation unit. Due to its performance of continuous removal the reaction products, this equipment enhances mass transfer and offers the benefit for the equilibrium-limited reaction; esterification reaction, and trans-esterification reaction. This also improves conversion and selectivity. According to the combined process, it lessens the process steps, reduces equipment, and simplifies the process flow sheet and operation. All mentioned advantages of the reactive distillation lead to lower cost in investment and operation, elevate income, and cause less harmful to the environment.

The goal of this study is to develop the simulation model for homogeneous catalyst catalyzed reactive distillation by introducing multiple feed using ASPEN PLUS. The process with single feed distillation is performed as a base case. Two different configurations of multiple feeds reactive distillation are performed. The catalyst presented in the process is sodium hydroxide. The comparative study of three different configurations is also investigated. The parameters consist of boil up ratio, reflux ratio and residence time in the reactive distillation column.

1.2 Objectives

1. To study and develop the simulation model of multiple feeds reactive distillation for biodiesel production.

2. To study the operating conditions in order to enhance the production

1.3 Scope of work

1. Simulation of biodiesel production by transesterification reaction with homogeneous catalyst (NaOH) will be performed in reactive distillation process.

2. Alternative configurations of multiple feeds with homogeneous catalyst in the simulation of reactive distillation process will be investigated.

3. Comparison the models with single feed and multiple feeds in reactive distillation process will be focused.

CHAPTER 2 THEORIES AND LITERATURE REVIEWS

This chapter presents about biodiesel and biodiesel production. The detail of transesterification which is selected as a production method is also mentioned. In addition, the reactive distillation and related literature reviews are stated simultaneously.

2.1 Biodiesel

Biodiesel, a mixture of mono-alkyl esters of fatty acids, is an alternative renewable energy that can be produced from biological sources of oils and fat. The oil and fat usually used in biodiesel production are animal fats, vegetable oils, microalgae oils, or even waste cooking oil (Helwani *et al.* (2009)). There are several advantages of biodiesel over fossil diesel:

1. Availability and renewability (Demirbas (2002))
2. Higher combustion efficiency (Demirbas (2002))
3. Lower emissions (Demirbas (2002))
4. Biodegradability (Demirbas (2002))
5. Non-toxicity (Kiss *et al.* (2006))
6. Possibility to be used in conventional diesel engine without significant modification (Mueanmas *et al.* (2010))
7. Prolongation the life of diesel engine (Kiss *et al.* (2006))

Biodiesel was first derived from peanut oil by Rudolph Diesel over 100 years ago. However, due to the cheap and plenty of fossil diesels, it has not been much attractive (Ma and Hanna (1999), Meher *et al.* (2006)). Recently, there is a large amount of diesel consumption owing to the expanding of industry. Biodiesel production becomes significant in the industrial world. There are many methods of biodiesel production:

1. Direct use and blend of vegetable oil (Ma and Hanna(1999))
2. Use of microemulsions with short-chain alcohols (Ma and Hanna (1999))
3. Thermal cracking (pyrolysis) of vegetable oils (Ma and Hanna (1999))
4. Transesterification of triglycerides catalyzed by bases, acids, or enzymes (Ma and Hanna(1999))
5. Esterification of fatty acids with alcohols, using acid catalysis (H_2SO_4) or solid acids (Kiss *et al.* 2006)

Be compared to other biodiesel production technologies, transesterification is currently used method in commercial (Myint *et al.* (2009), Helwani *et al.* (2009)). There are three major components involved in transesterification: triglycerides of oils or fat, alcohol, and catalyst. The various kinds of vegetable oils are normally introduced to complete the reaction. Their properties are presented in Table 2.1.

Table 2.1 Chemical properties of vegetable oil (Demirbas (2002))

Vegetable Oil	**Fatty acid composition, wt.%**								
	16:0	18:0	20:0	22:0	24:0	18:1	22:1	18:2	18:3
Corn	11.67	1.85	0.24	0.00	0.00	25.16	0.00	60.6	0.48
Cottonseed	28.33	0.89	0.00	0.00	0.00	13.27	0.00	57.51	0.00
Crambe	2.07	0.7	2.09	0.8	1.12	18.86	58.51	9	6.85
Peanut	11.38	2.39	1.32	2.52	1.23	48.28	0.00	31.95	0.93
Rapeseed	3.49	0.85	0.00	0.00	0.00	64.4	0.00	22.3	8.23
Soybean	11.75	3.15	0.00	0.00	0.00	23.26	0.00	55.53	6.31
Sunflower	6.08	3.26	0.00	0.00	0.00	16.93	0.00	73.73	0.00
Poppy seed	12.6	4	0.00	0.00	0.00	22.3	0.00	60.2	0.5
Safflower	7.3	1.9	0.00	0.00	0.00	13.6	0.00	77.2	0.00
Sesame seed	13.1	3.9	0.00	0.00	0.00	52.8	0.00	30.2	0.00
Linseed	5.1	2.5	0.00	0.00	0.00	18.9	0.00	18.1	55.1
Wheat grain*	20.6	1.1	0.00	0.00	0.00	16.6	0.00	56	2.9
Palm	42.6	4.4	0.00	0.00	0.00	40.5	0.00	10.1	0.2
Tallow	23.3	19.3	0.00	0.00	0.00	42.4	0.00	2.9	0.9
Hazelnut Kernel	4.9	2.6	0.00	0.00	0.00	83.6	0.00	8.5	0.2
Walnut Kernel	7.2	1.9	0.00	0.00	0.00	18.5	0.00	56	16.2
Almond Kernel	6.5	1.4	0.00	0.00	0.00	70.7	0.00	20	0.00
Olive Kernel	5	1.6	0.00	0.00	0.00	74.7	0.00	17.6	0.00

*Wheat grain oil contains 11.4 wt.% of 8:0 and 0.4 wt.% of 14:0 fatty acids.

When the reactions are completed, biodiesel must be checked standard. There are two international standards which are EN 14212 and ASTM D 6751 as shown in Table 2.2

Table 2.2 The biodiesel specification of EN 14214 and ASTM D 6751

Properties	**EN 14214**		**ASTM D 6751**	
	Unit	Limits	Unit	Limits
Ester content	% (m/m)	96.5	-	-
Density at 15 °C	kg/m^3	860-900	-	-
Viscosity at 40 °C	mm^2/s	3.5-5.0	mm^2/sec	1.9-6.0
Flash point	°C	120 min	°C	130 min
Sulfur content	mg/kg	10 max	% mass	0.05 max
Carbon residue	% (m/m)	0.3 max	% mass	0.05 max
Cetane number		51 min		47 min
Sulfated ash	% (m/m)	0.02 max	% mass	0.02 max
Water content	mg/kg	500 max	% volume	0.05 max
Total contamination	mg/kg	24 max	-	-
Copper strip corrosion	Rating	class 1		No. 3 max
Cloud Point	-	-	°C	Report
Oxidation stability	Hours	6 min	-	-
Acid Value	Mg KOH/g	0.5 max	Mg KOH/g	0.8 max
Iodine value	g/100g	120 max	-	-
Linoolenic acid ME	% (m/m)	12 max	-	-
Polyunsat ME	% (m/m0	1 max	-	-
Methanol content	% (m/m)	0.2 max	-	-
Monoglyceride	% (m/m)	0.8 max	-	-
Diglyceride	% (m/m)	0.2 max	-	-
Triglyceride	% (m/m)	0.2 max	-	-
Free glycerol	% (m/m)	0.02 max	% (m/m)	0.02
Total glycerol	% (m/m)	0.25 max	% (m/m)	0.24
Alkali metals (Na+K)	mg/kg	5 max	-	-
Phosphorus content	mg/kg	10 max	% mass	0.001 max
Distillation temperature	-	-	°C	360 max

2.2 Palm oil

Palm oil is dark yellow to yellow-red oil (high carotene content) of vegetable origin obtained by pressing or boiling the flesh of the fruit of the oil palm (Elaeis guineensis). Palm oil differs from palm kernel oil, the latter being obtained from the kernels of the oil palm. Palm oil and palm kernel oil are forms of edible vegetable oils obtained from the fruit of the oil palm tree. Palm oil and palm kernel oil are composed of fatty acids, esterified with glycerol just like any ordinary fat. Both are high in saturated fatty acids, about 50 wt.% and 80 wt.%, respectively. The fatty acids compositions of palm oil and palm kernel oil are shown in Table 2.3

The major difference between palm oil and palm kernel oil is in their fatty acid content. The main fatty acids of palm oil are palmitic, oleic, linoleic and stearic while the main fatty acids of palm kernel oil are lauric, myristic, oleic and palmitic. Note that amongst these fatty acids, lauric, myristic, palmitic and stearic are saturated fatty acids (12, 14, 16 and 18 carbons, respectively). Oleic acid is monunsaturated (18 carbons, 1 double bond) while linoleic acid is polyunsaturated (18 carbons, 2 double bonds) http://www.palmoilworld.org/PKO.htm (accessed 19 May 2011), and http://www.tis-gdv.de/tis_e/ware/oele/palmoel/palmoel.htm (accessed 19 May 2011)).

Palm oil is claimed to be the highest potential source among other vegetable oil in Thailand. Thai’s government has planned to produce 8.5 million liter per day in 2012 (Thai Parliament Ethanol and biodiesel. Alternative fuels. 2002).

Table 2.3 Fatty acid compositions of palm oil and palm kernel oil

Palm oil		**Palm kernel oil**	
Fatty acid	**wt.%**	**Fatty acid**	**wt.%**
Palmitic acid (16:0)	44.3	Lauric (12:0)	48.2
Myristic (14:0)	1.0	Myristic (14:0)	16.2
Stearic acid (18:0)	4.6	Palmitic (16:0)	8.4
Oleic acid (18:1)	38.7	Capric (10:0)	3.4
Linoleic acid (18:2)	10.5	Caprylic (8:0)	3.3
Other/unknow	0.9	Stearic (18:0)	2.5
Total saturated fatty acids	50	Oleic (18:1)	2.3
Total unsaturated acids	50	Other/unknown	0.9
		Total saturated fatty acids	80
		Total unsaturated acids	20

2.3 Transesterification

Transesterification is a chemical reaction which triglycerides react with alcohol and can promote the reaction rate by suitable catalyst. The products obtained from transesterification reaction are glycerin and fatty acid methyl ester; FAME. The reaction scheme is presented in Figure 2.1.

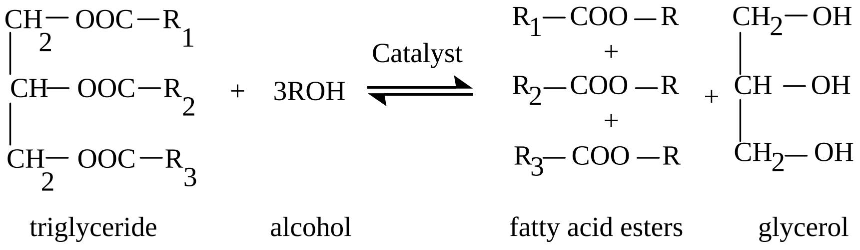


Figure 2.1 Transesterification

As previously mentioned, precursor to produce biodiesel can be any of animal fats, vegetable oils, microalgae oils, or even waste cooking oil. There are several of vegetable oils used in the production and the properties are shown in Table 2.4. The alcohol preferred in the reaction is the one with the low molecular weight such as methanol and ethanol. The reaction can be catalyzed by both homogeneous catalyst and heterogeneous catalyst.

- Homogeneous catalyst

Homogeneous catalyst includes alkalis and acid. The based catalysts, normally used, are sodium hydroxide, sodium methoxide, and potassium hydroxide. The preferable acid catalysts are sulphuric acid, hydrochloric acid, and sulfonic acid (Vicente *et al.* (2004)). However, transesterification using based catalyst is commonly used technique in industry since it is much faster than tranesterification using acid catalyst and the reaction condition are moderated (Helwani *et al.* (2009), and Vicente *et al.* (2004)).

- Heterogeneous catalyst

Although the use of homogeneous process is satisfactory due to its fast kinetic and feasibility in economic, it requires high energy consumption and costly separation biodiesel from the reaction products. There are attemptions to develop the heterogeneous process. Many alternative choices of heterogeneous catalyst, both base and acid are researched. The examples of heterogeneous are lipase (Marchetti *et al.* (2007)) ,hydrotalcite (CHT), magnesium oxide (MgO), titanium supported on silica (TiO_2/SiO_2), vanadyl phosphate ($VOPO_4.2H_2O$ (VOP)), metal-substituted vanadyl phosphate ($Me(H_2O)_xVO_{(1-x)}PO_4.2H_2O$)(Serio (2007)), oxides, γ-alumina (Helwani *et al.* (2009)), Zn/Al (Bournay *et al.* (2005)), sulfated titania (SO_4^{2-}/TiO_2), Sulfated tin oxide ($Sn(OH)_4$), Cs_2CO_3 (Kiss *et al.* (2006))

Transesterification consists of 3 steps in series with 2 intermediates, diglycerides (DG) and monoglycerides (MG). The steps are shown in Figure 2.2. Methanol is the common alcohol used in transesterification owing to its low cost, and physical and chemical advantages (polar and shortest chain alcohol). For the stoichiometry of transesterification, the ratio of alcohol to oil is 3:1 but an excess of alcohol is usually used in order to shift the reaction for more production of biodiesel.

$$\text{Triglyceride (TG)} + \text{ROH} \xrightleftharpoons{\text{Catalyst}} \text{Diglyceride (DG)} + \text{RCOOR}_1$$

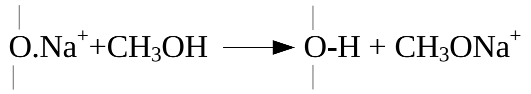
$$\text{Diglyceride (DG)} + \text{ROH} \xrightleftharpoons{\text{Catalyst}} \text{Monoglyceride (MG)} + \text{RCOOR}_2$$

$$\text{Monoglyceride (MG)} + \text{ROH} \xrightleftharpoons{\text{Catalyst}} \text{Glycerol (GL)} + \text{RCOOR}_3$$

Figure 2.2 General equation for transesterification of triglyceride (Meher *et al.* (2006))

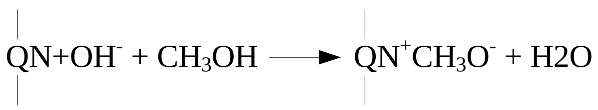
Reaction Mechanisms of heterogeneous acid and basic catalysts could be classified as Bronsted or Lewis catalysts, though in many cases both types of sites could be present and it is not easy to evaluate the relative importance of the two types of sites in the reaction. A detailed description of some reaction mechanisms can be found in the paper of Lotero *et al* (2006) here for brevity's sake, they will report only a general overview on reaction mechanisms of the different catalyst types

A mechanism is operative in the case of a heterogeneous basic Bronsted catalyst such as basic zeolite. Also in this case, the formed catalytic specie is a homogeneous alkoxide.



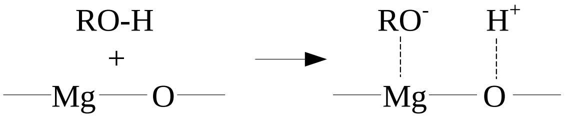
$$\text{O.Na}^+ + \text{CH}_3\text{OH} \longrightarrow \text{O-H} + \text{CH}_3\text{ONa}^+$$

In the case of heterogeneous basic Bronsted catalyst such as resin with quaternary ammonium functionality (QN+OH-), the positive counterions (organic ammonium groups), being bonded directly to the support surface, electronically retain the catalytic anions on the solid surface: The reaction occurs between methanol adsorbed on the cation and ester from the liquid (Eley–Rideal mechanism).



$$\text{QN+OH}^- + \text{CH}_3\text{OH} \longrightarrow \text{QN}^+\text{CH}_3\text{O}^- + \text{H2O}$$

The formation of alkoxide groups is also a fundamental step for heterogeneous basic Lewis catalyst. For example, in the case of ethylacetate transesterification, catalyzed by MgO, the reaction occurs between the methanol molecules adsorbed on a magnesium oxide free basic site and the ethyl acetate molecules.



The kinetic model of biodiesel formation was proposed by many researches (Freeman *et al.*, 1986; Noureddini and Zhu, 1997; Darnoko and Cheryan, 2000; Karmee *et al.*, 2004; Vicente *et al.*, 2005; Vicente *et al.*, 2006). The general form of governing differential equations involving three steps is following:

$$\frac{d[TG]}{dt} = -k_1[TG][A] + k_2[DG][E] \tag{2.1}$$

$$\frac{d[DG]}{dt} = k_1[TG][A] - k_2[DG][E] - k_3[DG][A] + k_4[MG][E] \tag{2.2}$$

$$\frac{d[MG]}{dt} = k_3[DG][A] - k_4[MG][E] - k_5[MG][A] + k_6[GL][E] \tag{2.3}$$

$$\frac{d[GL]}{dt} = k_5[MG][A] - k_6[GL][E] \tag{2.4}$$

$$\frac{d[E]}{dt} = k_1[TG][A] - k_2[DG][E] + k_3[DG][A] - k_4[MG][E] + k_5[MG][A] - k_6[GL][E] \tag{2.5}$$

$$\frac{d[A]}{dt} = -\frac{d[E]}{dt} \tag{2.6}$$

where A and E are the alcohol and ester concentrations, respectively.

In addition, the activation energy and reaction rate shown in Table 2.4 were estimated by the Arrhenius equation.

$$k(T) = AT^{n}e^{-E/RT} \tag{2.7}$$

Table 2.4 The energy of activation and reaction rate constant at 50 °C using NaOH (Noureddini and Zhu (1997))

Reaction	Energy of Activation (cal/mol)	Reaction rate constants
TG → DG	13145	4.80E+07
DG → TG	9932	5.81E+05
DG → MG	19860	2.70E+11
MG → DG	14639	9.98E+09
MG → GL	6421	5.38E+07
GL → MG	9588	2.17E+04

2.4 Reactive distillation

The reactive distillation is an operation which reactions and separations taking place in the same unit. This technique is especially useful for equilibrium-limited reactions such as esterification and transesterification reactions. Conversion can be increased by the ability to shift the equilibrium due to the continuous removal of products from the reactive zone. This approach can potentially reduce capital investment and operation costs. (De Lima da Silva *et al.* (2010), Mueanmas *et al.* (2010), Kiss *et al.* (2006), Kiss *et al.* (2011))

The advantages of the unit operation integration are**:** (1) capital savings due to the simplification or elimination of separation system, (2) increasing of conversion by continuously removing production, (3) prevention of the azeotropes mixture, and (4) reduction in the rates of side reactions and by product formation. (De Lima da Silva *et al.* (2009), Mueanmas *et al.* (2010), Kiss *et al.* (2006), and Kiss (2004))

Simasatitkul *et al.* (2011) proposed the production of biodiesel from soybean oil cataysted by sodium hydroxide via transesterification. Reactive distillation was applied to substitute the reactor and the distillation. HYSIS software was employed to perform the simulation of the production process. This work contained with the study of effect of various operating and design parameters: feed ratio of methanol and oil, feed temperature, reboiler heat duty, number of reactive stages, feed location of methanol. The simulation results revealed that the conversion and yield of product increased with the increasing of feed molar ratio, reboiler heat duty, number of reactive stages. However, the increasing feed temperature resulted in decreasing of conversion and yield. It was suggested that both reactants should be introduced at the first reactive stage. It was found that the optimal of the ratio was 4.5. The feed temperature can be at the temperature room due to the slightly effect of the change. The reboiler duty should be less than 20 GJ/hr. And the reactive distillation performance improves with when the reactive stages are higher than 3.

Meanmas *et al.* (2010) tested lab scale continuous flow reactive distillation and its applicability for biodiesel production. Palm oil and methanol was used as reactants and catalyzed by potassium hydroxide. The physical appearance of transesterified products was discussed. At high temperature, the rate of soap formation increased more than the rate of desired product produced which affected the difficulty in the separation and decreased the reaction conversion. The experimental results presented that the %weight of methyl ester decreased while the flow rate increased. The sufficient methanol vapor was generated with reboiler temperature higher than 900 °C, depending on the methanol concentrations. It was observed that the higher temperature has lower methanol contained in the product due to the easier evaporation. Moreover, the remaining of methanol in the product produced from reactive distillation was lower than the conventional process.

Singh *et al* (2004) proposed the laboratory scale for continuous-flow reactive distillation system for biodiesel production from seed oil. The objective was to promote the efficiency of production by reducing the alcohol-to-oil molar ratio. There were two setup cases which were the cases with and without a pre-reactor serving before the reactive distillation. The setup with a pre-reactor performed better reaction yield compared to the setup without pre-reactor. The methyl ester content promoted when the methanol-to-oil ratio increased. The optimum methanol-to-oil molar ratio was 4:1 while the ratio for the conventional process which reactor and distillation were set individually requires the stoichiometry ratio of 6:1. This result in the reduction of the methanol spent in the production process.

In this thesis, as sodium hydroxide is selected as a catalyst and mixed with methanol before entering to reactive distillation. The mixture is fed at the bottom of the reactive distillation. Then, the hypothesis is that the NaOH is not able to lift up to the top of the column. Therefore, to promote the reaction in the distillation, the new configurations of the reactive distillation are proposed to be an alternative configuration of this kind of column. Moreover, the investigation of the performance of the new design of the reactive distillation is also of interest.

CHAPTER 3 METHODOLOGY

The methodology to accomplish this work can be briefly illustrated in simple steps as followings:

3.1 Technical and data gathering of biodiesel production

Before start the simulation, the necessary information supposed to be collected. It might include the simple biodiesel production used in commercial, the catalyst employed in the process, all equipment involved, operating conditions, and other alternative methods in biodiesel production, etc.

Normally, the production of biodiesel could be provided by transesterification reaction between triglyceride, alcohol with catalyst. Thus, it could be categorized into two major techniques influenced by catalyst: homogeneous reaction and heterogeneous reaction. In this work, sodium hydroxide was presented as a homogeneous catalyst.

One of developed techniques in the biodiesel production that became significant was the reactive distillation. This technique provided less energy consumption, operating and investment cost, and raw material requirement. Moreover, it advanced reaction conversion.

3.2 Simulation of the production process

3.2.1 Simulation of single feed reactive distillation

The simulation began with performing the steady state model of the single feed. The biodiesel production reaction occurred in this work was transesterification of palm oil with methanol. There were three major components contained in palm oil which were tripalmitic, trioleic and trilinoleic acid. The reaction products which formed biodiesel were methyl palmitate, methyl oleate, and methyl linoleate. The catalyst introduced in the reaction was sodium hydroxide. The simulation procedures involved settling chemical components, selecting an appropriate thermodynamics property, defining plant capacity, choosing suitable operating units and setting up input conditions (flowrate, temperature, pressure and any other conditions).

3.2.2 Simulation of multiple feeds reactive distillation

After the single feed reactive distillation was settled, the alteration of the column's configuration was created to promote the more efficiency reactive distillation column. There were two proposed configurations. One was the multiple feeds reactive distillation with splitting feed stream of sodium hydroxide and another was the multiple feeds reactive distillation with splitting both feed stream of sodium hydroxide and oil.

The first configuration, the column with splitting sodium hydroxide feed, the sodium hydroxide feed stream was equally splitted and fed to every reactive stage. The second configuration, the column with splitting sodium hydroxide and oil feed, the sodium hydroxide and oil feed stream were equally splitted and fed to every reactive stage alike the first column.

3.3 Results and discussion

The results of each proposed process model were considered. They consisted of the temperature profile, the product generation which were methyl palmitate, methyl oleate and methyl linoleate, and the sodium hydroxide concentration in each stage. The profile of each parameter informed the behavior and capability of three different column configurations. In addition, the study of the effect of the change in operating condition which were boil up ratio, reflux ratio and residence time in the column were also determined in order to perform the comparative study among these configurations. The proper operating conditions of each condition were proposed from the presented results.

3.4 Conclusions and recommendations

According to the results, the conclusion was presented to determine the capability of the alteration of the column. The appropriate operating conditions were also defined. In addition, the recommendations were suggested for the further study.

3.5 Apparatus and computer

- Laptop computer
  1. CPU (Intel® Core™2 2.10 GHz (2CPUs))
  2. 3.00 GB of RAM
  3. 250 GB of hard disk

- Operating System: Microsoft Window 7 Ultimate
- Software: ASPEN PLUS version 7.1

CHAPTER 4 RESULTS AND DISCUSSION

This chapter covers the simulation models of three alternative reactive distillations and the simulation results. Furthermore, the results of the varied operating conditions are also presented.

4.1 Simulation model

Biodiesel production in this research is applied the tranesterification to produce biodiesel from palm oil. Sodium hydroxide was used as homogeneous catalyst to promote the reaction. The process included with the reaction section, separation of methanol and water washing section. The palm oil contained palmitic acids (44.3 wt.%), oleic acids (38.7 wt.%), linoleic acids (10.5 wt.%) and other fatty acids (7.5 wt.%) as reactant. In order to perform the simulation, the feed fraction is simplified and contained 47.38 wt.% of palmitic acid, 41.39 wt.% of oleic acid and 11.23 wt.% of linoleic acid (Chakton, 2009). This simulation used UNIFAC model (Myint, and El-Halwag, 2009) as the thermodynamic property method.

In the conventional production, the reactor and the distillation column are normally separated. However, in this work, the reactor and distillation column were combined into a single operating unit, called reactive distillation which is mentioned in a lot of research. In the single feed model, feed stream of each reactant introduced to the reactive distillation column. The heavier reactant is fed at the top of reactive zone, and the lighter reactant is fed at the bottom of reactive zone. These counter current feeds let the light reactant contact with the heavy reactant.

In this work, 1000 kg/h of palm oil is fed to react with 160 kg/h of methanol mixed with 1 kg/h of sodium hydroxide. Methanol and sodium hydroxide were mixed in the mixing tank (V-101). The reactant feed streams were fed at 25 °C and were preheated to 50 °C before entering the reactive distillation column (C-101). There are ten stages of distillation including with condenser and reboiler (Chakton, 2009). The reactive stages were started from fourth stage to eighth stage. The boil up ratio and the reflux ratio were determined as operating conditions and set at 1 and 0.6, respectively (Chakton, 2009). The residence time was set at 3.5 minutes. Palm oil was then fed to the top of reactive stage, stage forth. Methanol mixed with sodium hydroxide was fed to the bottom of reactive stage, stage eighth for the single feed model. Besides, for the multiple feeds model, the mixture of methanol and sodium hydroxide was fed to stage fourth, fifth, sixth, seventh and eighth to enhance the production. The bottom product was then sent to the decanter (V-103) to separate product, which contained methyl palmitate, methyl oleate and methyl linoleate, and glycerol. Product without glycerol was mixed with 500 kg/h of water in the mixing tank (V-103) to remove sodium hydroxide. It then entered another decanter (V-104) to separate water with sodium hydroxide from biodiesel by using liquid-liquid activity between water and methyl ester. Moreover, the remaining water in biodiesel product was evaporated in the evaporator (E-103 and V-105) to achieve the biodiesel specification.

4.2 Single feed reactive distillation

From the process production that was described above, the process flow diagram was illustrated in Figure 4.1. The product obtained was contained with 44.50 wt.% of methyl palmitate, 41.25 wt.% of methyl oleate and 11.24 wt.% of methyl linoleate and other results were expressed in Table 4.1

Table 4.1 The product property result from single feed reactive distillation

Parameter	Value
Product flow rates (kg/h)	997.65
Temperature (°C)	110
Pressure (atm)	1
Vapor fraction	0
Product purity (wt.%)	96.95 wt.%

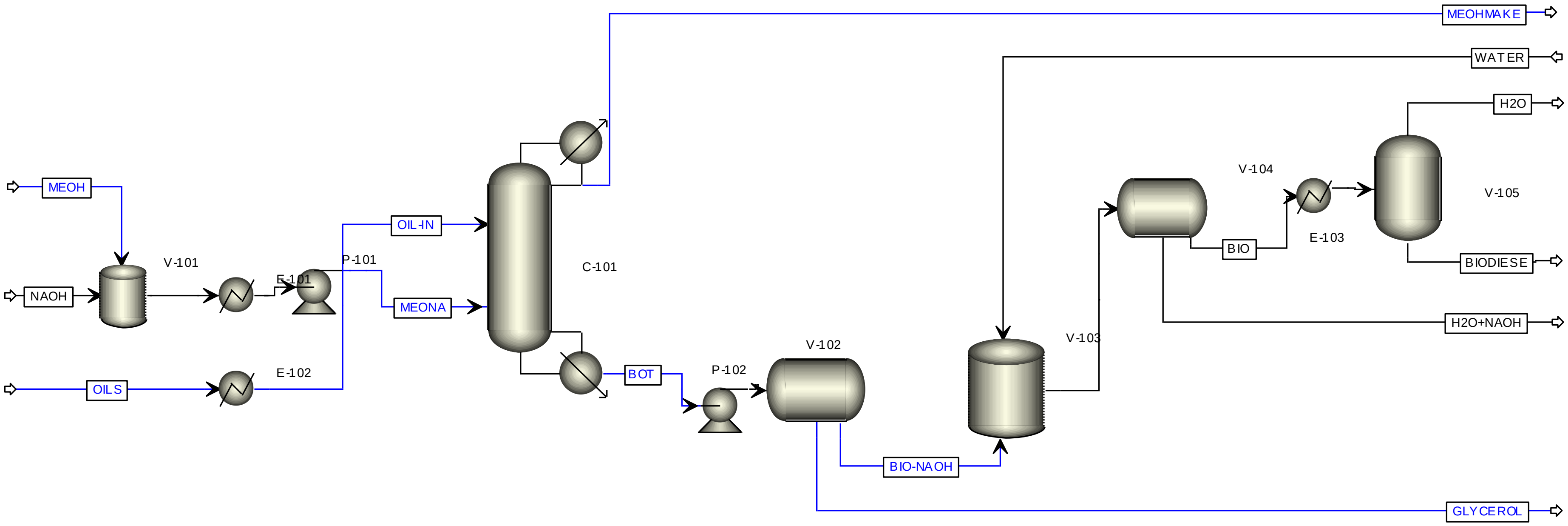


Figure 4.1 Process flow diagram of biodiesel production with single feed reactive distillation

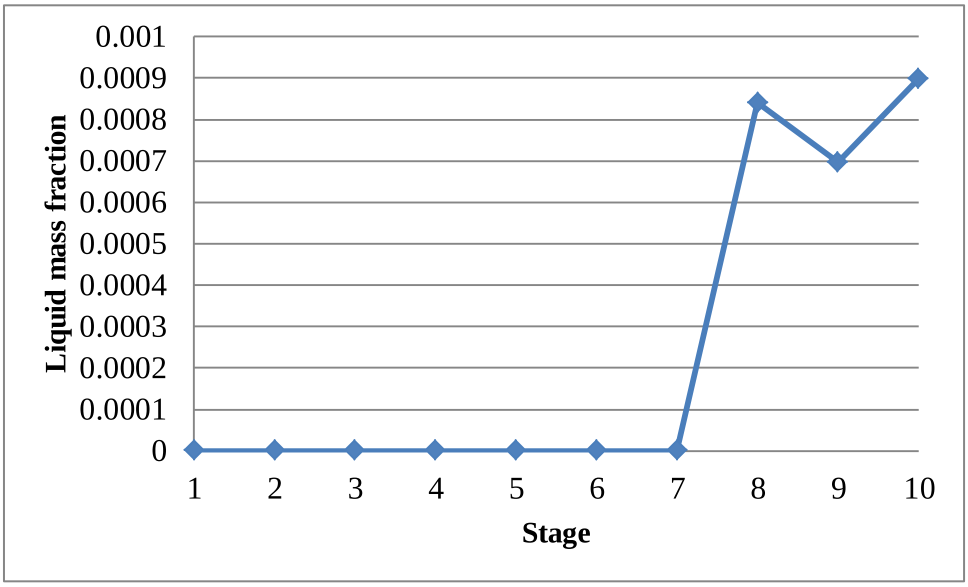


Figure 4.2 Sodium hydroxide concentration in single feed reactive distillation (RR=1 BR=0.6)

From Figure 4.2, the profile of sodium hydroxide concentration expressed that at its feed stage, the concentration of sodium hydroxide was the highest compared to the other stages in the reactive zone because sodium hydroxide was fed at the stage eighth and it cannot pass through the higher stage. In addition, this definitely affected to the product yield, as demonstrated in Figure 4.3, since the reaction depends on the concentration of sodium hydroxide.

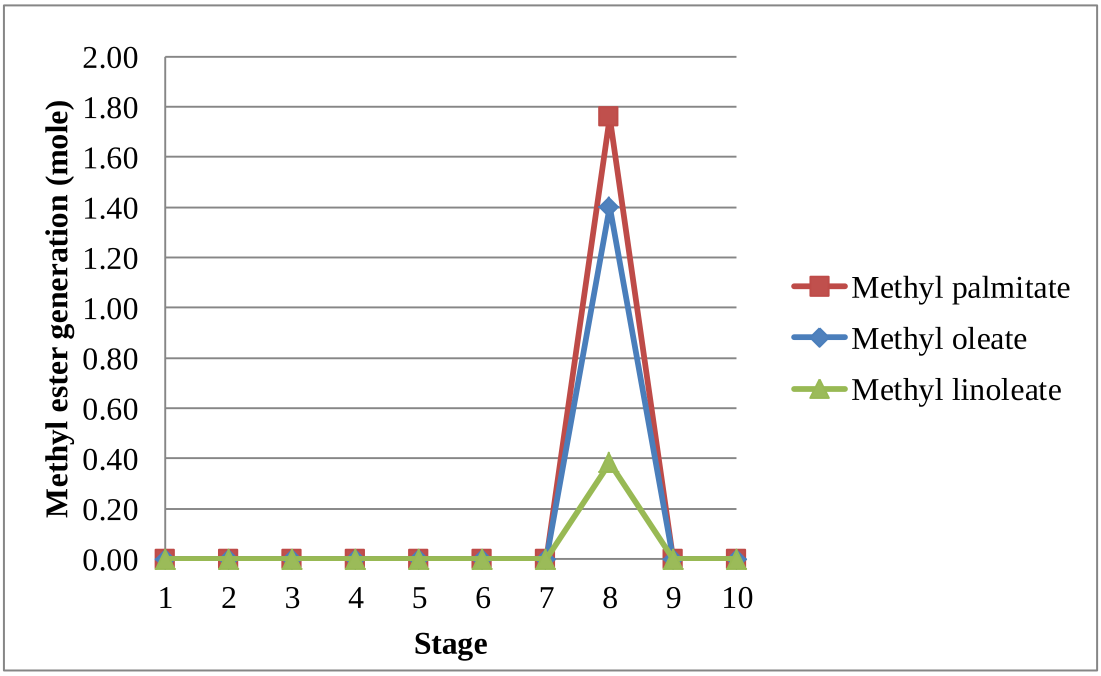


Figure 4.3 Methyl ester generated in each stage of single feed reactive distillation (RR=1 BR=0.6)

According to Figure 4.3, the highest yield of methyl ester was only produced in the column obtained at stage eighth due to the concentration of sodium hydroxide. The low concentration of sodium hydroxide in other stages in the reactive zone causes the low production of methyl ester in that reactive zone. The various production of each methyl ester conformed to the feed composition of each type of triglycerides.

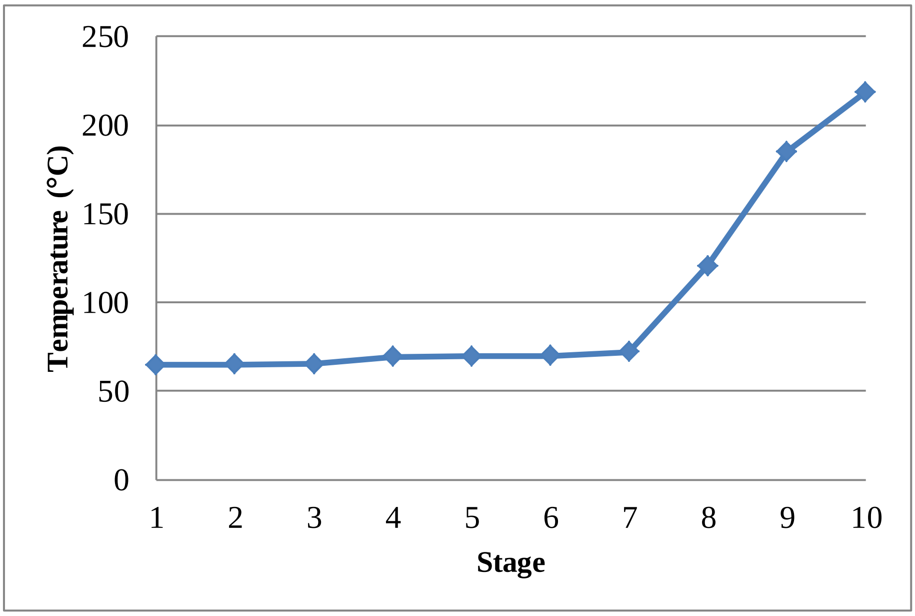


Figure 4.4 Temperature profile of single feed reactive distillation (RR=1 BR=0.6)

According to the temperature profile revealed in Figure 4.4, the temperature at the stage eighth was the highest compared to other reactive stages (stage forth to stage seventh) in the reactive zone. This was the result of the heat released from the exothermic reaction. This agrees to the concentration profile of sodium hydroxide shown in Figure 4.2.

4.3 Multiple feeds reactive distillation

4.3.1 Multiple feeds reactive distillation: feed stream of sodium hydroxide

After the single feed reactive distillation was performed, the results revealed that the reaction occurred only on the stage of sodium hydroxide feeding (stage eighth). Therefore, it must be an alteration of the distillation column configuration to perform the column with sodium hydroxide presented in every reactive stage. Then, the additional feed streams of sodium hydroxide were introduced to the column to keep sodium hydroxide existing in every reactive stage. This was an alternative method to promote the reaction in the reactive zone of the column. As it was mentioned in the beginning of this chapter, the mixture of methanol and sodium hydroxide was fed to the reactive stages which were stage fourth to stage eighth. This feed streams were equally splitted. Likewise, the overall process and operating conditions of equipment remained the same as the single feed and was displayed in Figure 4.5. The biodiesel product consisted of 44.73 wt.% of methyl palmitate, 41.40 wt.% of methyl oleate and 11.27 wt.% of methyl linoleate and other results were shown in Table 4.2.

Table 4.2 The product property result from multiple feeds reactive distillation sodium hydroxide splitted

Parameter	Value
Product flow rates (kg/h)	1000.34
Temperature (°C)	110
Pressure (atm)	1
Vapor fraction	0
Product purity (wt.%)	97.40 wt.%

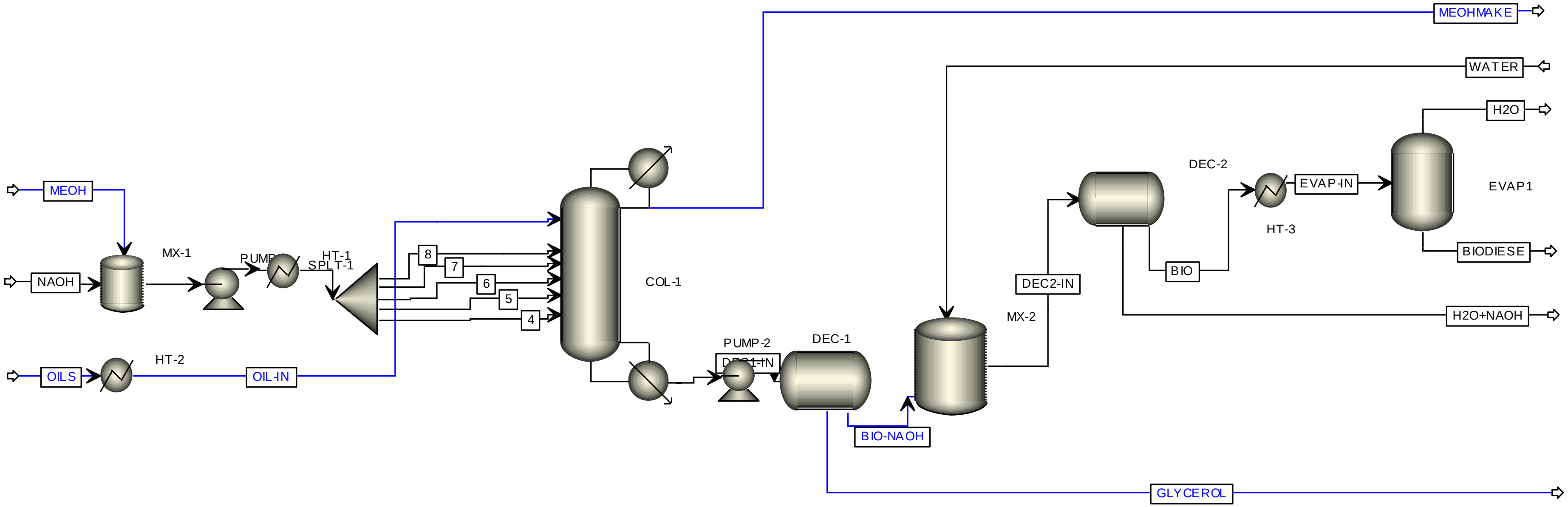


Figure 4.5 Process flow diagram of biodiesel production with multiple feeds reactive distillation sodium hydroxide splitted

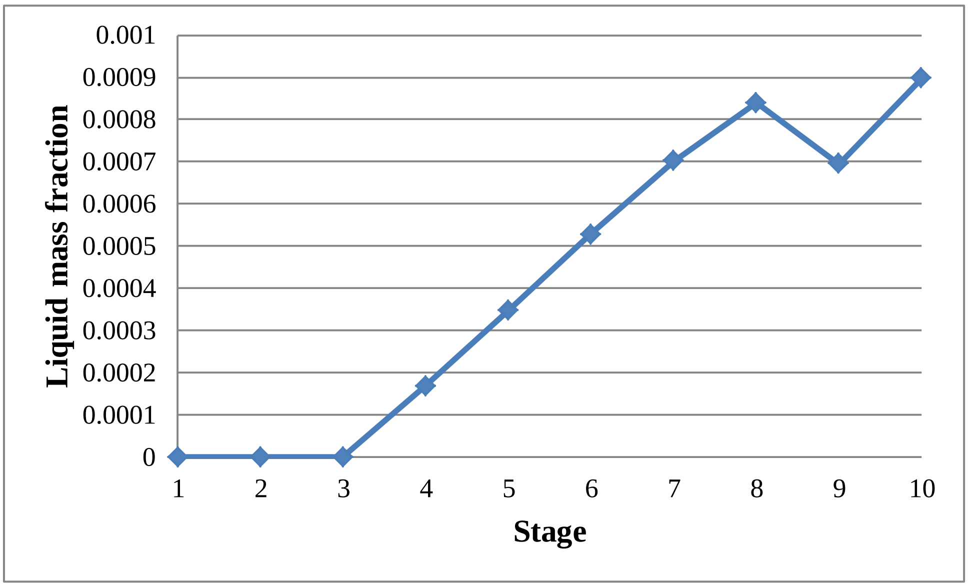


Figure 4.6 Sodium hydroxide concentration profile in multiple feeds reactive distillation sodium hydroxide splitted (RR=1 BR=0.6)

Figure 4.6 demonstrated the concentration of sodium hydroxide in the reactive column with the multiple feed streams of sodium hydroxide mixed with methanol. It presented that the concentration of sodium hydroxide got higher in the lower stage in the reactive zone since the sodium cannot pass through the higher stage. Sodium hydroxide, as it cannot go up to the higher stage, dropped to the lower stage. Each reactive stage obtained sodium hydroxide from stage above and got richer concentration of sodium hydroxide.

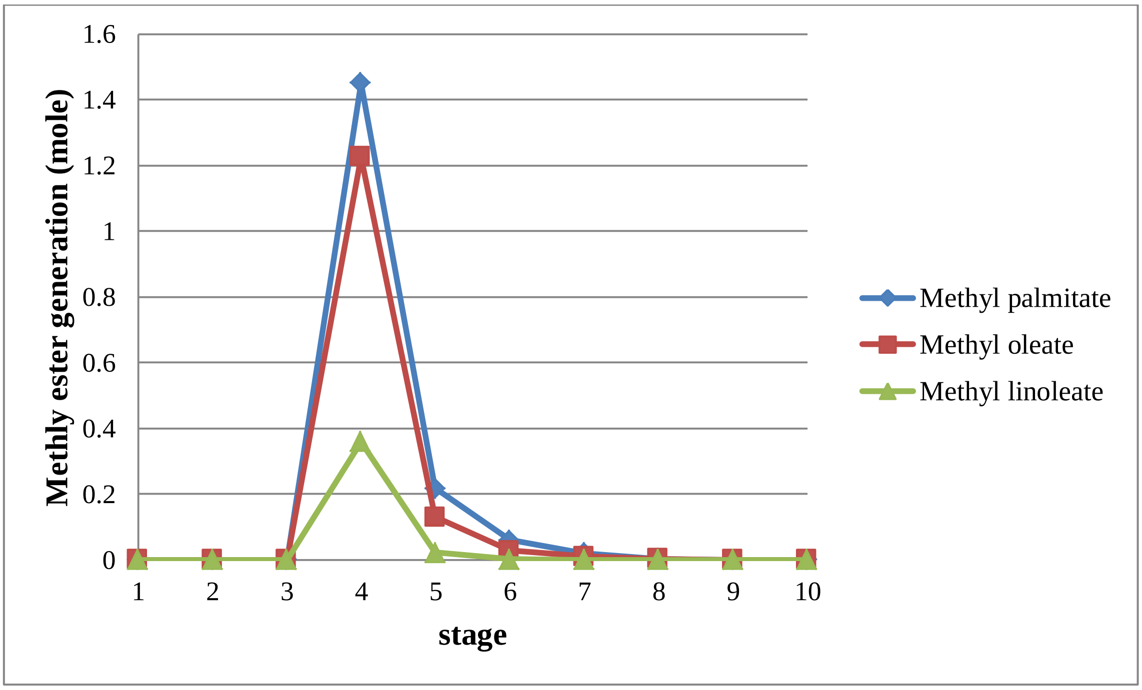


Figure 4.7 Methyl ester generated in each stage of multiple feeds reactive distillation sodium hydroxide splitted (RR=1 BR=0.6)

The highest yield of methyl ester generated in the column was on the stage fourth as seen in Figure 4.7 since the reactants, oil and mixture of methanol and sodium hydroxide, mixed at that stage. For other reactive stages, it may imply that the fed oil, triglycerides, was used up. Therefore, on other reactive stages, the product yield was not obtained as much as the fed oil stage (stage fourth).

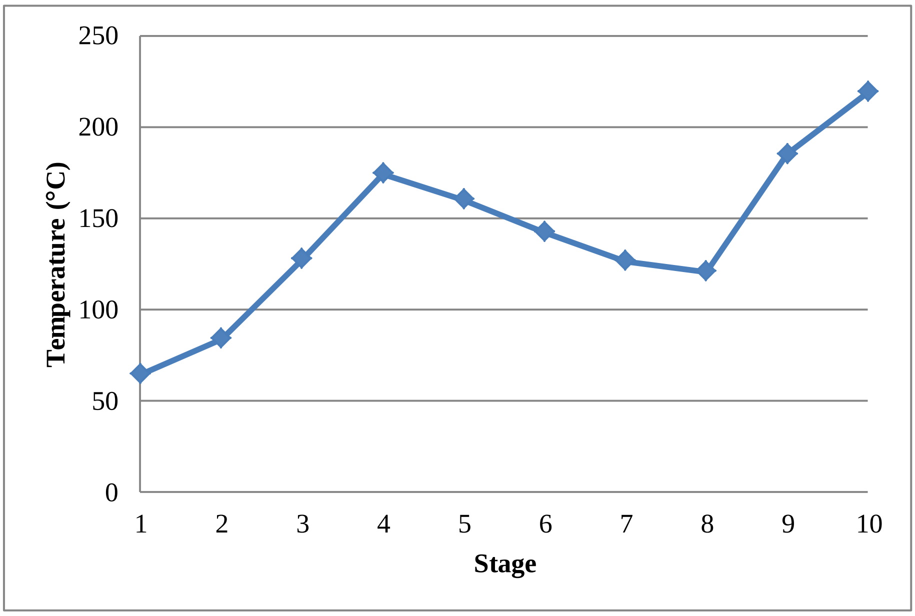


Figure 4.8 Temperature profile in multiple feeds reactive distillation sodium hydroxide splitted (RR=1 BR=0.6)

The curve in Figure 4.8 presented that the temperature profile in the reactive zone dropped from the higher stage to the lower since most of product produced at the stage fourth. This implied that most of heat released at the stage fourth due to the exothermic reaction. However, the temperature did not sharply drop at the lower stages because of the reboiler duty.

4.3.2 Multiple feeds reactive distillation: feed stream of sodium hydroxide and oil

In this configuration, not only the sodium hydroxide feed stream was splitted but also the oil feed stream, as demonstrated in Figure 4.9. It is the alternative configuration of the multiple feeds reactive distillation column. The production process remained the same as the two configurations that were mentioned above.

Table 4.3 The product property result from multiple feeds reactive distillation both sodium hydroxide and oil splitted

Parameter	**Value**
Product flow rates (kg/h)	1000.7
Temperature (°C)	110
Pressure (atm)	1
Vapor fraction	0
Product purity (wt.%)	97.25 wt.%

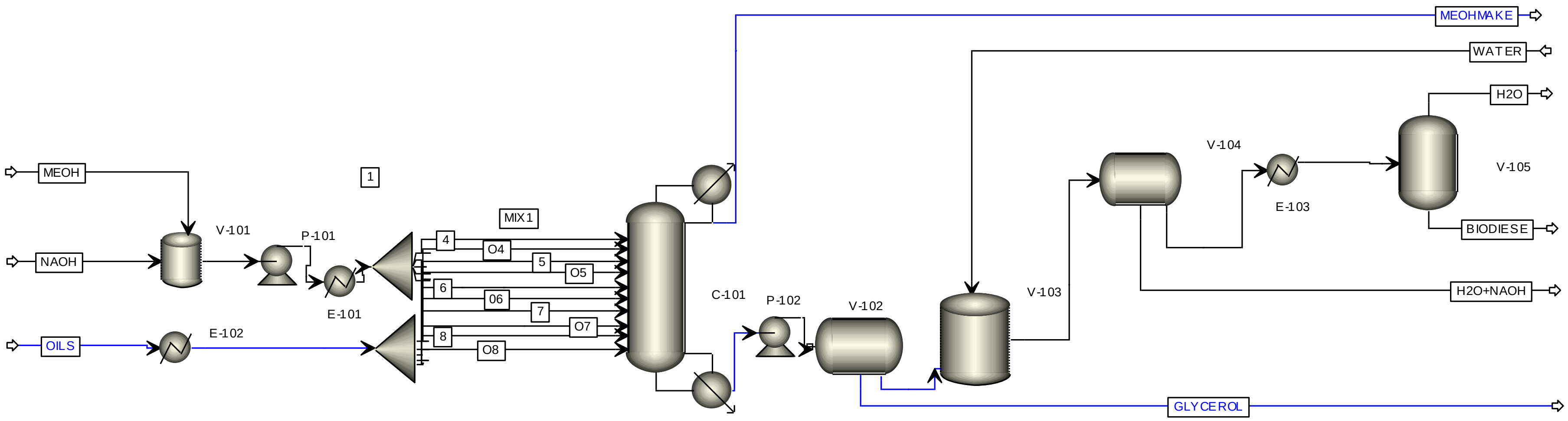


Figure 4.9 Process flow diagram of biodiesel production with multiple feeds reactive distillation both sodium hydroxide and oil splitted

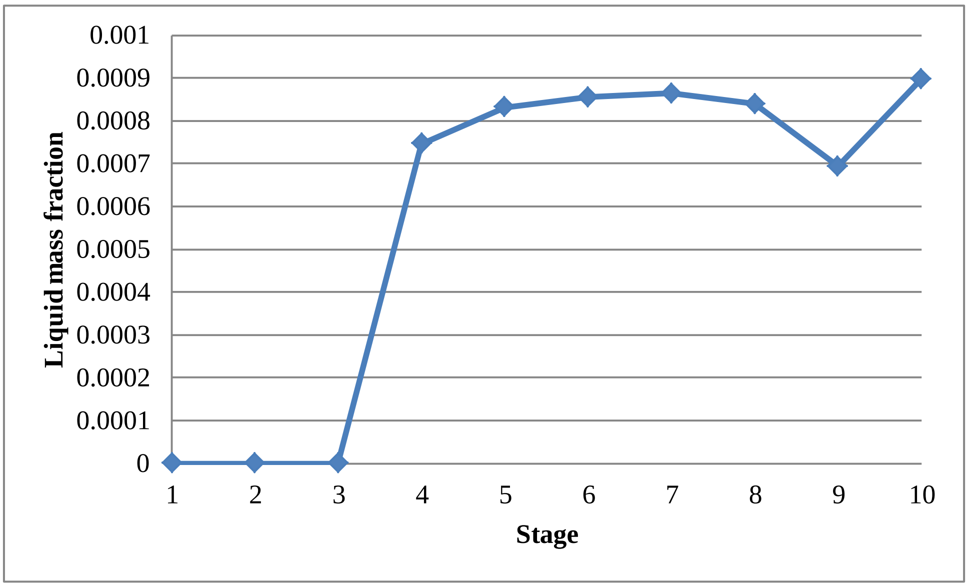


Figure 4.10 Sodium hydroxide concentration in multiple feeds reactive distillation sodium hydroxide and oil splitted (RR=1 BR=0.6)

According to the equally splited oil and sodium hydroxide fed to each reactive stage, the distribution of sodium hydroxide in each stage was rather the same which was different from the two previous configurations. This concentration distribution affected the reaction to equally generate methyl ester in every stage.

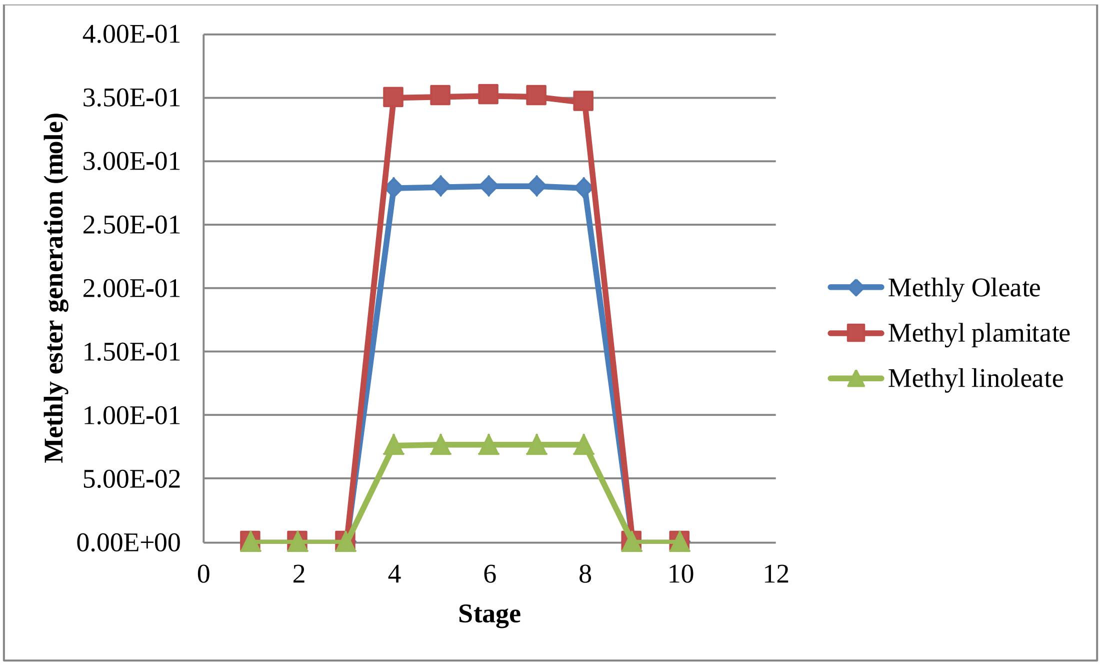


Figure 4.11 Methyl ester generated in each stage of multiple feeds reactive distillation both sodium hydroxide and oil splitted (RR=1 BR=0.6)

From Figure 4.11, the product was equally generated in each reactive stage since the amount of oil and sodium hydroxide were almost the same in each stage and oil.

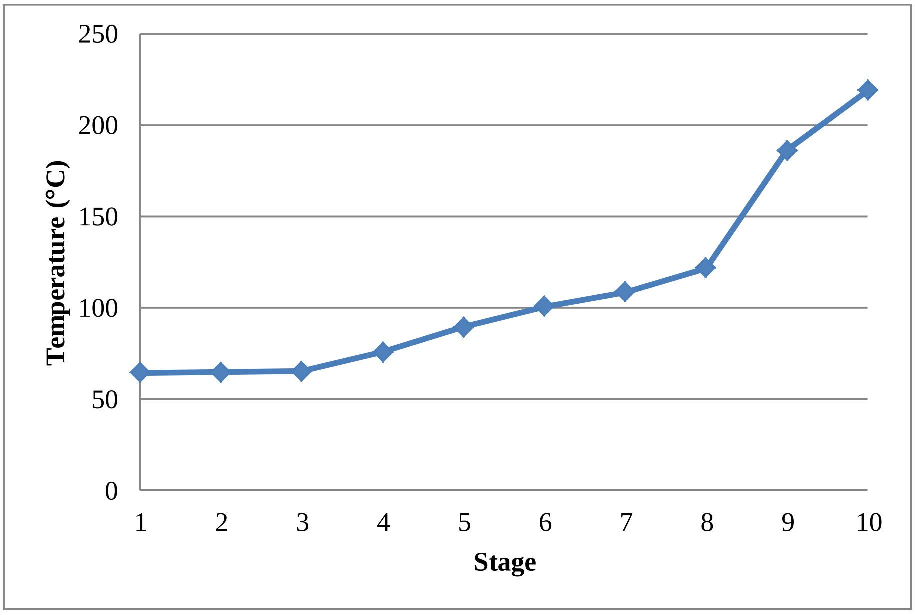


Figure 4.12 Temperature profile in multiple feeds reactive distillation both sodium hydroxide and oil splitted (RR=1 BR=0.6)

Since the reaction occurred equally in each stage, the temperature in the higher reactive stage was slightly increased, as displayed in Figure 4.12, which was more feasible in the operation than the two configurations presented before.

4.4 Comparative study of single feed reactive distillation and multiple feeds reactive distillation

After the three alternative configurations of the reactive distillation employed in biodiesel production were performed, the effects of operating parameters of the distillation were studied comparatively. Those sensible parameters were reflux ratio, boil up ratio and residence time.

4.4.1 Effect of reflux ratio and boil up ratio of reactive distillation

Figures 4.13 - 4.15 displayed the similar tendency of the methyl ester fraction when the boil up ratio and reflux ratio were varied. It has clearly seen that the product specification was strongly affected with the operating condition. The more boil up ratio set, the less methyl ester fraction obtained. On the other hand, the more reflux ratio set, the more methyl ester fraction can be produced. The reason is, at the higher boil up ratio, the higher temperature reached at the bottom of the column and affected the overall column temperature. However, this reaction is an exothermic reaction which the high temperature at the surrounding affected the low product conversion. Consequently, the increment of boil up ratio supported the vaporization of product to supply to the bottom of the column. That resulted in the backward reaction because the product was supplied to dissolve with the effluent stream. Besides, the increasing reflux ratio raised the amount of liquid which mostly contained with methanol. This methanol supply promoted the conversion of the forward reaction. Therefore, to obtain a higher methyl ester fraction, the boil up ratio must be high and the reflux ratio must be low.

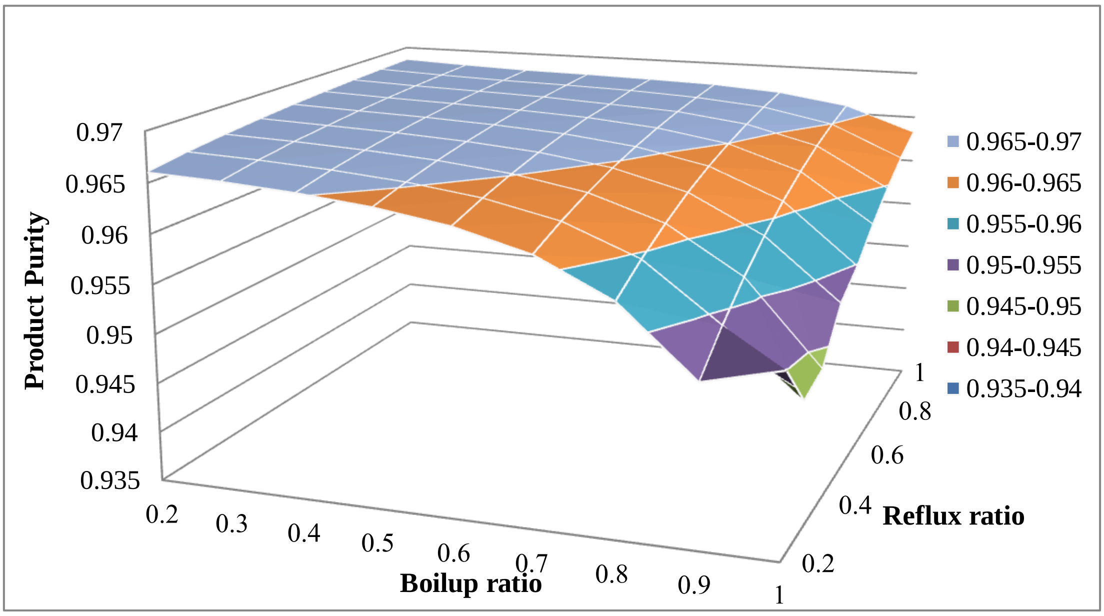


Figure 4.13 Product purity produced by single feed reactive distillation at different boil up ratio and reflux ratio

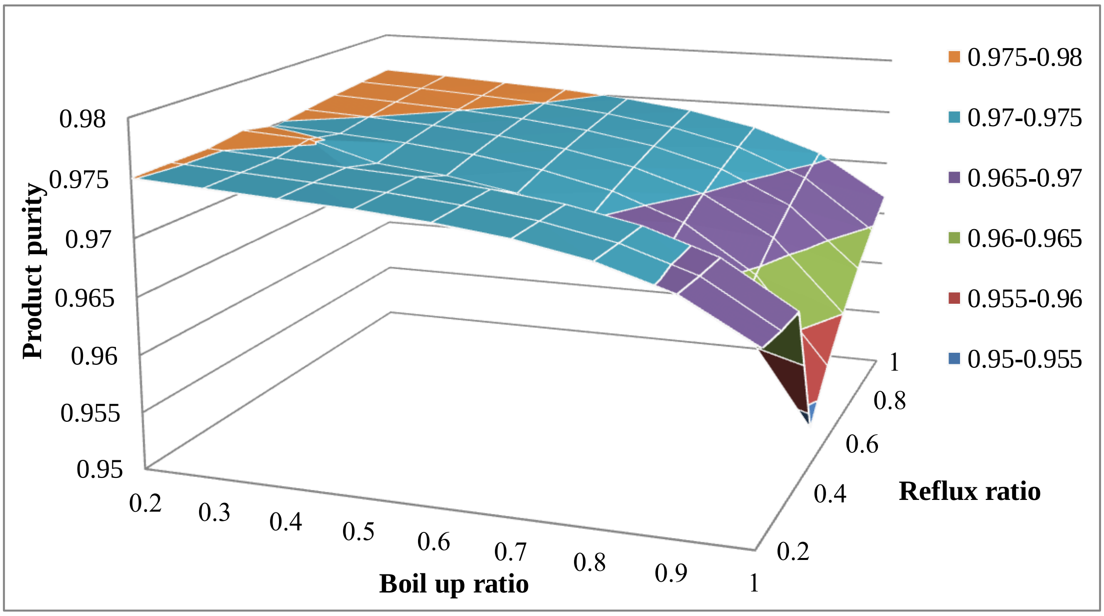


Figure 4.14 Product purity produced by multiple feeds reactive distillation sodium hydroxide splitted at different boil up ratio and reflux ratio

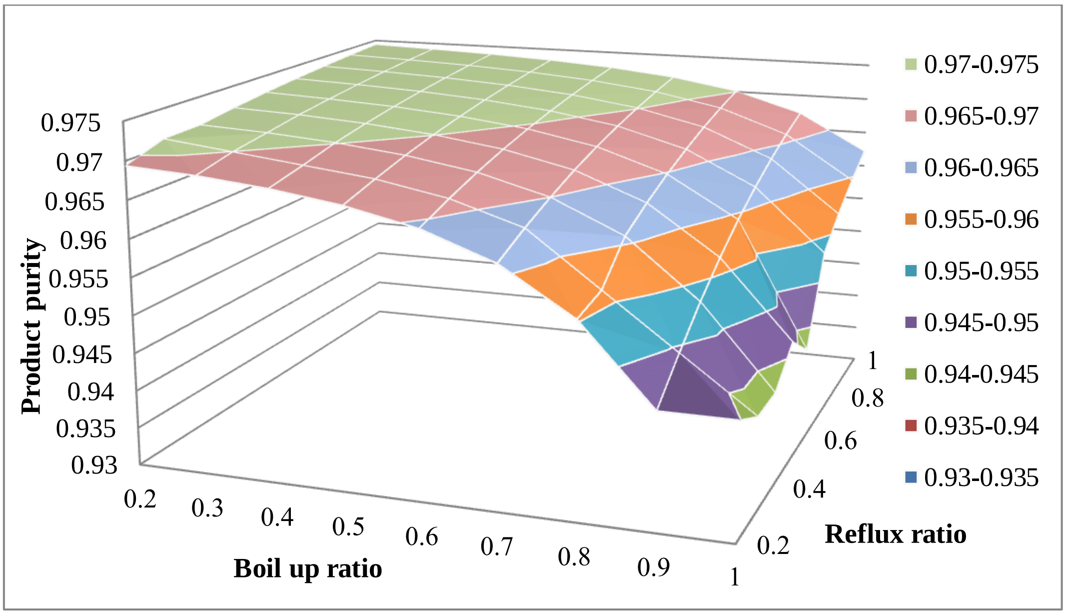


Figure 4.15 Product purity produced by multiple feeds reactive distillation both sodium hydroxide and oil splitted at different boil up ratio and reflux ratio

The comparison of the curve of the single feed reactive distillation in Figure 4.13, the curves of the multiple feeds reactive distillation in Figure 4.14 and Figure 4.15 was investigated. At the specified operating condition, methyl ester fraction obtained from the single feed reactive distillation was lower than the one from multiple feeds column. It was deduced that the equally splitted feed affected the better driving force of the reaction. Besides, the driving force in the single feed column was high at the feed stage but the driving force in other stage was low. This influences the product quality. However, the column with splitted oil and sodium hydroxide was less efficiency than the column with splitted only sodium hydroxide. Anyhow, its efficiency is better than the single feed column. The highest product purities were 0.967, 0.975 and 0.97, according to these figures.

4.4.2 Effect of residence time in reactive column

The study of effect of the residence time covered both in the single feed column and the multiple feeds column. The boil up ratio was fixed at 0.2 and the reflux ratio was varied from 0.2 – 1 and plotted with the varied residence time between 1 and 5.5 and methyl ester fraction.

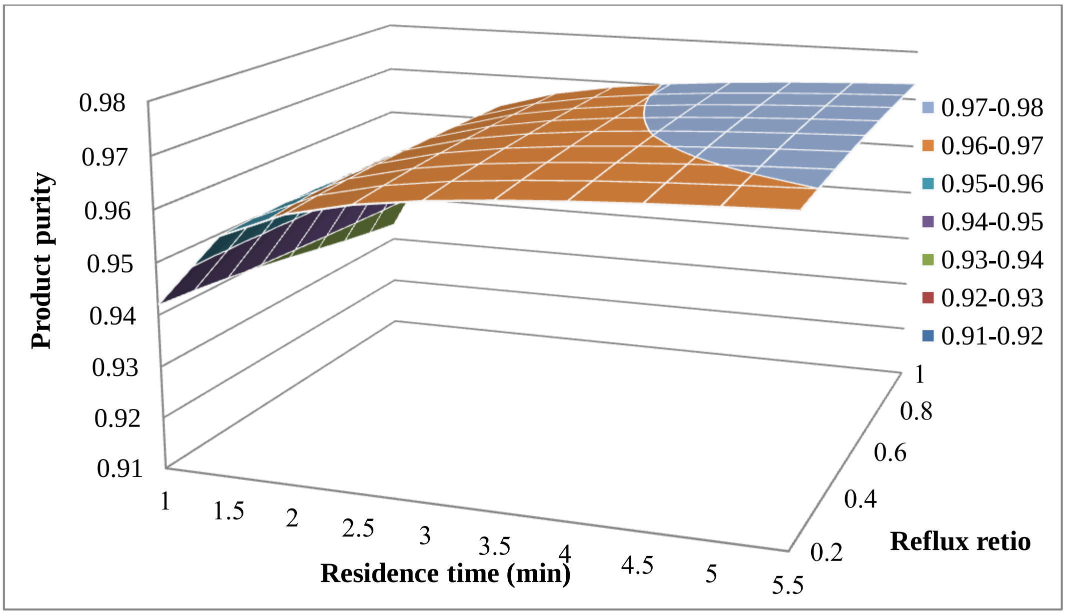


Figure 4.16 Product purity produced by single feed reactive distillation at different residence time and reflux ratio

As previous presented result, the low boil up ratio presented the higher yield. Then the low boil up ratio, 0.2, was selected to study the effect of varied reflux ratio at the fixed boil up ratio in the single feed column which displayed in Figure 4.16. It revealed that the highest yield obtained at the residence time around 2.5 – 3.0 minutes for each reflux ratio.

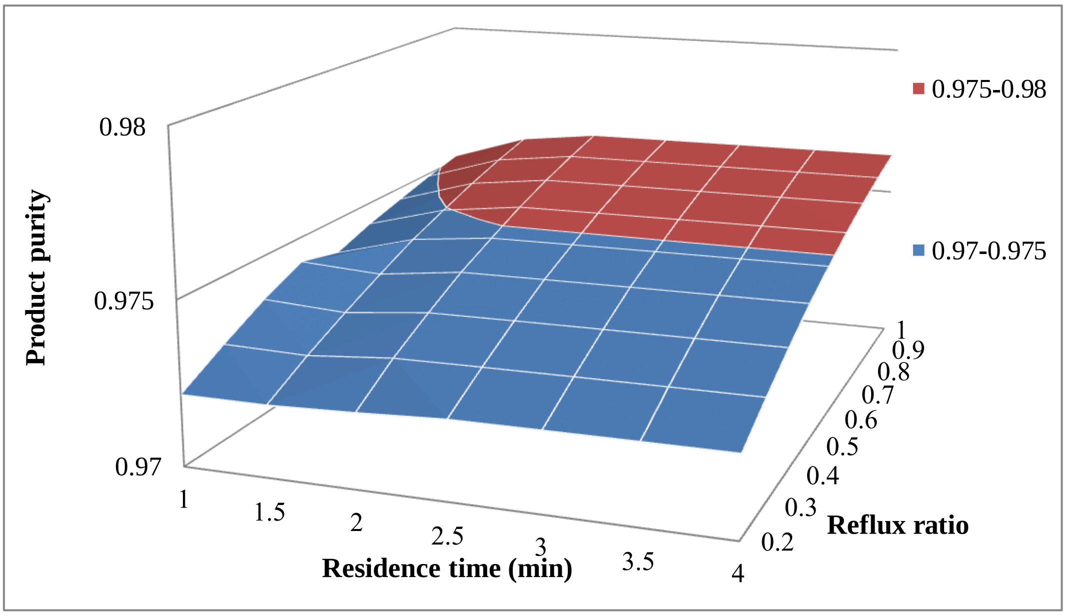


Figure 4.17 Product purity produced by multiple feeds reactive distillation sodium hydroxide splitted at different residence time and reflux ratio

The effect of the varied reflux ratio and the residence time to the product specification in the multiple feeds reactive distillation was illustrated by Figure 4.17. The highest product quality approached at 1-1.5 minutes in almost varied reflux ratio.

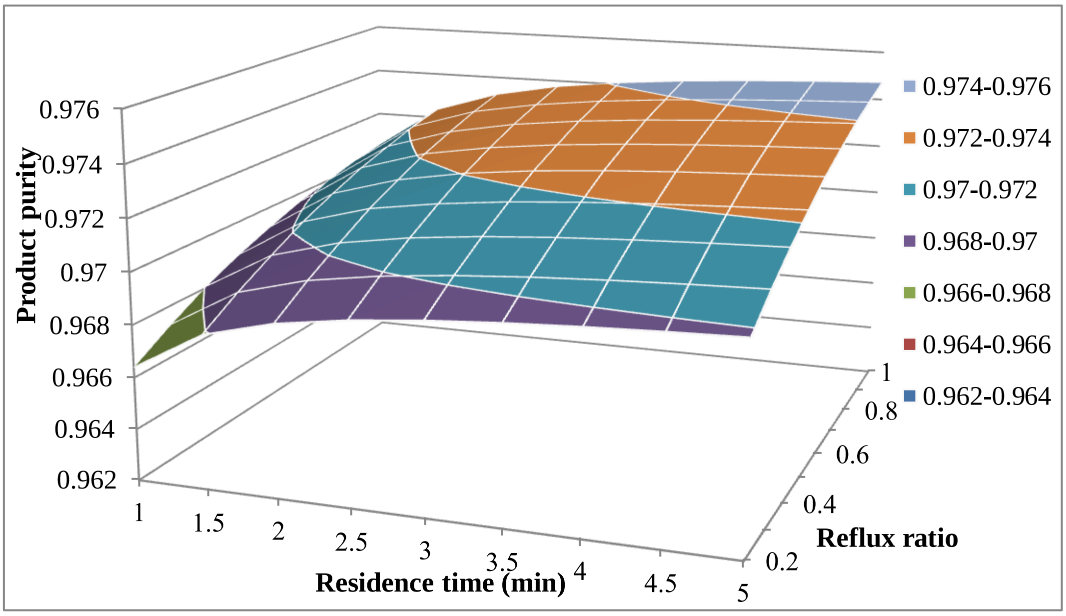


Figure 4.18 Product purity produced by multiple feeds reactive distillation both sodium hydroxide and oil splitted at different residence time and reflux ratio

According to Figure 4.18, the production reached the highest purity within 1.5-2.0 minutes. Therefore, it can be inferred that the multiple feeds models spent less time than the single feed model to reach the same product specification. Moreover, between the two multiple feeds models, the model with splitted oil and sodium hydroxide spent less time than the one with splitted only sodium hydroxide.

In this chapter, revealed results and discussion have been reported. It is quite obvious that the proposed multiple feeds reactive distillation can give more efficient productivity in terms of quality, quantity and reliability.

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This work focused on the reactive distillation applied in the biodiesel production plant. Transesterification reaction was selected as a main reaction in this production. The suitable catalyst introduced to transesterification reaction was sodium hydroxide. The reactive distillation had 10 stages equipped with reboiler and condenser. The reactive zone was set from stage fourth to stage eighth. The study covered three alternative configurations of the reactive distillation which were a single feed and two different designs of multiple feeds of the mixture of methanol and sodium hydroxide.

The work was firstly started with performing the production process with a single feed which the reactants were entered the reactive column at stage fourth and eighth. The heavier reactant; oil, was fed at the top of the reactive zone. It was found that the reaction occurred only on the stage where sodium hydroxide was fed (stage eighth) since sodium hydroxide cannot lift up to the higher stage. Thus, the product was formed only on the bottom stage of the reactive zone.

The multiple feeds reactive distillation was introduced to alter the configuration which sodium hydroxide existed in every reactive stage in order to promote the reaction efficiently. The result revealed that most of product was produced on stage fourth where the two reactants, oil and mixture of methanol and sodium hydroxide, were mixed. Another multiple feeds reactive distillation was performed by equally splitting methanol and oil. These two streams were fed to every reactive stage which the reactants were mixed in all reactive stages. It was found that the reaction took place in every reactive stage.

Then, the comparative study of three columns was investigated. The parameters consisted of boil up ratio, reflux ratio and residence time in the reactive distillation column. Both boil up ratio and reflux ratio were varied between 0.2 and 1. Residence time was varied from 1 to 4 minutes. The results presented that the more boil up ratio was, the less product quality obtained. Besides, the more reflux ratio was, the more product quality obtained. However, at 0.2 of reflux ratio, the product reached its standard specification, 96.5 wt.%. Thus, the optimum boil up ratio and reflux ratio were 0.2 and 0.2, respectively. In addition, at the specific condition, the multiple feeds columns produced high quality and more quantity of product than the single feed column. These happened in all configurations. Moreover, the single feed spent more time, 4.5 minutes, to obtain the same product specification as the two multiple feeds configurations, 1 minute and 2 minutes.

5.2 Recommendations

1. Economic analysis should be performed to investigate the investment cost, operating cost and payback period in order to compare the benefit of the three different configurations.

2. The control system should be considered to inform the control possibility of the multiple feeds reactive distillation columns in an industrial production.

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Appendix A

Calculation of rate constant

Appendix A: Calculation of rate constant depended on reactants and catalyst concentration

Regarding to Noureddini and Zhu (1997), the rate constant depended alone on the reactants concentration which the concentration of catalyst was fixed equalled to 0.2 wt.% However, in the reactive distillation, the catalyst concentration was fluctuated. Then, it is important to do a calculation of the rate constant which also depended on the catalyst concentration.

$$R = k'[A][B] \tag{A.1}$$

$$k' = k[NaOH] \tag{A.2}$$

$$R = k[NaOH][A][B] \tag{A.3}$$

$$R = k[NaOH][A][B] = k'[A][B] \tag{A.4}$$

At initial condition (Noureddini and Zhu (1997)),

NaOH in solution = 0.2 wt.%

Convert wt.% to concentration (mol/L)

$$Concentration = \frac{\frac{wt.}{wt.}\% \times \frac{1}{100} \times \rho\left(\frac{g}{m^3}\right) \times 1000\left(\frac{cm^3}{dm^3}\right)}{MW\left(\frac{g}{mol}\right)} \tag{A.5}$$

$$= \frac{\% \times 10 \times \rho}{MW}$$

Thus,

$$[NaOH] = \frac{0.2 \times 10 \times 0.9}{40}$$
$$= 0.045$$

From Equation 4,

$$R = \frac{k'[NaOH][A][B]}{0.045}$$

The new reaction rate constants were shown in Table A.1

Table A.1 The energy of activation and the modified reaction rate constant at 50 °C using NaOH

Reaction	Energy of Activation (cal/mol)	Reaction rate constants
TG → DG	13145	1.067E+09
DG → TG	9932	1.291E+07
DG → MG	19860	6.000E+12
MG → DG	14639	2.218E+11
MG → GL	6421	1.196E+09
GL → MG	9588	4.822E+05

Appendix B

Calculation of Antoine coefficients

Appendix B: Calculation of Antoine coefficients

According to Aspen physical property system, the extended Antoine equation was available to determine the vapor pressure of each component. However, the estimated coefficients from Aspen Plus estimation didn't perform very well. Then, the simple Antoine equation was considered the more correct vapor pressure.

The equation for the extended Antoine vapor pressure model is

$$\ln p_i^{*,l} = C_{1i} + \frac{C_{2i}}{T + C_{3i}} + C_{4i}T + C_{5i}\ln T + C_{6i}T^{C_{7i}} \text{ for } C_{8i} \le T \le C_{9i} \tag{B.1}$$

The equation for the simple Antoine vapor pressure model is

$$\ln p_i^{*,l} = C_{1i} + \frac{C_{2i}}{T} \text{ for } C_{8i} \le T \le C_{9i} \tag{B.2}$$

To determine the coefficients from a simple Antoine equation, at least, two points of temperature and pressure must be considered to perform a simple vapor pressure curve. One was a normal boiling at 1 atm of each component. Another was temperature and pressure at the critical point. The normal boiling points were gathered from www.chemspider.com (20 August 2011) and the critical temperature and pressure were provided from the estimation of Property Constant Estimation System (PCES) in Aspen Plus. The points of each component were displayed in Table B1. By applying the plots, C_{1i} and C_{2i} could be specified from the intercept and the slope of vapor pressure curves. The Antoine coefficients obtained from vapor pressure curves were illustrated in Table B.2. After all coefficients were defined, they were input to PLXANT parameter in Aspen Plus

Table B.1 Normal boiling point at 1 atm, critical temperature and critical pressure of each component

Component	T_b (°C)	T_c (°C)	P_c (kPa)
Tripalmitate	759.80	2735.68	269.54
Trioleate	818.70	3746.15	235.89
Trilinoleate	816.50	3392.09	247.61
Dipalmitate	620.80	1388.62	500.93
Dioleate	670.80	1612.97	443.59
Dilinoleate	669.40	1581.45	463.68
Monopalmitate	451.30	1235.48	802.51
Monoolate	483.30	868.10	1122.31
Monolinoleate	485.00	870.97	1162.45
Methyl palmitate	332.10	1235.48	538.37
Methyl linoleate	343.85	602.16	1162.45

Table B.2 Antoine coefficients of each component from simple Antoine equation

Component	C_1	C_2
Tripalmitate	5.9729	-1029.2
Trioleate	5.6977	-885.3
Trilinoleate	5.7951	-960.84
Dipalmitate	7.5086	-1797.3
Dioleate	7.1462	-1695.7
Dilinoleate	7.2554	-1765.3
Monopalmitate	7.8808	-1474
Monoolate	10.044	-2622
Monolinoleate	10.124	-2670.4
Methyl palmitate	6.9025	-758.58
Methyl linoleate	10.306	-1955.8

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