COMPARISON OF KENICS AND SMX STATIC MIXERS FOR USE IN BIODIESEL PRODUCTION WITH CIRCULATION SYSTEM

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**A THESIS SUBMITTED AS A PART OF THE REQUIREMENTS
FOR THE DEGREE OF MASTER OF SCIENCE
IN ENERGY TECHNOLOGY AND MANAGEMENT**

**THE JOINT GRADUATE SCHOOL OF ENERGY AND ENVIRONMENT
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ABSTRACT

Static mixers are interesting devices for using in mixing applications and heat transfer capabilities, including biodiesel production. Static mixers have various designs for any proper purposes, but suitable models for biodiesel production process have not much been reported. In this study, standard types of static mixers, Kenics (a series of elements with short helixes of length equal to 3 times compared with the pipe radius and a twist angle of 180^o) and SMX (a complex series of cross-bars mixing elements) mixers, were used to produce biodiesel from coconut fatty acid via acid catalyst esterification in pilot-scale process using circulation system. Biodiesel production reactor with circulation system consisted of fatty acid tank, methanol tank, mixing tank, biodiesel tank, pump, and electric heaters, was employed to produce biodiesel. With 6:1 coconut fatty acid to methanol molar ratio, catalyst concentration of 0.7% v/v sulfuric acid (H_2SO_4) compared with fatty acid, and reaction temperature of 60 ^oC, SMX mixer can reached the highest fatty acid (FFA) conversion (88.40%), while Kenics mixer can achieve FFA conversion of 85.08%. Both types of static mixers can achieve FFA conversions more than referent cases, *i.e.* plain pipe and mechanical stirring (FFA conversions of 75.18 and 72.23%, respectively). In summary, the SMX mixer can be introduced as the most proper type static mixer for biodiesel production process (compared with Kenics mixer, plain pipe, and mechanical stirring), which it can provide FFA conversion and FAME yield more than 90% within 10 min of reaction.

Keywords: Coconut fatty acid, Esterification, Biodiesel, Static mixer, SMX, Kenics

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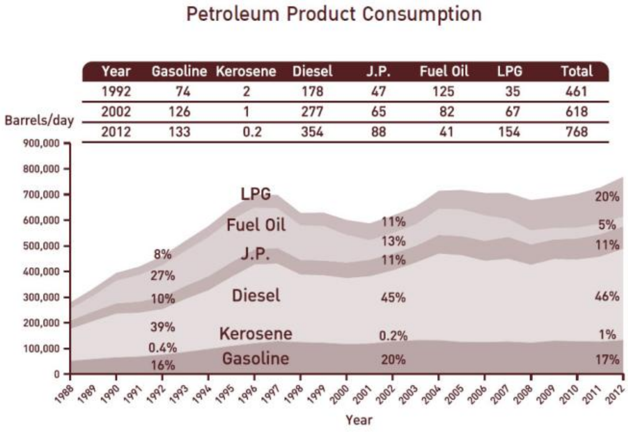
CHAPTER 1
INTRODUCTION

1.1 Rationale

The present world energy situation is entering into a crisis due to the increasing energy demand, rising of energy prices and also global warming problem. Fossil fuel resources, which are non-renewable energy resources (oil and coal), are continue increasing consumed. Without the any control measures, these energy resources may deplete in near future. Increasing renewable energy resources role for the energy need in the world is an interesting way to solve this problem.

There are several forms of renewable energy sources in the earth, such as solar power, nuclear power, wave energy, and energy from biofuels. Increasingly, renewable energy in the form of biofuels, especially biodiesel, is getting attention from the world because of environmentally friendly properties, and it is able to use with diesel engine without any specific modifications requirement [1].

In Thailand, the final energy demand in 2012 was growing rapidly due to economic growth and the energy policies of the government, while petroleum product was the most important part that accounted for 48.3% [2]. Figure 1.1 shows the trends of petroleum product consumption in Thailand. Diesel consumption increase significantly from 178 barrels/day, accounted for the largest share of 46%, in 2012 to 354 barrels/day, accounted of 10% in 1992.



Year	Gasoline	Kerosene	Diesel	J.P.	Fuel Oil	LPG	Total
1992	74	2	178	47	125	35	461
2002	126	1	277	65	82	67	618
2012	133	0.2	354	88	41	154	768

Figure 1.1 Petroleum product consumption in Thailand [3]

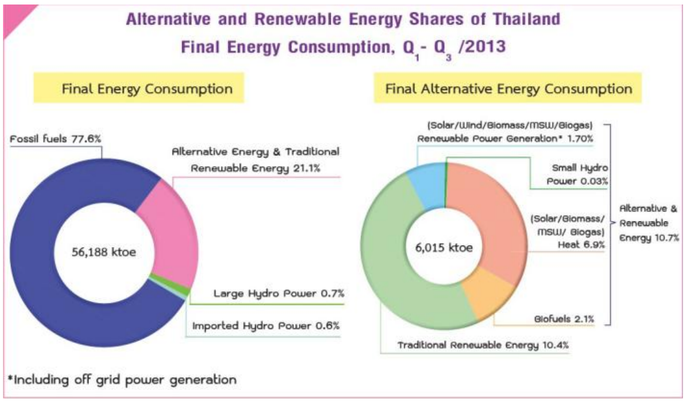


Figure 1.2 Alternative and renewable energy shares of Thailand final energy consumption, Q_1-Q_3/2013

Due to the continuous increase of petroleum product consumption, alternative energy was promoted by government to reduce the domestic petroleum fuel demand. Alternative energy consumption of Thailand in 2013 is accounted of 22.4%, as shown in Figure 1.2. Due to Thailand is an agricultural country, biodiesel can be considered as alternative fuel to petroleum diesel. Therefore, biodiesel production is expected to significantly growing due to the increasing of diesel consumption. Thai's government promoted policy in 2008, which require replacing petroleum diesel with B2 and B5 biodiesel (a mixture of diesel with 2% and 5% biodiesel, respectively).

Biodiesel or fatty acid methyl ester (FAME) is a renewable organic biofuel represented as a fossil diesel fuel. It produced from agricultural fuel crops or animal fat, so it can reduce the implication from fossil fuels such as high fuel cost and impact on environment because of its benefits *i.e.* high degradability, low pollution emission and. In addition, the production cost is a major obstacle in biodiesel production process. The most important factor of production cost is the feedstocks cost, mostly are edible-grade refined oils that containing low amount of free fatty acids (FFA), which appropriate for biodiesel trans-esterification. Typically, biodiesel in Thailand was manufactured from vegetable oil, like palm or jatropha.

In fact, biodiesel can be made by two methods. First, transesterification of many kinds of renewable feedstocks such as pure vegetable oil, waste cooking oil or animal fats with methanol or ethanol in the presence of base catalysts. Second, esterification of free fatty acid (FFA) from waste cooking oil and waste from refined oil those have high fatty acid content, *i.e.* some vegetable oils such as coconut oil and mahua oil, animal fats and also palm fatty acid distillate (PFAD) with methanol over the acid catalyst. According to the problem with high edible-grade feedstock cost, esterification of low quality feedstocks can reduce the production cost and making biodiesel has high competitive with petroleum-based fuel.

Nowadays, the developments of alternative energy resources become an important topic for sustainable and environmental saving. But, there are some problems in biodiesel production those are mass transfer limited, possibility of backward reaction and most industrial processes are run in a batch mode that the advantages of continuous process cannot obtain [4]. Increasing productivity and operating conditions safety, reduce production waste and energy consumption are main objectives of process improvement. Many researchers introduce the novel technologies for improve these problems, *i.e.* oscillatory flow reactors, spinning tube reactors, microwave reactors, and static mixers.

Static mixers, known as motionless mixers, consist of series of fixed mixing elements enclosed within a tubular pipe. Static mixers become the interesting devices that using in mixing applications and heat and mass transfer abilities due to its benefits compared with mechanically stirring processes. It requires lower energy consumption because it exploited energy of the flow stream of fluids that flow through it to create mixing, and it can reduce the maintenance requirements and also maintenance cost follow to there are no moving parts. Static mixers are more efficiency in fluids mixing that cannot mix together under normal conditions. Moreover, the smaller space requirement, low equipment operation, reduce residence time, byproduct decreasing and enhanced safety are the major advantages of using static mixer in industries such as chemical reactions, pharmaceutical, food processing, etc. Regularly, static mixers have various designs for any proper purposes, but industry processes use only few models and the model that optimize for use in biodiesel production process are infrequent.

In this work, the biodiesel production processes of coconut fatty acid in circulation operation using static mixer via acid-catalyst esterification in pilot-scale experiment were used to determine the performances of widely industrial used static mixers, Kenics and SMX mixers, base on criteria of residence time (min) and FFA conversion (%). The results were compared with biodiesel production processes by using plain pipe in pilot-scale experiment and also those processes with employing the mechanical stirrer in laboratory-scale experiment.

1.2 Literature Review

Most research has studied the comparative performance of biodiesel production processes between using the static mixer and mechanical agitation.

Sungwornpatansakul, et al. [5] studied the mean droplet diameters of methanol in oil from both of mixing methods, mechanical mixing, and helical type (HT) static mixer. Static mixer generated almost droplet diameter less than 5 μm, which smaller than mechanical mixer since the start of reaction. Figures 1.3 and 1.4 show the droplet sizes images of static mixer and mechanical mixer for initial and end of reaction, respectively. Furthermore, droplet size of static mixer distribution was more uniform, as shown in Figure 1.5. In addition, they also studied about reaction rate constant (k). They found that the reaction rate constants for static mixer were higher than mechanical mixer due to static mixer can generate smaller droplet sizes.

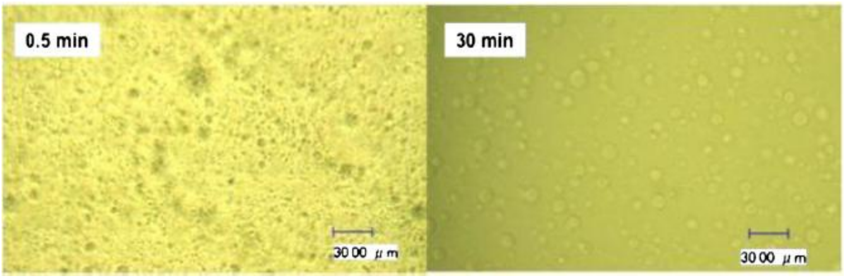


Figure 1.3 Methanol droplets from the static mixer at 0.5 and 30 min of reaction times

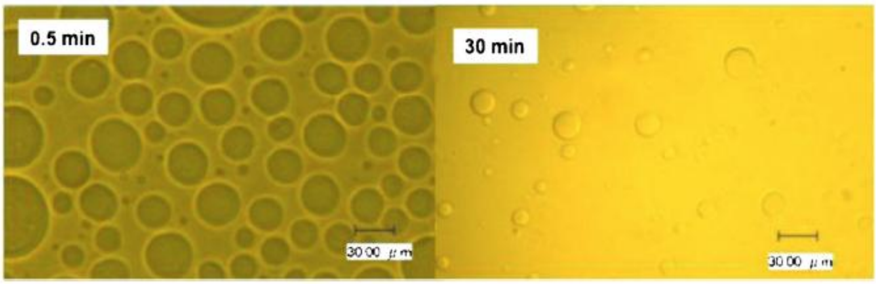


Figure 1.4 Methanol droplets from mechanical mixer at 0.5 and 30 min of reaction time

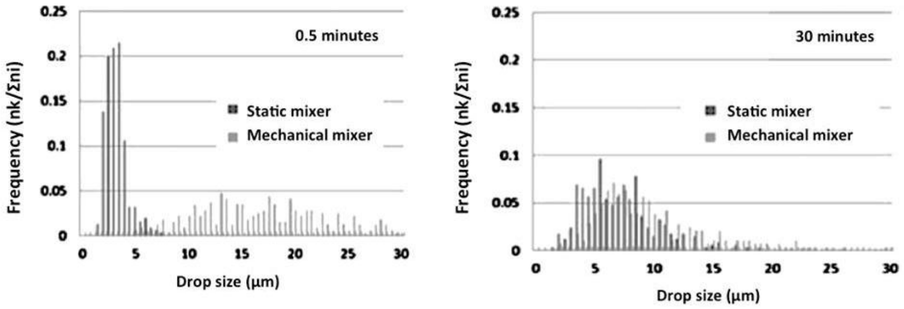


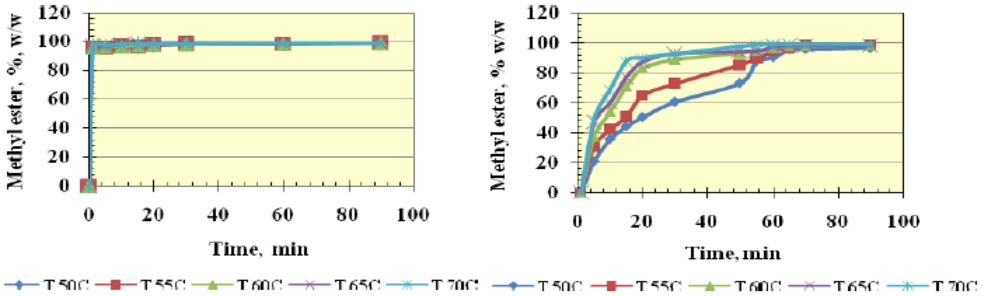
Figure 1.5 Droplet size distributions

Moreover, they studied the mass transfer coefficient (kc) and reaction rates constant (k) for transesterification in biodiesel production process. The consequences are shown in Table 1.1. For mass transfer coefficient (kc), according to the droplet size distribution, they confirmed that static mixer had more effect to increase the interface surface area between oil and methanol. Thus, mass transfer coefficients of static mixer were higher than those of mechanical mixer. In addition, for reaction rate constant (k), reaction rate constants for static mixer were also higher than mechanical mixer due to it can generated small droplet size of methanol, so the reaction can be considered as a pseudo-homogenous. The forward reaction rate of rate determining step was higher than the reversible reaction rate because of an excess amount of methanol were used.

Table 1.1 Mass transfer coefficient (k_c) reaction rate constant (k) comparative between static mixer and mechanical mixer

Methanol (molar ratio to oil)	**KOH (%wt.)**	**Static mixer**		**Mechanical mixer**	
		k_c	**k**	**k_c**	**k**
6	1.8	1.867	1.998	0.655	0.701
	1.2	0.597	0.639	0.446	0.477
	0.6	0.270	0.289	0.225	0.241
4.3	1.8	1.268	1.357	0.416	0.446
	1.2	0.276	0.296	0.230	0.353
	0.6	0.097	0.104	0.063	0.068

Comparison of kinetic reactions of biodiesel production process between a static mixer and a blade agitator reactor was introduced by Alamsyah, et al. [6]. The experiments were conducted by reacting palm oil with methanol at 50, 55, 60, 65, and 70 ^{o}C in using of potassium hydroxide (KOH) as catalyst. Molar ratio of methanol and oil was 10.5:1 and KOH used was 1% wt. The consequences of experiments, as shown in Figure 1.6, exhibited that static mixer can reach required 96.5%wt of fatty acid methyl ester (FAME) in the early step of reaction for all temperature levels while blade agitator reactor used more time.



(a) (b)

Figure 1.6 Effect of temperature on FAME formation using (a) static mixer; (b) blade agitator

Thompson and He [7] studied about biodiesel production continuous flow reactor by using static mixers, which canola oil and methanol play as raw materials and sodium hydroxide (NaOH) was used as alkali catalyst. The system consisted of two-stainless steel static mixers (4.9 mm internal diameter and 300-mm long) including 34 fixed right- and left-hand helical mixing elements.

Table 1.2 Levels of variables and experimental results: (A) mixing intensity (low or high), (B) concentration of catalyst (%wt) and (C) temperature of reaction (^oC) [7]

Exp. No.	**Variables**			**Results**	
	A	**B**	**C**	**Total Glycerides (%wt)**	
	Mixing	**Conc. (%wt)**	**Temp. (^oC)**	**Avg.**	**SD**[a]
1	Low	0.5	30	4.19	2.07
2	Low	0.5	60	0.40	0.05
3	Low	1.5	30	0.71	0.17
4	Low	1.5	60	0.17	0.03
5	High	0.5	30	4.09	0.94
6	High	0.5	60	0.29	0.05
7	High	1.5	30	0.87	0.46
8	High	1.5	60	0.18	0.00

Table 1.2 shows the variables and the result of the criteria of: mixing intensities, catalyst concentrations, reaction temperatures. At higher temperatures and catalyst concentrations can made the static mixer to had greater effect to decrease total glycerides, conversely, mixing intensity did not affect to reaction as the catalyst concentration and reaction temperature. Moreover, they were recommended the most effective conditions for reaction that are at 60 °C and 1.5% catalyst for 30 min.

The previous research confirms the effect of static mixer in biodiesel production process with investigated criteria of: increase the interfacial of methanol by generates smaller droplet size, increase the rate of reaction and reduce the residence times. Moreover, the parameters effect on optimal condition was determined. Furthermore, researchers have tried to examine the esterification of PFAD and coconut oil, the popular raw materials with high content of FFA.

Chongkhong et al. [8] determined the optimal condition for esterification of PFAD in biodiesel production, which have high FFA content. The influences of reaction temperatures of 70-100 ^oC, molar ratios betwwen methanol and PFAD of 0.4:1–12:1, concentration of acid catalyst of 0-5.502%wt (related to PFAD) and reaction times of 15-240 min were investigated by batch operation via esterification. The optimal condition for esterification that achieved from this experiment is molar ratio to PFAD of 4.3:1 over the acid catalyst quantity of 1.834%wt at 70-100 ^oC, while the reaction time is 90 min.

The potential using of PFAD as a feedstock to produce FAME by non-catalytic process in supercritical methanol was described by Duangkamol et al. [9]. With the molar ratio between PFAD to methanol of 1:6 at 300 ^oC over 30 min of reaction time, 95% conversion of FAME can be occurred. The result was correlated with the conventional acid-catalyzed esterification of PFAD and purified palm oil (PPO) in transesterification with supercritical methanol. With PPO to methanol molar ratio of 1:45, FAME was produced at the maximum yield of 80% at 300 ^oC and 75% of FAME gained by the common acid-catalyzed esterification in 5 h. Moreover, they were studied about effect of hydrolysis reaction from water content in reaction. The presence of water has significantly decreasing the yield of FAME. Nonetheless, using high amount of methanol can minimized the impact of water. Only 8% of FAME was hydrolyzed in the presence of methanol, while 20% was observed when the reaction without the presence of methanol.

Nakpong, P. and Wootthikanokkhan, S. [10] used coconut oil to study the potential of raw material for produced biodiesel in Thailand. The coconut oil that contained free fatty acid (FFA) of 12.8% was used to produce biodiesel by acid-catalyzed esterification follow with alkali-catalyzed transesterification. After that, coconut biodiesel was analyzed with gas chromatography method with flame ionization detector (GC-FID). In the first step, they found that FFA content in coconut oil was reduced to 0.6% with the optimal condition (0.35 v/v of methanol to oil ratio, catalyst concentration of 0.7% v/v compared with oil, reaction temperature of 60 ^oC over 60 min of reaction time. Moreover, esterified oil was followed by alkali catalyzed transesterification with 0.4 v/v of methanol to oil ratio and 1.5% w/v of catalyst concentration compared with oil with the same optimal temperature and reaction time for previous step. The methyl ester content of 98.4% wt was content in coconut biodiesel when analyzed by GC-FID. The GC chromatogram of biodiesel from coconut is shown in Figure 1.7.

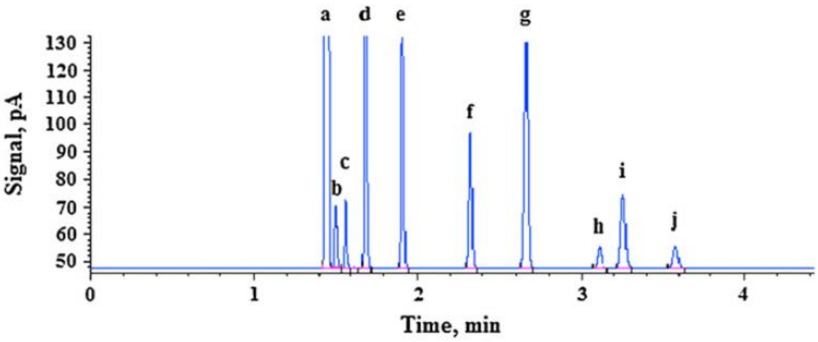


Figure 1.7 Chromatogram of coconut biodiesel: (a) n-heptane, (b) methyl caprylate, (c) methyl caprate, (d) methyl laurate, (e) methyl myristate, (f) methyl palmitate, (g) methyl heptadecanoate (used as internal standard), (h) methyl stearate, (i) methyl oleate and (j) methyl linoleate

Finally, they determined the physical and chemical properties of coconut biodiesel and compared with those of Thai Biodiesel (B100) specifications. The results are shown in Table 1.3.

Table 1.3 Properties of coconut biodiesel in comparison with Thai biodiesel (B100) specifications [10]

Test item	**Limit**	**Result**
Density at 15 °C, kg/m^3	860-900	874.8
Kinematic viscosity at 40 °C, mm/s	3.5-5.0	2.937
Copper strip corrosion (3 h at 50 °C)	Max No.1	1a
Total acid number, mm KOH/g	Max 0.50	0.29
Water content, % w	Report	0.028
Carbon residue on 10% distillation residue, % w	Max 0.30	0.24
Iodine value, g I_2/100 g	Max 120	30
Gross heat of combustion, MJ/kg	Report	38.1
Oxidation stability at 110 °C, h	Min 6	14.98
Triglyceride, % w	Max 0.2	0.000
Diglyceride, % w	Max 0.2	0.000
Monoglyceride, % w	Max 0.8	0.2049

In addition, some of the previous work dealt with performances of commercial static mixers, Kenics and SMX mixer, and performance comparative between each mixer.

Hobbs and Muzzio [11] used the dynamical systems to analyze the performances of the Kenics mixer. The twist direction of mixing elements and the length to diameter of element ratio with constant twist per element were used as variations to study the standard Kenics mixer. The R-R configuration mixer is the mixer that has same twist direction of all elements. It has important separated regions that play as barrier to mixing uniformly. Conversely, those regions were not observed in the R-L configuration, as shown in Figure 1.8. As a result, the R-L configuration is considered as the preferred mixer for the mixing applications.

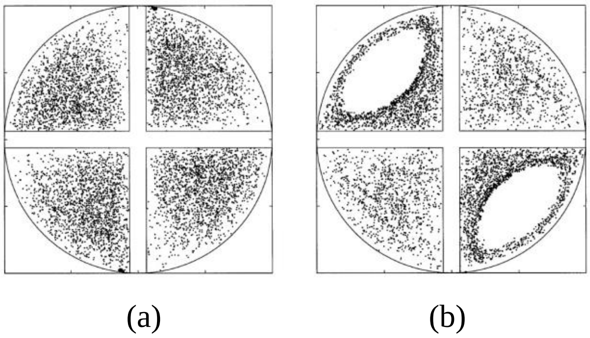

(a) (b)

Figure 1.8 Poincaré sections on the cross-sectional plane of: (a) R-L configuration, (b) R-R configuration

The ranges of element length to diameter ratio (α) in the R-L configuration were investigated of: α = 1.0 to α = 2.0. Mixing formats of different α were very similar and the normalized mixer efficiency (β), stretching rate per pressure drop, was significantly constant along the range of α studied. Figure 1.9 shows α has no impact on the efficient of Kenics mixer. However, elements with smaller α could be used in the mixing applications due to it used shorter residence times.

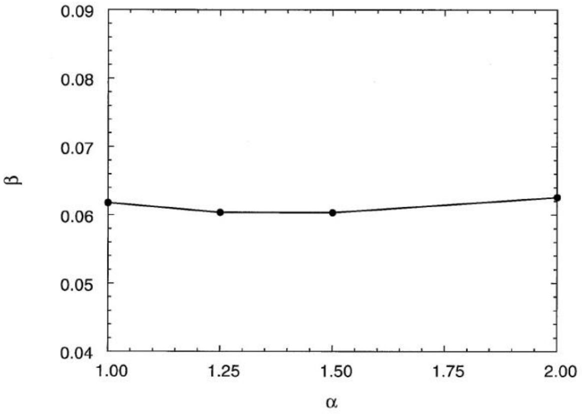


Figure 1.9 Mixer efficiency (β) vs element length to diameter ratio (α)

The element twist angles (θ) were investigated of: $\theta = 30^o$ to $\theta = 210^o$. Figure 1.10 shows Poincaré sections indicating the segregated regions, which were observed at $\theta = 60^o$ and $\theta = 30^o$. The maximum efficiency of mixer was found at of twist per element of: $\theta = 120^o$, which it can provide more energy efficiency of mixer than the standard configuration (180^o) about 44%.

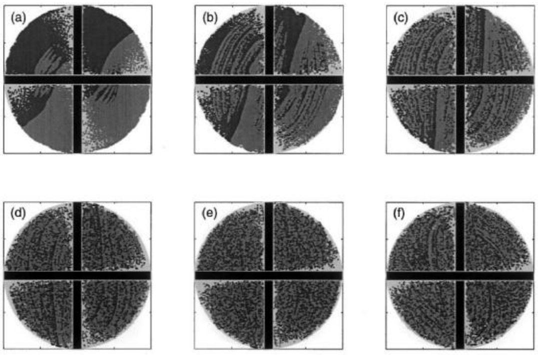


Figure 1.10 Poincaré sections on the cross-section of: (a) $\theta = 30^o$, (b) $\theta = 60^o$, (c) $\theta = 90^o$, (d) $\theta = 120^o$, (e) $\theta = 150^o$ and (f) $\theta = 210^o$

Rauline et al. [12] compared the performance between Kenics and SMX mixers. Table 1.4 shows results of four comparisons of: pressure drop (ΔP), mixer length (L), mean shear rate ($\bar{\dot{\gamma}}$) and Lyapunov exponent (δ), when two parameters are fixed. The fixed parameters are bold and underline show in the four double rows. These comparisons based on two mixing intensities of: easy mixing, blending of two similar polymers in equal proportions, and difficult mixing, the dispersion of a low viscosity fluid in a high viscosity fluid.

Table 1.4 Summary of performance of Kenics and SMX mixers

	Variable	**Constraints**		**Dispersive mixing**		**Distributive mixing**	
	D	**ΔP**	**L**	$\bar{\dot{\gamma}}$	**δ**		
SMX	1.1	$\underline{1}$	1	1.3	2.6	$\underline{1}$	‘easy’ mixing
Kenics	1	$\underline{1}$	3.3	1	1	$\underline{1}$	
SMX	3.7	1	$\underline{1}$	1	1	$\underline{1}$	
Kenics	1	36	$\underline{1}$	26	14	$\underline{1}$	
SMX	1.3	1	1	$\underline{1}$	1.9	$\underline{1}$	‘difficult’ mixing
Kenics	1	1.4	3	$\underline{1}$	1	$\underline{1}$	
SMX	1.6	1	1	1	$\underline{1}$	$\underline{1}$	
Kenics	1	2.6	2.4	1.9	$\underline{1}$	$\underline{1}$	

For the same pressure drop and mixing intensity (the first double lines), Kenics has a larger diameter due to pressure drop depending on the diameter. Moreover, Kenics have to longer than SMX of 3.3 times. Therefore, if the space is not limited, Kenics could be choosing for easy mixing applications due to its lower diameter and cheaper.

On the other hand, if space restricts, the length of mixer could play an important role for selecting the mixer. The second double rows show results of comparison based on criteria of same mixer length and mixing intensity. SMX is preferred than Kenics mixer because of Kenics has 36 higher pressure drop.

In case of same shear rate and distributive mixing, Kenics is 3 times longer than SMX and generates higher pressure drops of 1.4 times. Moreover, SMX mixer has more chaotic flow region due to it has Lyapunov exponent (δ) more than Kenics of 1.9 times. In addition, Kenics also has length and generates pressure drop more than SMX for case of same Lyapunov exponent and intensity of segregation. Although, Kenics has higher shear rate that has to consider between the cost of the mixer (higher for SMX) and the cost of capital of operation (higher for Kenics). However, it can be said that SMX is preferred to Kenics mixer for the difficult mixing task.

1.3 Research Objective

The main objective of this study is to determine the performances of standard types of static mixers used in circulation biodiesel production process in pilot-scale experiment. The specific objectives according the main objective are:

- To compare the performance of biodiesel production processes via esterification by using conventional static mixers that are used in industry, Kenics and SMX mixers, with those productions by employing the mechanical stirring in laboratory-scale experiments.
- To determine the suitable conditions for biodiesel production process via esterification by using static mixers.

1.4 Scope of Research Work

This research studied on biodiesel production process in circulation operation via acid catalyst esterification. Coconut fatty acid and methanol were used as raw materials to produce FAME. A few of designs of standard static mixers that used in industry, Kenics and SMX mixers, were used to mix coconut fatty acid and methanol in the catalyst solution.

The coconut fatty acids to methanol molar ratios were varied from 3:1, 6:1 and 9:1. Sulfuric acid (H_2SO_4) 0.7%v/v of coconut fatty acid was used as a catalyst. The reaction temperatures were used of 50 ^{o}C, 60^{o}C and 70 ^{o}C.

These experiments were carried out to determine the suitable type of static mixer, which diameter is 1 inch, based on the criteria of shorter residence times (min) and higher FFA conversion (%). In addition, the appropriate conditions for biodiesel production process in continuous operation via acid catalyst esterification by using static mixer that having the FFA conversions more than 90% were investigated.

CHAPTER 2

THEORIES

2.1 Introduction of Biodiesel

Biodiesel was developed and used in diesel engines in 1893 by Rudolf Diesel, who is shown in Figure 2.1. Diesel demonstrated that his primary diesel engines, a single 10 feet iron cylinder with a flywheel, can be powered by peanut oils. Diesel believed that future of engine depend on biomass fuel resources utilization as he saying "the use of vegetable oils for engine fuels may seem insignificant today, but such oils may become, in the course of time, as important as petroleum and the coal-tar products of the present time" in his speech in 1912 [13]. However, the process to obtain fuel from a fat occurred in the early of 1853 before the first diesel engine became completely practical, when the first transesterification of a vegetable oil was conducted by E. Duffy and J. Patrick.

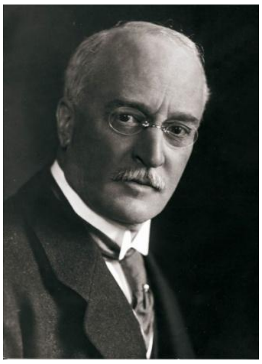


Figure 2.1 Rudolf Diesel (1858-1913)

At present, biodiesel accounts for an alternative promising diesel fuel produced from vegetable oil or animal fat and alcohol. The most frequently alcohols were used as acyl acceptors are methanol and ethanol. Propanol, butanol can also be used to produced biodiesel but they are more expensive. FAME produced from methanol is more volatile than FAEE (fatty acid ethyl esters) because methanol is more reactive than ethanol. Conversely, ethanol origin is less toxic and more renewable due to it can be made from fermentation of renewable resources, while non-renewable fossil sources is the mainly feedstock of methanol, such as natural gas. For the characteristics when used as fuels, FAEE has slightly higher viscosities than FAME. However, FAME has higher pour and cloud points. Moreover, the chemical reactions, which are used to produces FAME or biodiesel, requires a catalyst, *i.e.* NaOH and KOH.

Biodiesel is defines as a mixture of long-chain mono-alkylic esters produced from fatty acids that can be used in diesel engines by American Society for Testing and Materials (ASTM). Moreover, ASTM also specifies the properties of biodiesel as shown in Table 2.1. Biodiesel is viscous clear yellow liquid, non-flammable and non-explosive. Biodiesel is biodegradable and non-toxic; in addition it can reduce toxic and other emissions significantly when it burned.

Table 2.1 Properties of biodiesel, B100, defined by ASTM [14]

Property	ASTM Method	Limit	Unit
Flash Point	D93	93.0	°C
Alcohol Control			
1. Methanol Content	EN 14110	0.2 max	%wt
2. Flash Point	D93	130 min	°C
Water & Sediment	D2709	0.050 max	% vol
Kinematic Viscosity, 40 °C	D445	1.9 - 6.0	mm^2/sec
Sulfated Ash	D874	0.020 max	%wt
Copper Strip Corrosion	D130	No. 3 max	
Cetane Number	D613	47 min	
Cloud Point	D2500	Report to customer	°C
Carbon Residue 100% sample[a]	D4530	0.050 max	%wt
Acid Number	D664	0.50 max	mg KOH/gm
Free Glycerin	D6584	0.020 max	%wt
Total Glycerin	D6584	0.240 max	%wt
Distillation, T90 AET	D 1160	360 max	°C
Oxidation Stability	EN 14112	3 min	hours
For use in temperatures below -12 ^{o}C	Annex to D6751	200 max	Seconds

[a] The carbon residue shall be run on the 100% sample.
T90=Temperature 90% recovered; AET=Atmospheric equivalent temperature.

Biodiesel can blend with diesel fuel in any proportion indicated as ‘‘Bx’’, where ‘‘x’’ accounted for percentage in volume of biodiesel in the mixture. Presently, the most frequently concentrations of biodiesel are used of; pure (B100), blends (B20–B30), additive (B5) and lubricity-additive (B2). Biodiesel is absolutely miscible and it has resembles physical and chemical properties with petroleum diesel that make the conventional diesel engines can use biodiesel without significant modification.

2.2 Biodiesel Advantages and Disadvantages

Some of the advantages and disadvantages of biodiesel when used as a substitution for diesel oil are shown in Table 2.2.

Table 2.2 Advantages and disadvantages of biodiesel [15]

Advantage	**Disadvantage[a]**
• Low toxicity when compared with diesel fuel.	• Lower calorific value result in slightly higher fuel consumption.
• Higher degradability causes in more rapidly degrades than diesel fuel.	• Slightly higher nitrous oxide (NO_x) emissions.
• Lower emissions of pollutions: carbon monoxide (CO), particulate matter, polycyclic aromatic hydrocarbons, aldehydes.	• Higher freezing point cause in inconvenience in cold climates.
• No sulfur dioxide (SO_2) emissions.	• Teflon components is required due to it can degrade plastic and natural rubber when used in pure form.
• Higher flash point (100^oC minimum). • May be blended with diesel fuel at any proportion. • Can be use as efficient lubricant.	• Cleaning of storage tanks and fuel line before filling with biodiesel is required due sediments and other contaminants from diesel fuel can be cause problems in the valves and injection systems.

[a] These disadvantages are significantly reduced when biodiesel is used in blends with diesel fuel.

2.2.1 Advantages of Biodiesel

2.2.1.1 Availability and Renewability of Biodiesel

The low percentage of biofuel in biofuel and petroleum fuel mixture can run in less or non-modified conventional engines, is the property of only biodiesel in various alternative fuel. It can be stored in the same place with petroleum diesel fuel. Biodiesel decrease dangers in handling, transporting and storing steps than those of conventional diesel because it has higher flash point and it is not provide explosive vapor. Biodiesel can be produce from renewable resources, which made in domestic.

2.2.1.2 Lower Emissions from Biodiesel

Biodiesel has low emission values. Accordingly biodiesel represents as an alternative fuel with minimum global air pollution and it can help to reduce the emission levels of carcinogens.

Mainly emissions from biodiesel are carbon monoxide (CO), carbon dioxide (CO_2), oxides of nitrogen (NO_x) and smoke [15]. Over 90% of total unburned hydrocarbons (HC) and 75–90% of polycyclic aromatic hydrocarbons (PAHs) can be reduced in combustion of pure biodiesel. Nevertheless, biodiesel provides slightly increase in NO_x. Figure 2.2 shows average emission impacts of biodiesel for heavy-duty highway engines.

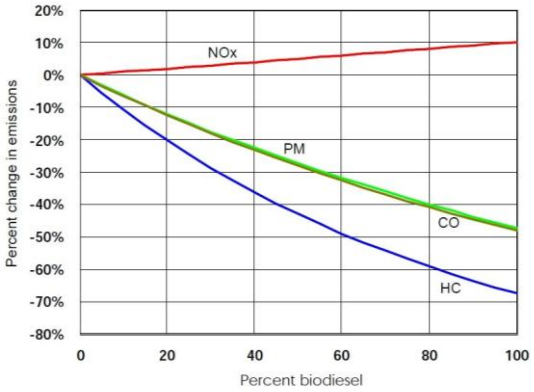


Figure 2.2 Average emission impacts of biodiesel for heavy-duty highway engines [16]

2.2.1.3 Biodegradability of Biodiesel

Biodiesel has high oxygen content that contributes to biodegradation make it degrades rapidly than petroleum diesel.

Pure biodiesel, it degraded more than 98% after 28 days, while diesel fuel and gasoline was decomposed for 50% and 56%, respectively. Moreover, B5 and B20 were decomposed for 50% in 22 and 16 day at the room temperatures.

2.2.1.4 Higher Lubricity

Biodiesel has better lubricant properties than petroleum diesel. This property is very important to reduce wear in the engine and the injection system.

Biodiesel has oxygen that contains about 11%wt and contains no sulfur. The oxygen content of biodiesel enhances the efficiency of combustion. In addition, the oxygen content can decrease the oxidation potential of biodiesel. So, the combustion efficiency of biodiesel is higher than petroleum diesel. Using of biodiesel has higher lubricating properties than petroleum diesel make it can preserve diesel engines than petroleum diesel.

2.2.1.5 Higher Cetane Number

Cetane number (CN) is the parameter for defined diesel fuel performance. It refers to the ignition delay time and combustion quality, which higher cetane number refers to better ignition quality. The ISO 5156 test method is used to measure CN for diesel and biodiesel. Furthermore, the theoretical estimation of CN without running engine tests can also determine CN. Some of biodiesel from various feedstocks has been estimated by the theoretical estimation of CN. According to biodiesel has contains the more saturated and longer the fatty-acid carbon chains molecules, so the CN of biodiesel is higher than conventional diesel. Moreover, CN of biodiesel from animal fats is higher than those of vegetable oils.

2.2.2 Disadvantages of Biodiesel

The main disadvantage of biodiesel is low temperature flow properties. This problem is very critical for using biodiesel in aviation applications. However, blending with biodiesel obtained from unsaturated feedstocks can enhance this problem. Moreover, higher viscosity, lower energy content, higher NO_x emissions are also disadvantages of biodiesel.

Relevant operating disadvantages of biodiesel compared with petroleum diesel are the lower energy content, higher copper strip corrosion and higher viscosity that make it difficult to pump the fuel in to engines. These problems are increases biodiesel consumption when using as alternative fuel, hence production costs and cost of application of biodiesel are higher than using petroleum diesel.

Economic and environment are also affected from biodiesel production. Over 95% of biodiesel is made from edible oil crops or food. The large scale production of biodiesel is the reason of global imbalance in the food supply and demand market. Beside, the negative impacts on the agriculture of edible oil crops, especially deforestation, have been mentioned by environmentalists. Therefore, the economics of biodiesel production and food industry are competing for the limited land availability.

2.3 Biodiesel Feedstocks

First of mostly used feedstocks in biodiesel production process are vegetable oils. Vegetable oils are alternative fuels for diesel engines due to their high heat content. However, high viscosity properties and they also have high content of unsaturated fatty acids, mainly oleic and linoleic acid, limit their directly consumption in diesel engines since it leads to many problems. The edible vegetable oils that are widely used in transesterification are soybean, sunflower, palm, corn, cottonseed, canola and olive. Although, edible oil has higher quality to produce biodiesel by transesterification, but they have major concerns in economically viability of biodiesel since refined vegetable oils are expensive and use of high value edible vegetable oil also caused food crisis. Hence, non-edible oils, *i.e.* jatropha curcas, rubber seed tree, tobacco, are needed for make biodiesel production more economical and decrease cost of production.

Vegetable oils are becoming a hopeful alternative to diesel fuel due to their sustainable properties: renewable, friendly with the environment and they can be produced domestically. Canola and soybean oil in the USA, palm oil in Thailand and Malaysia, rapeseed oil in Europe and corn oil were the popular edible vegetable oils that have been used for biodiesel production. Furthermore, some of non-edible vegetable oils have also been used in biodiesel production.

The oil yield from the vegetable is a major feedstock for biodiesel production. In order to decrease the production cost of biodiesel, crops that give higher oil yields are more suitable since they always have lower cost than lower oil yield crops. Typically, the cost of raw materials is accounts for 70–80% of the total production cost of biodiesel. Table 2.3 shows the oil yields in terms of kg oil/ha and wt% and the prices of several edible and non-edible oils types [17].

Table 2.3 Oil yields for major non-edible and edible oil sources [17]

Type of oil	Oil yield (kg oil/ha)	Oil yield (%wt)	Price (USD/ton)
Japtropha	1590	Seed: 35-40 Kernel: 50-60	N/A
Rubber seed	80-120	40-50	N/A
Castor	1188	53	N/A
Pongamia pinnata	225-2250	30-40	N/A
Soybean	375	20	684
Palm	5000	20	478
Rapeseed	1000	37-50	683

The main characteristics of typical oil crops that suitable for biodiesel production are summarized as follows:

2.3.1 Rapeseed and Canola

Rapeseed and canola is the most important feedstock for produced biodiesel in the Europe with a high oil yield (37–50%). However, the usefulness of rapeseed in Central and South American countries was limited due to the lower prices than wheat, main crop rotation competitor, and the lack of knowledge about fertilization, cultivate and storage.

2.3.2 Soybean

Soybean seeds have the oil content around 20%. The biodiesel produced from soybean can used to produce other valuable products such as glycerin.

2.3.3 Palm Oil

Palm oil has 2 types: oil from the pulp (called palm oil) and oil from the nut of the fruit (called palm kernel oil).

Palm oil can uses for cooking, used as raw material in margarine production, used as an additive in butter and bakery production and used as feedstocks in alternative fuel.

2.3.4 Peanut

Mainly using of peanut is a feedstocks for produce peanut butter, candy and other foods. The waste peanuts from food industries, low quality peanuts, are used to produce oil.

2.3.5 Sunflower

The significance of sunflower, which is extracted from the seeds, is the outstanding quality of edible oil. The sunflower oil can be stored for long times due to it has a very low content of linoleic acid. Moreover, sunflower has the oil content in the range of 48–52%.

2.3.6 Flax

Flax seeds have oil content about 30 to 48%. This oil, called linseed oil, has high content of polyunsaturated fatty acids, linolenic acid.

2.3.7 Jatropha

Jatropha (Jatropha curcas) is an oilseed species that has the potential as a feedstock for biodiesel production. It is a tropical America bush or low-growing tree. Jatropha is known as a diesel fuel plant, which its seed can be extracted oil that can be burnt directly or converted into biodiesel without prior refining [18].

Oil yield of jatropha depends on the method of extraction. It is 28–32% when using presses while solvent extraction can extract oil up to 52%. However, jatropha oil is nonedible due to the toxicity of jatropha seed. The toxicity is emanate from the presence of curcasin and jatrophic acid.

2.3.8 Avocado

The oil content in avocado is in the range of 12–30%. It has high content of essential fatty acids, mono-unsaturated fatty acids (mostly is oleic acid) and nutrient. Moreover, the oil has low content of saturated fatty acids.

2.3.9 Microalgae

Microalgae have a lot of oil quantities for biodiesel production. Microalgae oil, in term of liters per hectare, is higher than other raw materials about one to two times. Oil content is 20 to 50%, although in some species it can be higher than 70%.

2.3.10 Palm Fatty Acid Distillate

Palm fatty acid distillate or PFAD is a by-product from refining crude palm oil. It is a light brown semi-solid at room temperature and becomes brown liquid on melting. PFAD comprises FFA more than 80%, which palmitic acid and oleic acid are mainly components. Other components are triglycerides, partial glycerides and unsaponifable matters, *i.e.* vitamin E, sterols, squalenes and volatile substances.

Ping and Mohtar [19] determined the characteristics and properties of PFAD. Table 2.4 shows the general characteristics and properties of various parameters of PFAD from their studies.

The fatty acids composition of PFAD is shown in Table 2.5. The main fatty acids content are palmitic acid and oleic acid with percentage of 43.0-49.1% and 34.7-37.2%, respectively. In conversely, the least component in PFAD is caprylic acid with percentage of 0-0.2%.

Table 2.4 General characteristics of PFAD [19]

Parameter	**Range**	**Mean**
Iodine value (g/100g)	46.3-57.6	54.8
FFA (%)	72.7-92.6	86.4
Conventional mass per volume at 50 ^{o}C (kg/l)	0.8640-0.8880	0.8725
Titre (^{o}C)	46.0-48.3	46.7
Water content (%)	0.03-0.24	0.104
Unsaponifiable matter (%)	1.0-2.5	1.61

Table 2.5 Fatty acid composition of PFAD (%wt methyl ester) [19]

Fatty acid	**Range**	**Mean**
C8:0 capric	0 – 0.3	0.2
C10:0 caprylic	0 – 0.2	0.17
C12:0 lauric	0.1 – 2.4	0.46
C14:0 myristic	0.9 – 1.6	1.20
C16:0 palmitic	43.0 – 49.1	46.9
C16:1 palmitoleic	0.1 – 0.3	0.15
C18:0 stearic	4.0 – 4.5	4.30
C18:1 oleic	34.7 - 37.2	36.7
C18:2 linolenic	8.5- 9.7	9.03
C20:0 arachidic	0.0 – 0.4	0.28

The PFAD biodiesel has properties as follows: calorific value is 38600 MJ/kg, density is 879 kg/m3, flash point is 147 °C, viscosity is 3.96×10^{-6} mm^{2}/s and cetane number is 49 [20].

The second important raw material is animal fats or oils. Animal oils differ from vegetable oils for the fatty acid component. Vegetable oils have high amount of unsaturated fatty acids, while animal fat has higher saturated fatty acids. Commonly animal fats that use to produce biodiesel are lamb meet, beef tallow and chicken fat. The prefer qualities of animal fats for biodiesel are non-corrosive, high cetane number, and renewable. In the other hand, high FFA (5-30%) and water content that led to soap formation in chemical transesterification process [21]. In addition, higher saturated fats make animal fats oxidized and crystallized at high temperatures. Moreover, animal fats generally contain phospholipids or gums that cause the insoluble precipitate occur in aqueous phases.

One mole of glycerol and three moles of fatty acids (called as triglycerides) are the major compents of Vegetable oils and animal fats. The length of carbon chain and the number of unsaturated bonds makes fatty acids differ. The fatty acids found in vegetable oils are revealed in Table 2.6. Moreover, Table 2.7 shows typical fatty acid compositions in common oil sources.

Table 2.6 Chemical properties of vegetable oil

Vegetable oil	**Fatty acid composition, % by weight**									**Acid value**	**Phos ppm**	**Peroxide value**
	16:0	**18:0**	**20:0**	**22:0**	**24:0**	**18:1**	**22:1**	**18:2**	**18:3**			
Corn	11.7	1.9	0.4	0.0	0.0	25.2	0.0	60.6	0.5	0.1	7.0	18.4
Cottonseed	28.3	0.9	0.0	0.0	0.0	13.3	0.0	57.5	0.0	0.1	8.0	64.8
Crambe	2.1	0.7	2.1	0.8	1.1	18.9	58.5	9.0	6.9	0.4	12.0	26.5
Peanut	11.4	2.4	1.3	2.5	1.2	48.3	0.0	32.0	0.9	0.2	9.0	82.7
Rapeseed	3.5	0.9	0.0	0.0	0.0	64.4	0.0	22.3	8.2	1.1	18.0	30.2
Soybean	11.8	3.2	0.0	0.0	0.0	23.3	0.0	55.5	6.3	0.2	32.0	44.5
Sunflower	6.1	3.3	0.0	0.0	0.0	16.9	0.0	73.7	0.0	0.2	15.0	10.7

Table 2.7 Typical fatty acid compositions in common oil sources

Fatty acid	**Soybean**	**Cottonseed**	**Palm**	**Lard**	**Tallow**	**Coconut**
Lauric	0.1	0.1	0.1	0.1	0.1	46.5
Myristic	0.1	0.7	1.0	2.8	2.8	19.2
Palmitic	10.2	20.1	42.8	23.6	23.3	9.8
Stearic	3.7	2.6	4.5	14.2	19.4	3.0
Oleic	22.8	19.2	40.5	44.2	42.4	6.9
Linoleic	53.7	55.2	10.1	10.7	2.9	2.2
Linolenic	8.6	0.6	0.2	0.4	0.9	0.0

2.3.11 Coconut

Coconut oil has oil content about 60-65%. This oil is contains 92% of saturated fatty acids in the form of triglycerides, which amount of carbon atom chains are vary from 6-18. The main fatty acid component is lauric acid, myristic acid and plamitic acid as shown in Table 2.8 and physical and chemical characteristics of coconut oil are exhibited in Table 2.9.

Table 2.8 Fatty acids contained in coconut oil (%wt)

Fatty acid		**Range**	**Mean**
Caproic	C6:0	0.4-0.6	0.5
Caprylic	C8:0	6.9-9.4	7.8
Capric	C10:0	6.2-7.8	6.7
Lauric	C12:0	45.9-50.3	47.5
Myristic	C14:0	16.8-19.2	18.1
Palmitic	C16:0	7.7-9.7	8.8
Stearic	C18:0	2.3-3.2	2.6
Oleic	C18:1	5.4-7.4	6.2
Linoleic	C18:2	1.3-2.1	1.6

Table 2.9 Physical and chemical characteristics of coconut oil

Properties	**Virgin coconut oil from wet coconut**	**Unrefined coconut Oil from copra**	**Refined coconut oil**
Appearance	Colorless	Slight brownish	Colorless
Odour	Coconut smell	Coconut smell	Coconut smell
Melting point °C	24	24	24
Moisture (%)	<0.1	<0.1	<0.1
Iodine value (cg I_2/g)	12-15	12-15	10-12
Saponification value (mg KOH/g)	245-255	245-255	250-255
Phospholipids (%)	0.1	0.1	0.0
Unsaponifiable matter (%)	-	0.42	0.19
Tocopherols mg/kg	150-200	150-200	4-100
Total phenolics mg/Kg	640	618	20
Saturates Fatty acid (%)	92.0	92.0	92.0
Monounsaturates Fatty acid (%)	6.0	6.0	6.0
Polyunsaturates Fatty acid (%)	2.0	2.0	2.0

2.4 Trends of Biodiesel Production

In the present, energy demand is continue increasing because the rapid growth of population and urbanization. It increased from 5.9 GJ to 6.2 GJ in 5 year (from 2000-2005). Petroleum was the major of energy demand that the transportation segment is the main consumption, followed by the industrial, domestic and other sectors. Coal, petroleum and natural gas, the crucial conventional energy resources, are becoming depleted. Biofuels can be introduced as an alternative environmentally friendly renewable energy.

Currently, transportation is one of the main energy consuming segments. Bio-ethanol and biodiesel are biomass based liquid transportation fuels that are used to replace gasoline and diesel fuel, while bio-ethanol is used as gasoline and biodiesel is considered as the alternative renewable transportation fuel to fossil diesel fuel. Therefore, the current potential use of biodiesel supply for transportation sector increases in the energy market to replace petroleum products *i.e.* gasoline and diesel.

The world and region biodiesel capacity between 1991 and 2003 is shown in Figure 2.3. Moreover, biodiesel in Europe is represented as the biggest share with 82% of the whole biofuel production.

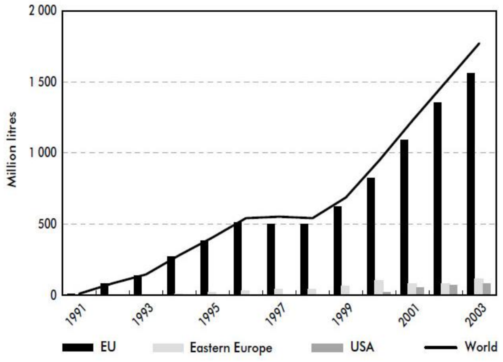


Figure 2.3 World and region biodiesel capacity (million liters per year) in 1991-2003

Recently, biodiesel has become more interesting due to its environmental profits. However, the cost of biodiesel production is the major problem to commercialization. Germany can produce biodiesel more than half of world total capacity, about 1.9 billion liters. Moreover, Biodiesel price in Germany is less than fossil diesel fuel. The production capacity of France, USA, Italy and Brazil accounted for only 11% of world biodiesel consumption. The European Union (EU) set the goal to carry out 5.75% of transportation biofuel demands in 2010. In 2010, the USA is anticipated to be the largest market of biodiesel in the world that accounting for 18% of world biodiesel consumption. In addition, China, India and Brazil are also expected to be the new large markets for biodiesel.

The large capacity of biomass energy resources in the EU regions could become exporters of biofuels to the regions that have lower capacities for biofuels production, to enlarge the total use of biomass energy in countries. As this situation, the inter-regional and international biofuels trading is growing due to the increasing of biomass energy use.

Biodiesel production costs are mostly depended on feedstock prices followed by ethanol prices, another main component in biodiesel production. The scale of ethanol production is an important impact but only smaller share of overall cost, which costs for production via continuous process are lower than batch processes.

In the US, biodiesel production is mainly uses soy oil more than rapeseed oil, which is mainly feedstock in Europe. The US biodiesel production costs are estimated to ranging from about 0.48-0.73$ per diesel equivalent liter, which based on soy oil, which costs of 0.38-0.55$ per liter of biodiesel produced, production costs of 0.20-0.28$ per liter and glycerol costs of about 0.10$ per liter [22].

Biodiesel produced from waste greases and oils have lower prices due to the lower feedstock price. However, these waste sources have limited quantities although some of organization of collection methods can increase significantly the availability of these waste sources. Costs for biodiesel from waste greases and oils are 0.25$ per liter. In the cases of feedstock is free, companies are willing to pay to remove these wastes from their sites. However, biodiesel production from waste feedstocks needs some additional processing, like purification of fatty acid, before conversion into methyl ester that can increase capital and operating costs.

However, the cost of biodiesel production can decline due to larger scale plants being built and optimal designs of technologies are being used. However, the high costs of the feedstock are also the dominant factor to make the biodiesel price still highly. Biodiesel can be cheaper when produce with lower cost of oilseed crop from the developing world or agricultural countries. Figure 2.4 shows cost ranges of diesel fuel and various biodiesel in US and EU between 2002 and post 2010. It reveals that costs of biodiesel have not significantly change from their past levels because of costs of biodiesel that produced from

FAME can be reduced due to scale and technology improved, but they can be compensated easily by higher crop prices.

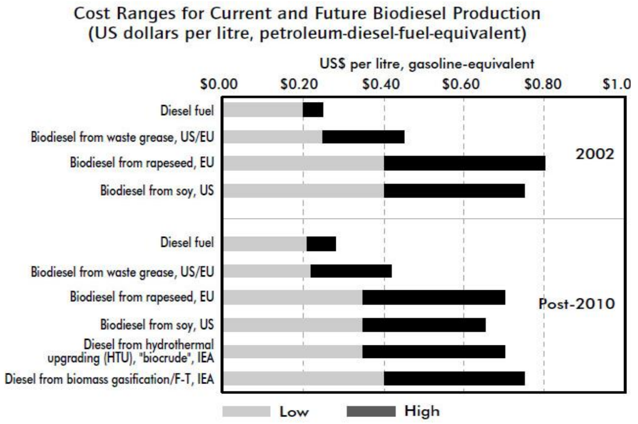


Figure 2.4 The cost ranges of diesel fuel and various biodiesel fuels in US and EU between 2002 and post 2010

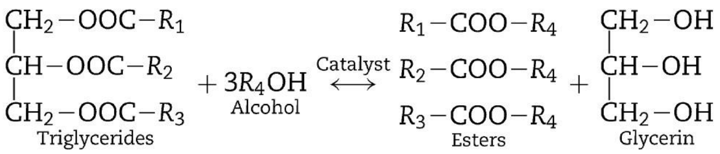
2.5 Biodiesel Production

Biodiesel, a biodegradable fuel derived from renewable sources, can be obtained from chemical reactions with alcohol (transesterification and esterification) in the existence of a catalyst.

2.5.1 Transesterification Reaction

Biodiesel can be made from several feedstocks including palm oil, coconut oil, jatropha oil, soybean oil, wasted cooking oil, and animal fats via transesterification reaction with alcohol in the presence of a catalyst.

Transesterification (sometimes is called alcoholysis) is the reaction of oil or fat with alcohol to provide esters and glycerol. The reaction rate and yield are usually improved by catalyst. The reaction is shown in Figure 2.5.



$$\underset{\text{Triglycerides}}{\begin{array}{l} CH_2-OOC-R_1 \\ | \\ CH-OOC-R_2 \\ | \\ CH_2-OOC-R_3 \end{array}} + \underset{\text{Alcohol}}{3R_4OH} \overset{\text{Catalyst}}{\longleftrightarrow} \underset{\text{Esters}}{\begin{array}{l} R_1-COO-R_4 \\ R_2-COO-R_4 \\ R_3-COO-R_4 \end{array}} + \underset{\text{Glycerin}}{\begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array}}$$

Figure 2.5 Transesterification reaction of FFA

Transesterification reaction is reversible, so excess amount of alcohol is used to shift the equilibrium to the forward direction (products side).

Alcohols that can be used in biodiesel production are short-chain alcohols including methanol, ethanol, propanol and butanol. Although methanol and ethanol are mostly used alcohol in the reaction, but methanol is more preferred to ethanol regardless of it has high toxicity since it has lower cost and it has more suitable physical and chemical properties *i.e.* polar and shortest chain alcohol. Methanol can quickly react with triglycerides. According to theoretical, transesterification needs 3:1 molar ratio between alcohol and triglycerides. However, in order to obtain the maximum ester yield, the higher ratio is needed to drive the equilibrium.

The conventional transesterification process of oils and fats is a homogeneous system, with alkalis, or enzymes used to catalyze the reaction. The alkalis that can be used as catalyst include sodium hydroxide (NaOH), potassium hydroxide (KOH), and sodium and potassium alkoxides. For acid catalysts, sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) are often used.

Transesterification can be catalyzed by alkali. If glycerides and alcohol are not in the form of anhydrous before use, the saponification reaction can occurred and soap is produced. This soap can decrease the yield of esters. In addition, the separation of ester and glycerol has more difficult. Moreover, triglycerides that suitable for alkali catalyzed transesterification must have low FFA content. If the water and free fatty acids content in triglycerides are high, acid catalyzed transesterification can be used.

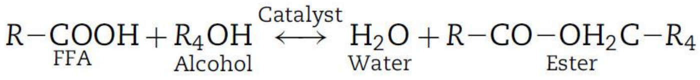
Soaps and FFA cause degradation of engine components. Furthermore, free water that can obstruct with the acid number of biodiesel and induce hydrolysis and biological contamination under non-adequate storage conditions.

The main problem of transesterification is that the purification of methyl esters and glycerin step. Becaused glycerin, another high commercial value chemical, must be recovered in good condition. In order to obtain pure methyl esters from mixture, glycerol, alcohol, catalyst and mixture of glycerides (tri-, di- and monoglycerides), is so complicate and need more processes since impurities are difficulty to separate. Furthermore, the monoglycerides make the mixture has more turbidity and crystalline. These impurities increase the cloud and pour points of methyl esters that become a disadvantage of biodiesel.

Although glycerol can be used as an industrial chemical, however, the presence of glycerin in biodiesel is problematic since it can dehydrate during combustion and produce a toxic unsaturated aldehyde, acrolein that can pollute to atmospheric, producing the carbon soot that block filters and reduce the engine performance. Glycerol is separated by gravitational settling or centrifuging method. Moreover, methyl esters from detergents and cosmetics can also make by transesterification.

2.5.2 Esterification Reaction

Waste cooking oil or residue is one of the interesting feedstocks for producing biodiesel because of it is cheaper and environmentally friendly than refined or crude oil. Conversely, the FFA contain is higher than the maximum suitable quantity for used with alkali catalysts that the high amounts of soap is made. In order to avoid this drawback, some of alternative technologies, *i.e.* homogeneous acid catalyst, solid resins, enzymes and supercritical process, can be exploited in the production processes. But if selecting the simplest and cheapest process, the direct esterification of the FFA in the existence of acid catalyst is selected as the popular method. The esterification reaction of FFA is summarized in Figure 2.6 [23].



$$\underset{\text{FFA}}{R{-}COOH} + \underset{\text{Alcohol}}{R_4OH} \overset{\text{Catalyst}}{\longleftrightarrow} \underset{\text{Water}}{H_2O} + \underset{\text{Ester}}{R{-}CO{-}OH_2C{-}R_4}$$

Figure 2.6 Esterification reaction of FFA

As with the transesterification reaction, the esterification reaction is also an equilibrium reaction, so the molar ratio between alcohol and oil should be over the stoichemetrically amount to be driving the equilibrium to give the maximum conversion of the FFA.

The conventional homogeneous esterification processes uses Brønsted acids such as H_2SO_4 or HCl as a catalysts. However, corrosion in reactor components and pipelines occurred when these catalysts were widely used. Also, the purification of the FAME produced from this reaction is also expensive and may require additional washing steps and distillation.

2.6 Biodiesel Production Technologies

According to the commercial biodiesel production via transesterification is mostly operate in batch processes, which is an agitator or stirred tank. Therefore, three major challenges of these processes occurred. First, reaction rate can be limited by mass transfer of oils and alcohol. Second, there is an upper limit to conversion in the absence of product removal due to transesterification is a reversible reaction. Finally, they do not gain some of the advantages of continuous operation. In order to overcome these problems, some technologies have been developed.

2.6.1 Micro-Channel Reactor

Micro-channel reactor utilizes high ratio of surface area to volume and small diffusion distance that can develop the efficiency of heat and mass transfer, so the reaction rate is increased. The zigzag micro-channel reactors configuration with narrower channel size is shown in Figure 2.7.

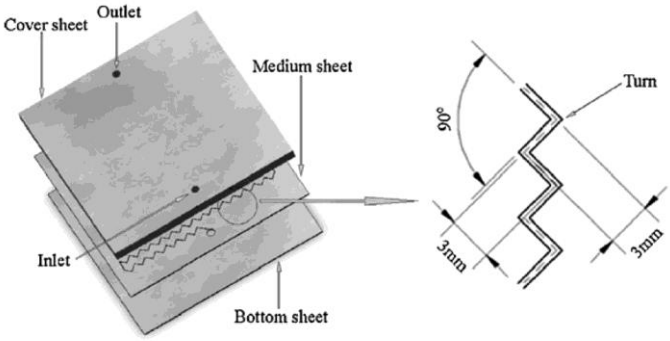


Figure 2.7 Configuration of a zigzag micro-channel reactor

The zigzag micro-channel improves biodiesel production process by producing smaller droplets of methanol and oil than does the conventional agitator. It can provide 99.5% yield of methyl ester by using 9:1 molar ratio between methanol and oil and 1.2 % wt NaOH is used as catalyst concentration with 28 s of residence time and reaction temperature of 56 ^{o}C. Moreover, less energy consumption is required to produce the same volume of biodiesel than conventional stirred reactor. The micro-channel reactor has smaller size, so it can reduce the construction requirements and operating costs.

2.6.2 Oscillatory Flow Reactor

An oscillatory flow reactor, which is a tubular reactor with equal spaced orifice plate baffles, produces oscillatory flow to intensify the performance of mixing, as shown in Figure 2.8.

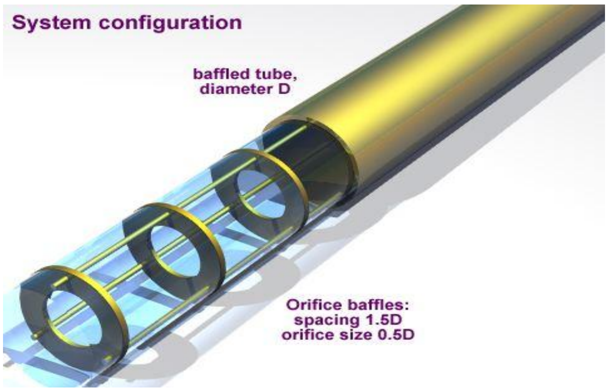


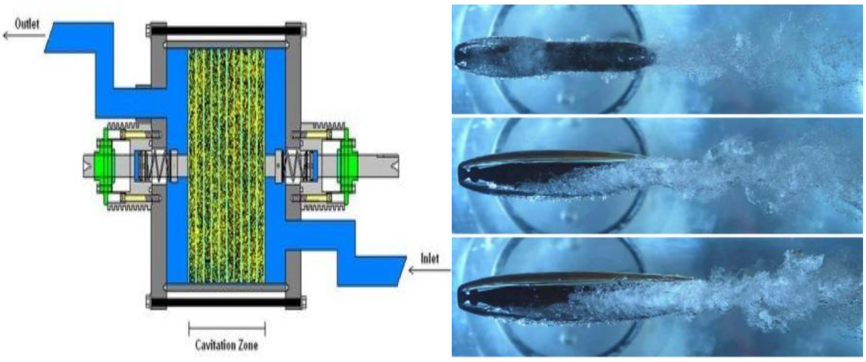
Figure 2.8 Oscillatory flow reactor [24]

Inside the reactor, fluid that flows into the reactor is interacted by oscillatory motion, then mass and heat transfers are enhanced and radial mixing is increase. The degree of mixing depends on the oscillatory conditions, so it can be created with a short length to diameter ratio.

The major advantages of this reactor are very low molar ratio of methanol to oil can be used. Moreover, the short length to diameter can reduce capital cost and enhance the economy of biodiesel production.

2.6.3. Cavitational Reactor

A cavitational reactor uses sound or flow energy to make cavitation phenomena occurs. This phenomenon generates turbulence and liquid micro-circulation to increase the rate of mass transfer. The large magnitude of energy, which releases from sound and flow energy over a small area, make area has very high temperatures and pressures that make the cavities forcibly break. The shock waves generated by the large magnitude of sound or flow energy enlarge the surface area of the compounds, so the mixing is enhanced with higher mass transfer rate. Moreover, this reactor can use with a range of raw materials with any FFA concentrations due to saponification and emulsification steps are reduced by the short residence time. The hydrodynamic cavitational reactor and its cavitation are shown in Figure 2.9.



(a) (b)

Figure 2.9 (a) Hydrodynamics cavitational reactor [25], (b) Hydrodynamics cavitation

2.6.4. Spinning Disk Reactor

A spinning disk reactor (SDR) is a technology that employs high gravity fields to intensify mixing processes. SDR consists of a rotating disk within a stationary housing. Figure 2.10 reveals the main structure of the SDR. Usually, SDR is used in gas-liquid reactions. When the disk rotating, high gravity field and centrifugal force are generated at disk surface, then liquid is dispersed as a thin film and contact with a gas. The thin film is forms the waves between the gas-liquid interface that uniform of micro-mixing is occurred and the outstanding mass and heat transfer are accomplished. Residence times on the SDR can vary from fractions of a second to a few seconds. Advantages of the SDR are enhancing mixing process with increasing heat and mass transfer coefficients and reduce the reaction times.

Morever, SDR is also used in liquid–liquid reactions because it can acheive the better mass transfer and more uniform micro-mixing characteristics. Furthermore, SDR can be used in polymerization and production of micro- or nano-particles by precipitation.

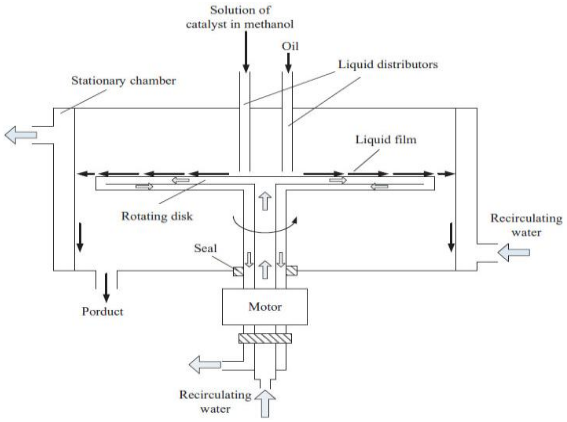


Figure 2.10 Structure of the SDR [26]

2.6.5 Microwave Reactor

A microwave reactor intensifies mixing processes by utilizing microwave irradiation to transfer energy directly into reactants, which rate of chemical reaction is accelerated. Accordingly, conversions are done in lower residence time than the reactors that use the conventional thermal heating. Presently, microwave reactors have been intensified for use in biodiesel production of vegetable oil and alcohol that microwave irradiation can heat the reactants up to the designed temperature in the shorter time. Figure 2.11 shows some types of industrial microwave reactors that are used in biodiesel production.

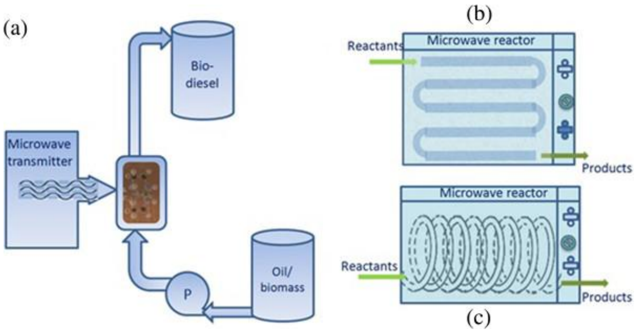


Figure 2.11 Industrial microwave reactor for biodiesel production (a) focused microwave reactor, (b) serpentine plug-type reactor and (c) helical coil-type reactor [27]

The important advantages of microwave reactor in biodiesel production are increase the quality and yield of product with lower molar ratio of alcohol to oil in the shorter residence time, provide less quantity of by-products decrease the energy consumption and it is more friendly with environmental.

Besides the above novel technologies, there is one more reactor that is the simplest but can achieve the very high performance of mixing due to it can increase the efficiency of mass and heat transfer of immiscible fluid, namely static mixer.

2.7 Static Mixers

Before 1970, static mixers were not popularly used in the process industry. Until 1874, a single-element with multi-layer motionless mixer was used to mix gaseous fuel with air. The staged/helical elements were installed in tube for mixing process in 1931. The multi-element design was introduced for blending solids in 1949. Moreover, in the early 1950, staged elements designed for heat transfer were created [28].

Recently, there are more than 8000 literature articles describing static mixers and their applications due to it having become standard equipment in the mixing process in industry. They are promoted as an alternative to traditional agitation for use in continuous processes. The performance of static mixer are better than mechanical agitation with lower cost and require less energy consumption and maintenance due to it has no moving equipments. Furthermore, static mixers require smaller space, lower equipment cost and lower installation cost. The obvious more advantages than conventional stirred tanks are the motionless can generated homogenization of the mixture streams with a minimum reaction time and they can be manufactured from most materials of construction.

A static mixer consists of a specific geometrical series of stationary inserts, called elements, within a pipe, channel, or duct. These elements use only the pumping energy of flowing fluid to influences to flow structure by divide and redistribute the fluid stream in the directions transverse to the main flow that are radial and tangential directions, which can intensified mass and heat transfer in the cross section.

Motionless inserts such as blades, corrugated plates, holes, channels, helical elements, and oblique blades induce changes in the acceleration and stretching of the fluid streamlines. They separate incoming fluid streamline into more than 1 layer, after that, recombine these layers into a new streamline. The mixing actions by convection induce flowing fluid stream into distributive mixing stream more than does diffusion. Despite the diffusion is greater at the extent of stream, which distributive mixing is high.

The commercial static mixers that are widely used in mixing process in industry have been created in various types. Table 2.10 shows list the top static mixer manufacturers and Figure 2.12 illustrates some of the available commercial designs.

Table 2.10 Commercially available static mixers and their corresponding manufacturers

Manufacture	**Static mixer models**
Chemineer	KM, HEV, KMX, KME, Thermogenizer, Ultratab, WVM
Sulzer	SMF, SMN, SMR, SMRX, SMV, SMX, SMXL, SMI
Ross Engineering	ISG, LPD, LLPD
Komax Systems	Komax, Custody Transfer, Ozone Mixer, GGM, FRP
Alfa Laval	ART Plate Reactor
Westfall Manufacturing	Model 2800 Plate Type Mixer
Fluitec	CSE-XR
Wymbs Engineering	HV, LV
Lightnin	Inliner Series 45, Inliner Series 50
Toray	Hi-Toray Mixer
UET	Heliflo (Series, I, II and III)
Noritake	N10, N16, N26, N60

KMX-V (Chemineer, Inc.)

SMX (Sulzer, Inc.)

Custody Transfer (Komax Systems, Inc.)

Standard LPD (Ross Engineering, Inc.)

Kenics KM (Chemineer, Inc.)

ZT-MX (ZelenTech, Ltd)

SMI (Sulzer, Inc.)

Corrugated channel reactors
(Laboratory pilots)

Figure 2.12 Commercially available in-line static mixers

The composition of Kenics and SMX mixers are as follows: Kenics mixer consists of a series of mixing elements that each has a short helix of length (L) equal to three times of the pipe radius a with a twist angle of 180^o and the standard Sulzer SMX element consists of eight cross-bars.

The applications of these devices include mixing of miscible fluids, creating an interface between immiscible fluids in high shear rate dispersive mixing and heat transfer operation to provide thermal homogenization phases. Flow instabilities reach oscillation of downstream fluid at Reynolds numbers greater than a few hundreds. Even in creeping flow, mixing elements in series also approach chaos condition at downstream fluids.

2.7.1 Mixing in Static Mixer

2.7.1.1 Mixing in Laminar Flows

Laminar flows are mostly found in high viscosity fluids *i.e.* food, paint, dairy, cosmetic, polymer, adhesive, and detergent industries. Conventional static mixers are used to redistributing the fluid streamline in the radial and tangential directions for homogenize that fluid. The transient non-homogeneities are provided by undisturbed laminar flow due to the low levels of mixing. Static mixers redistribute the fluid in undisturbed laminar flow, in which spatial mixing is occurred and also gives temporal mixing. In the ideal case of plug flow, fluids that enter the mixer with segregate phases will be uniformly redistributed and all the molecules will have mixing together.

2.7.1.2 Mixing in Turbulent Flows

Static mixers can create turbulence and intense radial mixing, in which eddy diffusion generates sufficient mixing level for intensification in most industrial processes, in fluids in turbulent flows, even near the pipe wall. Static mixers can significantly reduce contact time or increase heat transfer compared to a plain pipe by increase the level of turbulence without changing pipe diameter and flow rate, although pressure drop is higher. The presence of inserts and perturbators usually generate a complex vortex system, which is simultaneously enhance mass and heat transfer phenomena.

Three important applications that use the static mixer to intensify the mixing process in the turbulent regimes include gas mixing, blending of aqueous solutions and blending of polymer melts or solutions.

2.7.1.3 Mixing Applications

The most common use of static mixers in industry is in the mixing of miscible fluids such as mixing enzymes in milk to make yogurt. Static mixers can also be used for blending of particulate solids such as cereal grains, bread and cake mixes, and concrete components. Gas mixing and gas-liquid dispersion, like ozonation of drinking water, are common applications of motionless mixers as well. Figure 2.13 shows static mixer configurations commonly used in mixing of gaseous processes that provide effective contact, small bubble size, and global homogeneity with minimum length requirement.

SMV Spray evaporator
(Sulzer, Inc.)

Ozone Mixer
(Komax Systems, Inc.)

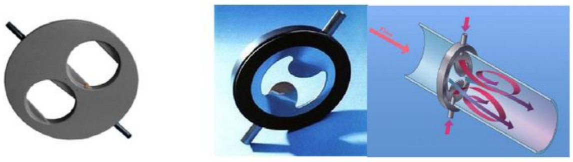
Gas/Gas Mixer
(Komax Systems, Inc.)

Figure 2.13 Static mixer designs for mixing of gaseous phase fluids

In the case of mixing in laminar flows, static mixers are used in various common processes. Additives, plasticizers and internal lubricants, stabilizers, colorants, fillers and flame retardants, are use static mixer to blend with polymer melts. The compact additive dosing mixers, as shown in Figure 2.14, provide efficient mixing for many polymer processes and many other applications by rapidly mixing secondary fluids that are injected into the main flow with combination of vortex flow and shear zone turbulence. Moreover, motionless mixers are also used to process glues and disposable static mixers are used to blend two-part epoxy resins.

CompaX (Sulzer, Inc.)

Kenics UltraTab (Chemineer, Inc.)



FRP Wafer Mixer
(Komax Systems, Inc.)

Model 2800 Plate Type Mixer and mechanism
(Westfall Manufacturing, Ltd.)

Figure 2.14 Compact static mixers with additive dosing features for secondary fluid injection

Other common applications of static mixers are in the food production industry. Typically, food products are highly viscous; in addition they are non-Newtonian fluids and usually are processed in the laminar regime. Static mixers can be used to mix acids, juices, oils, beverages, chocolate, milk drinks, or sauces in food production. Figure 2.15 shows some types of static mixers using in food production industry. These mixers surfaces are usually electropolished, mostly made from 316-stainless steel and housed in sanitary tubes of similar materials.

SMR for chocolate cooling (Sulzer, Inc.)

In-line sanitary static mixer (Komax, Inc.)

SMX plus (Sulzer, Inc.)

Figure 2.15 Some types of static mixers used in the food industry

Furthermore, water clarification and sludge treatment can also use these devices. Static mixers are used to disperse a flocculating agent in clarification of turbidity in drinking water, in which turbulent flow play important role; although shear is excess, leading to higher consumption of the flocculating agent.

Static mixers are widely used in chemical reactions as well. They are good device for mixing gases and pre-vaporized liquid fuels prior to a reaction. Despite the high diffusivities of gases mixtures do not immediately achieve homogeneity and additional mixing is required. Static mixers are often used as pre-reactor prior feeding to improve reaction yields. They are used in nitric acid (HNO_3) production by placed their at the upstream of a reactor in order to mix air with ammonia to increase nitric acid yield and eliminate hotspots that can damage the costly platinum catalyst. Many chemical reactions relate with gaseous can be intensified by using static mixers, for example production of vinyl chloride, ethylene dichloride, styrene, xylene and maleic anhydride. Moreover, static mixers have great potential in reducing NO emission in combustors. Static mixers are also used as both post-reactors and pre-heaters in devolatilization in polystyrene, nylon, urethane and sulfonated compounds production. Commercial reaction injection molding (RIM) machines use an impingement mixer followed by a static mixer to blend the reactive components in polyurethanes making, which the reaction is moderately exothermic.

Other types of chemical reactions can benefit from the use of static mixers include reactive extrusion process for glycol glucoside synthesis, production of starch ethers *i.e.* hydroxypropyl starch for the food and pulp and paper industry, and cultivation of attenuated hepatitis A virus antigen. Moreover, nuclear industry is also using static mixer in a conventional applications to improve sampling and analysis of contaminants in an air flow.

2.7.2 Heat Transfer in Static Mixer

Typically, conventional agitators, such as stirred tanks, are already involving heat transfer at the wall of the vessel. However, isothermal operation in these devices is difficult because thermal non-homogeneities are generated by the significant distance between the heat transfers device and the chemical reaction regime where heat is generated. Consequently, static mixers, where mixing, chemical reaction, and heat transfer can occur simultaneously in the same equipment, are promotes to use as heat exchanger/reactor (HEX reactor). The aim of using static mixers as HEX reactors is to take out the distance by contributing or removing heat almost as rapidly as it is absorbed or generated by the reaction.

Besides the conventional thermal homogenization and heat transfer of viscous fluids in heat exchangers in the laminar regime, static mixing can also be used in turbulent flows in order to reduce the size of the exchanger and increase the intensity of turbulent systems. Moreover, they can be used in highly exothermal chemical reactions where heat rejection is rapidly. Static mixers change the hydrodynamics of fluids by redistributing flow into cross sectional and then combination, which make the heat transfer coefficients significantly increase. In addition, they are also used for thermal regulation and heat injection, catalyst removal, esterification reactions or any other applications that heat transfer participate in reaction. Figure 2.16 reveals some static mixer configurations that can be used as HEX reactors.


Helical Kenics (Chemineer, Inc.)
LPD (Ross Engineering, Inc.)
HEV (Chemineer, Inc.)
SMXL (Sulzer, Inc.)
CSE-XR (Fluitec, Inc.)
KME (Chemineer, Inc.)
Thermogenizer (Chemineer, Inc.)

Figure 2.16 Commercial static mixers that can be used as heat exchangers/reactors

2.7.2.1 Thermal Homogenization

Normally, thermal diffusion is the heat transfer mechanism in the radial direction only in undisturbed laminar flow in a plain pipe. Therefore, static mixers are introduced for inducing radial flow to reduce radial temperature gradients. The main purpose is generates thermal homogenization in the processes. Moreover, they can also decrease composition differences in polymer blending and coloring process. Typically, flow patterns in conventional extruders, which are used to produce polymers, have only radial mixing, but lack tangential symmetry. Thus, motionless mixers become popular devices in polymer processes due to they can provided some tangential mixing.

A typical application of thermal homogenization is in the polymer production processes. In order to obtain a thermally homogeneous polymer melts, static mixers can be installed immediately downstream from screw extruder in polyethylene, polypropylene, and polystyrene processing. Furthermore for film blowing or sheet extrusion, static mixers can provide uniform temperature distribution to eliminate position dependent variations in thermoplastics product.

Besides, mixing elements are most beneficial in undisturbed laminar flow. These devices can be used for turbulent flow and boiling heat transfer as well as for laminar flow to improve heat transfer coefficients. Some typical uses of static mixers as heat exchangers in the turbulent regime to enhance thermal homogenization in the polymer industry include heating and cooling of polymer and polymer solutions prior to devolatilization, cooling polymer melts before filling plants to avoid thermal damage to packaging or before granulation to raise the viscosity and cooling polyester melts between the reactor and the fiber spinning unit.

In addition, static mixers can be used in the catalyst tubes of a reformer furnace. They can increase heat transfer coefficients, eliminate channeling within the catalyst bed, avoid cocking and prevent catalyst deterioration due to hot spots and improved yield. Other applications of static mixers are treatment of coal tar oil residues and naphtha cracking, these processes using static mixer as heat exchangers to intensify processes. Motionless mixers are effective solutions to many problems found in heat exchanger operations. Furthermore, static mixers can significantly reduce effects in cooling process include crystallization, polymerization and biological growth that resulting films with low thermal conductivity and cause significant resistance to heat transfer in reactor.

On the other hand, static mixing has some of disadvantages compared to plain tubes such as higher pressure drop, greater potential for fouling and difficulty of cleaning that make greater cost.

CHAPTER 3
METHODOLOGY

3.1 Reactor Construction

Two raw material tanks, a mixing tank, a biodiesel tank, a static mixer, an electric heater, a pump, gauges for monitoring temperature and pressure, and sampling valves were the main components of this reactor. Coconut fatty acid was heated until the desired temperature, and then methanol and sulfuric acid solution was fed to mix with coconut fatty acid in the mixing tank. The first sampling valve, located at before static mixer, was used to kept biodiesel sample before the feeding pump was turned on, while another sampling valve, located at after static mixer, was used to collected other samples when it passed static mixer at any designed times. Kenics and SMX mixers types were used in this experiment due to they can plugged in and out at the mixer position. After 60 min of reaction, two ball valves were used to changed flow direction of biodiesel from circulation direction to direction that product went to biodiesel tank. The reactor scheme is shown in Figure 3.1.

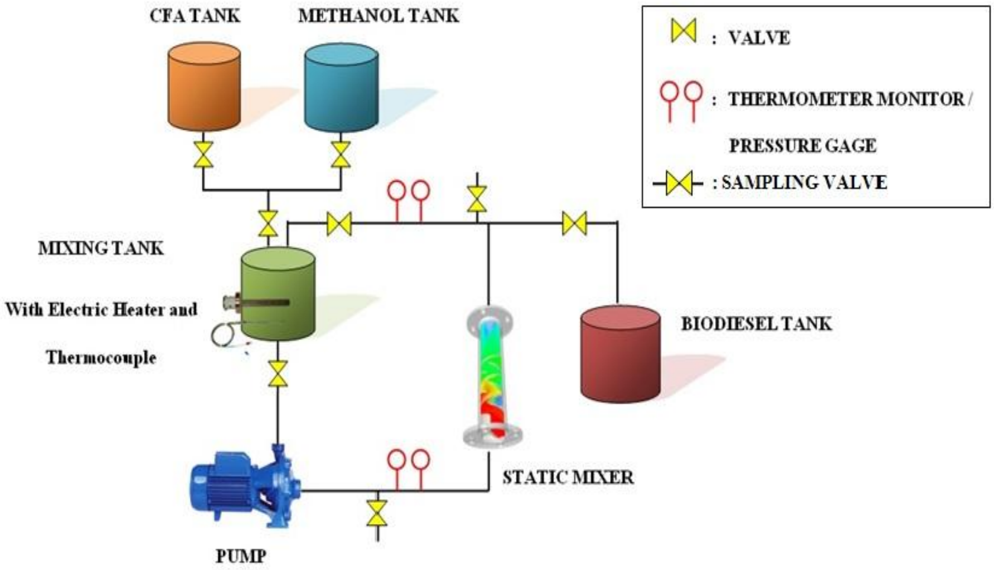


Figure 3.1 Reactor scheme

3.2 Acid Catalyzed Esterification with Mechanical-Stirring in Laboratory-scale

The equipment for mechanical-stirring laboratory-scale experiment consists of a three-neck and flat-bottom flask (500 ml), a hot plate with a magnetic stirrer, a condenser, and a thermometer as shown in Figure 3.2.

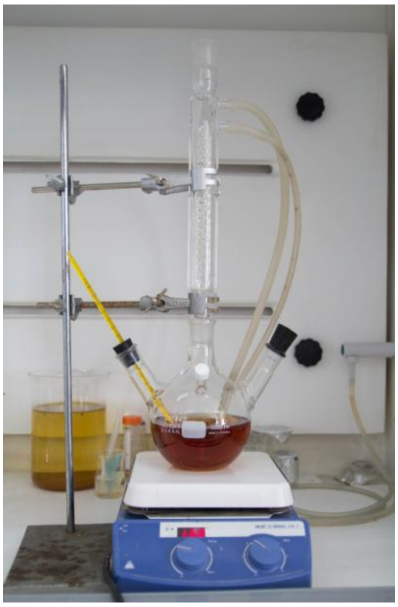


Figure 3.2 Laboratory equipment set up

The experiment started with pouring the coconut fatty acid into the flask with magnetic bar. The coconut fatty acid was then heated to 60 ^oC with a constant speed of stirring. Sulfuric acid (0.7 %v/v compared with fatty acid) was mixed with methanol, which the molar ratio of methanol to coconut fatty acid was 3:1. Finally, methanol and sulfuric acid solution was added to the preheated coconut fatty acid. The first sample (represented as a sample at retention of 0 min) was suddenly collected and the reaction time was also started. After that, biodiesel samples were collected every 10 min of reaction. These samples were allowed to settle for 2 h in a separating funnel. The upper layer consisted of esterified fatty acid (or biodiesel), which separated from lower phases (or methanol, sulfuric acid and water phases) as shown in Figure 3.3. The biodiesel was then purified by washing with hot distilled water at 60 ^oC until the washing water had a similar pH with distilled water. After that, the biodiesel layer was dried at over 100 ^oC (Figure 3.4). Finally, biodiesel samples were analyzed with the FFA conversion.

Figure 3.3 Phase separation of biodiesel and another phase in separating funnel after esterification

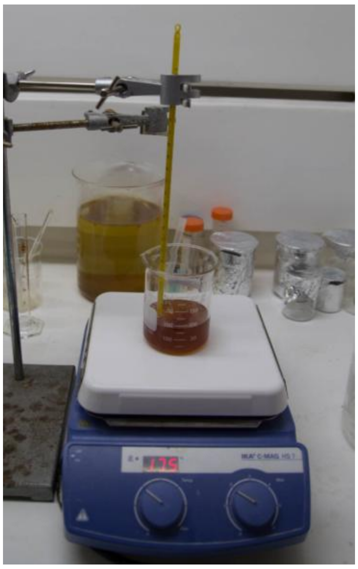


Figure 3.4 Removal of water from produced biodiesel

3.3 Investigation of Mixer Type for Continuous Biodiesel Production process

The acid catalyzed esterification reactions were conducted in a pilot-scale experiment, which had 2 types of static mixers, Kenics and SMX mixers, and a plain pipe were used as mixer in the process. The coconut fatty acid was poured into the coconut fatty acid tank, then flowed to mixing tank and heated it to 60 ^{o}C. Methanol and 0.7%v/v of sulfuric acid (related with fatty acid) solution was then added to the preheated coconut fatty acid with a ratio of methanol to coconut fatty acid of 3:1. The first sample was suddenly collected from sampling vale (located at before static mixer) after the methanol and sulfuric acid solution was added. Finally, feeding pump was turned on and measurement of reaction time was started. Other samples were collected at every 10 min of the reaction from sampling vale after the static mixer. Those samples were allowed to settle for 2 h in a separating funnel. The other processes were same with the laboratory-scale experiment. Finally, FFA conversions of biodiesel samples from pilot-scale were compared with those of mechanical stirring method in laboratory-scale experiment. The most suitable mixer type was determined by considering the mixer type that can provided highest FFA conversion, which also higher than 90%.

3.4 Investigation of Conditions for Continuous Biodiesel Production

The proper condition was studied from the effect of methanol to coconut fatty acid molar ratio and temperature of reaction. The acid catalyzed esterification processes were conducted in pilot-scale experiment with the appropriate static mixer's type. The methanol to coconut fatty acid molar ratios of 3:1, 6:1 and 9:1 were used while the reaction temperatures were varied from 50 ^oC, 60 ^oC and 70 ^oC, respectively. The mostly steps were same as laboratory-scale experiment. But in the separation step of samples that produced with methanol to coconut fatty acid molar ratios of 6:1 and 9:1, biodiesel was in the lower layer while the upper layer was methanol, sulfuric acid and water phases as shown in Figure 3.5. When the proper value of each parameter was obtained, it was kept as a constant value for the next parameter investigation. The suitable condition was considered as the condition that can reach FFA conversion more than 90% by using lowest methanol to coconut fatty acid molar ratio and lowest temperature in the minimum reaction time.

(a) (b)

Figure 3.5 Separation of biodiesel sample in separating funnels produced from methanol molar ratio 6:1 and 9:1

3.5 FFA Conversion Analysis

FFA conversion was used to indicate the completion of the acid esterification reaction. It can be calculated by Eq. (1):

$$FFA\ Conversion(\%) = \frac{A(i) - A(f)}{A(i)} \times 100 \qquad (1)$$

where A(i) is an initial acid value (mg KOH/g) and A(f) is a final acid value (mg KOH/g).

Acid value was determined by titration of 2 g of coconut biodiesel sample with KOH, while 1% phenolphthalein was used as an indicator. The calculation of acid value was followed by Eq. (2):

$$Acid\ Value\,(mg\ KOH/g) = \frac{56.1 \times C \times V}{M} \qquad (2)$$

where C is concentration of KOH (normality), V is volume of KOH (mL), and M is weight of sample taken to analyze (g).

3.6 GC Analysis

The coconut biodiesel product was analyzed by gas chromatography equipped with a flame ionization detector (GC-FID). Gas chromatograph (model of Shimudzu GC2014AFsc) was used with Omegawax 320 column (30 m × 0.32 mm ID). The helium was used as a carrier gas with flow rate of 1.02 ml/min. The temperature of the oven was kept at 200 ^{o}C for 12 min. The n-hexane was used as solvent for preparing sample solution. The analysis started with injection of 5 µL sample solution into GC. Comparing with their retention times to those of the standard methyl ester of fatty acids method was used identified the methyl esters.

CHAPTER 4
RESULTS AND DISCUSSION

4.1 Reactor Design

The components and all pipe lines were made from 304-stainless steel, the stainless type was used in the food industries, because it can be used with chemicals and acid also. This reactor was designed as circulation operation mode. The fabricated pilot reactor is shown in Figure 4.1.

Figure 4.1 Circulation biodiesel production reactor

Figure 4.2 Raw material tanks (methanol and coconut fatty acid tanks)

The raw materials were filled in the tanks on the top of the reactor (Figure 4.2). Coconut fatty acid was flowed to the mixing tank and then heated with a 200 W electric heater. After that, it was allowed to mix with methanol and sulfuric acid solution and the mixture also heated by same electric heater into designed temperature. There is a thermocouple for control the temperature of mixture by sending the control signal to the magnetic relay to control the electric heater in the tank. Moreover, it had a vapor release valve that is used as a safety valve. Since the biodiesel production process proceed in high temperature condition, so methanol became to vapor that made the pressure in the tank was too high and it can made the tank explode. The mixing tank with vapor release valve and the components in the mixing tank show in Figures 4.3 and 4.4, respectively.

Figure 4.3 Mixing tanks

Figure 4.4 Electric heater and thermocouple in the mixing tank

The feed pump (with 1 hp, 50 Hz and 220 V) was selected to feed the mixture through a static mixer and pipe line. Figure 4.5 exhibits the 1 hp feed pump.

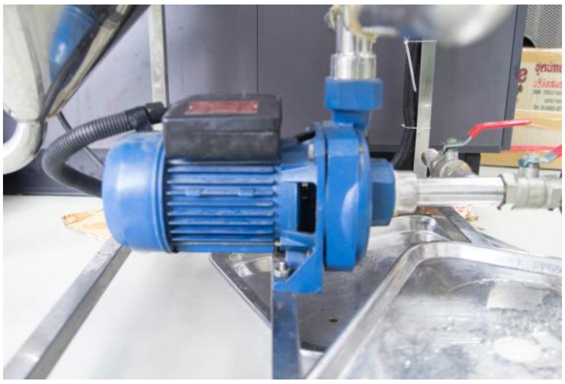


Figure 4.5 Feed pump

Static mixer, with 1-m length and 1-inch diameter, consists of the element piece, host pipe and PTFE gaskets. It can plugged –in and –out from the flanges for change with the other mixer types. Figure 4.6 shows the 2 types of static mixer and their mixing elements used in this experiment.

(a)

(b)

Figure 4.6 Static mixers and their element pieces (a) SMX mixer and (b) Kenics mixer

The pipe line has the temperature and pressure gauges for monitoring the temperature and the pressure in the pipe. In addition, it also had 2 sampling vales for kept the coconut biodiesel samples at the designed reaction time (located at before- and after-static mixer). The temperature and pressure gauges and the sampling vales are shown in Figure 4.7 both before- and after-the static mixer.

(a) (b)

Figure 4.7 The temperature and pressure gauges and the sampling vales (a) before- and (b) after- static mixer

Another component is the electrical control cabinet. It consists of control switches (of main power (220V), electric heater, and feed pump) and LED lights for showing the status of the reactor, as shown in Figure 4.8.

(a) (b)

Figure 4.8 The electrical control cabinet for this reactor (a) outside and (b) inside

4.2 Effect of Static Mixer Type on Circulation Biodiesel Production

The type of mixing is one of important factor in mixing efficiency. Moreover, the different types of static mixer can create different flows of fluid flowing through them. Kenics and SMX mixers were used to produce biodiesel with acid catalyzed esterification. Biodiesel sample, which collected before turn the pump on from sampling valve located at before-static mixer, was account for sample at 0 min of reaction. The other samples, kept from sampling valve located at after-static mixer in every 10 min, referred to samples at 10 to 60 min of reaction. The results were compared with mechanical stirring, laboratory-scale experiment, and also plain pipe in pilot-scale experiment.

The results reveal that the acid catalyzed esterification can reduce the acid value of the coconut fatty acid due to its changing into FAME (or biodiesel). Figure 4.9 exhibits the acid value of biodiesel, which obtained from acid catalyzed esterification from both pilot-scale experiments with static mixers and plain pipe and mechanical stirring in laboratory-scale experiment.

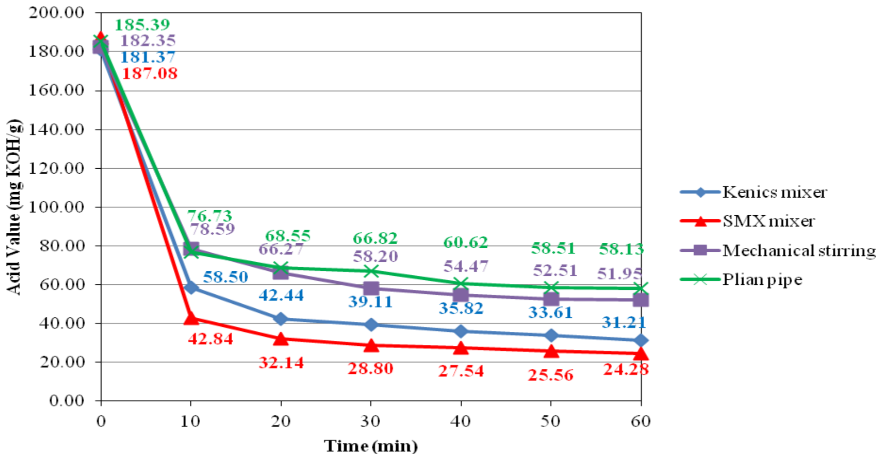


Figure 4.9 Acid value of biodiesel obtained from acid catalyzed esterification from both laboratory-scale (accounting for mechanical mixing) and pilot-scale (accounting for static mixing with circulation) experiments at different reaction times

In addition, biodiesel produced from the static mixing processes with both types of static mixers (Kenics and SMX types) can reach higher FFA conversion of coconut fatty acid (88.40 and 85.90%, respectively) than mechanical stirring experiment (75.18%) and static mixers used shorter time to obtain FFA conversion at higher levels than the highest FFA conversion obtained from mechanical stirrer (at 10 min, SMX mixer reached 79.53% and Kenics mixer reached 79.72% in 20 min) (Figure 4.10).

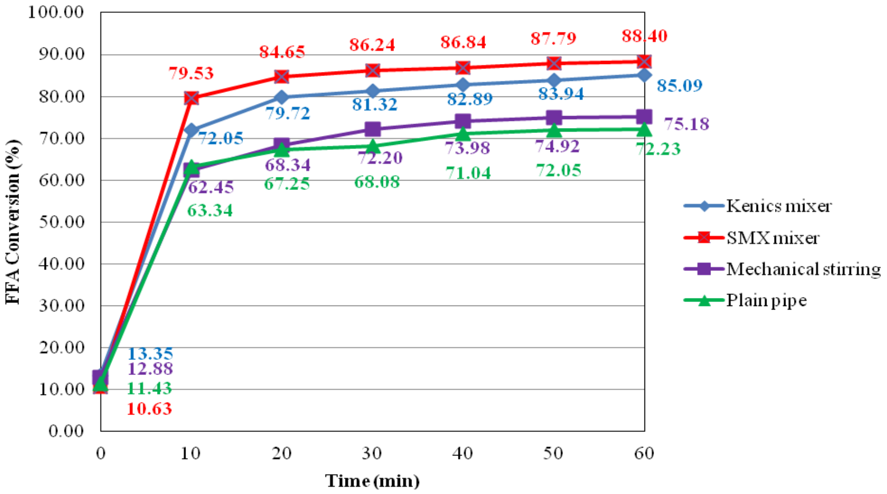
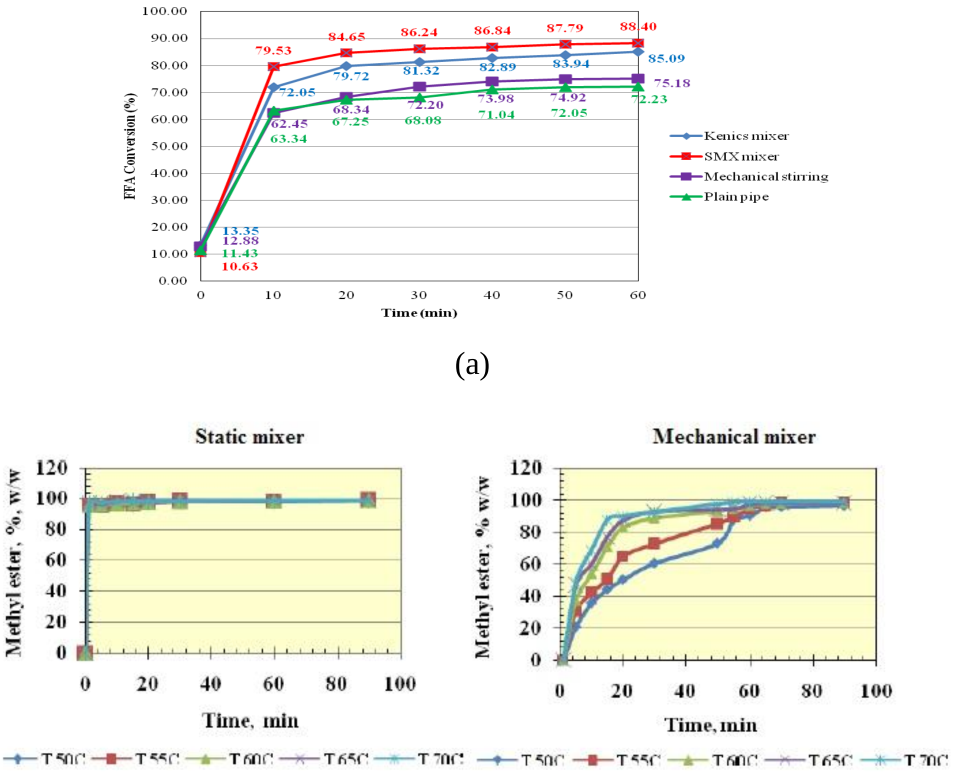


Figure 4.10 Comparative FFA conversion of both biodiesel production experiments (mechanical stirring in laboratory-scale and static mixing in pilot-scale experiments) at different reaction times

These results also reveal that static mixers, both Kenics and SMX mixers, can create the effective mixing of methanol and coconut fatty acids better than can the mechanical stirring method. Mixing mechanism of static mixer was employed the mixing elements in order to generated smaller droplet size of methanol than mechanical stirring (Sungwornpatansakul et al, 2013), which employed the magnetic field to induced the moving of materials, that can increase the interfacial of methanol to reacted with coconut fatty acid, so the mixing performance of static mixers had higher level than another method.

Figure 4.11 shows the FFA conversion comparison between this work and the previous work from Alamsyah, R., et al., who produced biodiesel from palm oil by using static mixing and mechanical stirring in the laboratory-scale via transesterification.

These graphs have the same trend of conversion that static mixer can provide high FFA conversion faster than the mechanical stirrer although the feedstock, type of reaction and experiment scale were different. It confirms that static mixer was more suitable to use to produce biodiesel than was the mechanical mixer with the several feedstocks for both reactions of transesterification and esterification.



(a)

(b)

Figure 4.11 FFA conversions comparison between (a) this work and (b) work from Alamsyah, R., et al. [6]

Moreover, the SMX mixer has more compact mixing elements than does the Kenics mixer and the flow in the SMX mixer was induced by the difference of pressure between inlet and outlet of the tube. When methanol and coconut fatty acid moved through the SMX mixer and the interface between them were touched by the crossed bar elements that played as mixing combs that move the their flow into the direction from wall to another wall in perpendicular from their orient direction, then 8 times of stretched and folded were occurred with interface of them [29], while Kenics mixer elements split and change rotation of materials to created the mixing from the vortices and stretching of the materials in laminar region. So, SMX mixer can generate the higher effectiveness of mixing and it can be promoted as the more suitable static mixer type for biodiesel production when compared with Kenics mixer.

In addition, the challenge of the biodiesel production process is that the esterification reaction was a reversible reaction, so the rate of FFA conversion in mechanical agitation (batch mode) usually had a lower percentage. Since the product cannot move out from the system. These results confirm that the static mixer can increase the rate of reaction due to the reduction of acid value and increasing of FFA conversion.

A static mixer can generate greater mixing efficiency than can a mechanical stirrer, which can confirm about mixing of methanol with coconut fatty acid, which were not readily mix together in the normal condition, improve. Static mixer can be used in continuous process that allow the industries to gain more benefits from continuous operation, such as higher production capacity and yields of product and reducing costs of operation and maintenance.

4.3 Effect of Molar Ratio of Methanol to Coconut Fatty Acid on Circulation Biodiesel Production

Another factor that can affect the FFA conversion was molar ratio. Coconut biodiesel was produced with the methanol to coconut fatty acid molar ratios, which varied of 3:1, 6:1 and 9:1, in the pilot-scale experiment by using the SMX mixer. The sample collection was same as a previous part (mixing type investigation). Acid value and FFA conversion of biodiesel samples with each molar ratio are exhibited in Figures 4.12 and 4.13, respectively.

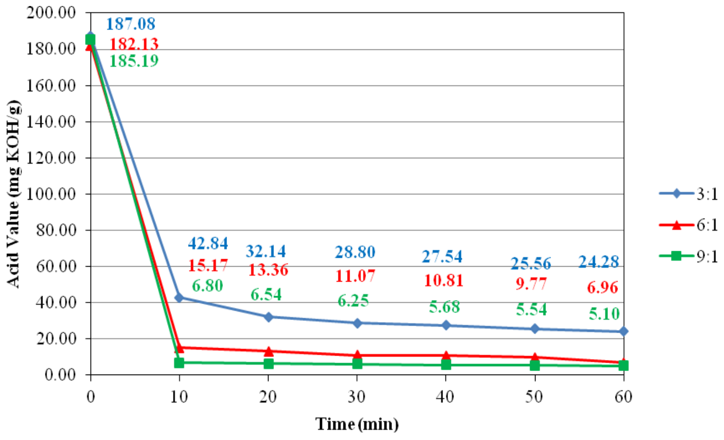


Figure 4.12 Acid value of biodiesel produced from different molar ratios

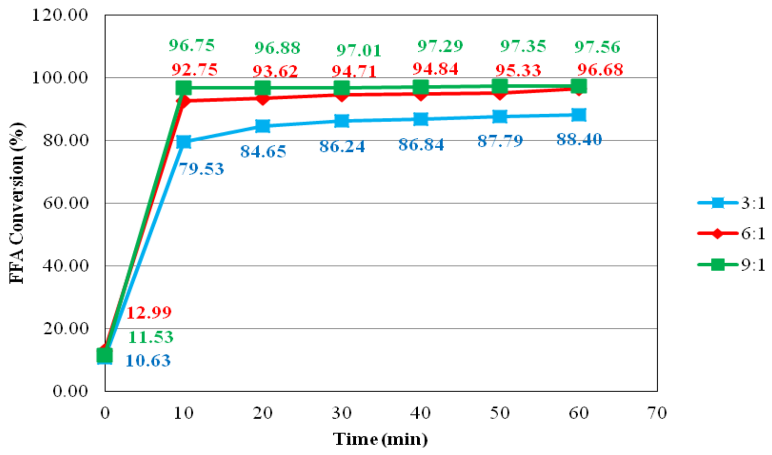


Figure 4.13 FFA conversions of biodiesel produced from different molar ratios

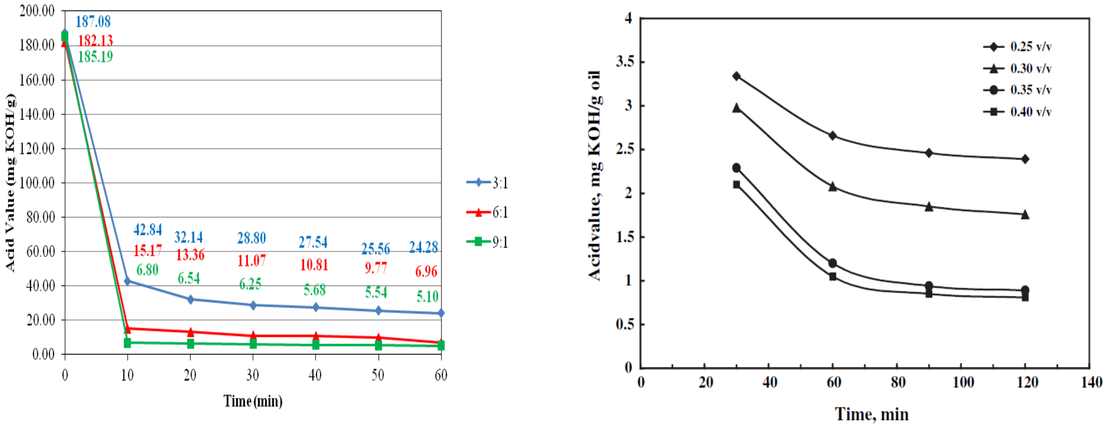
Since the esterification reaction was a reversible reaction, so the excess amount of raw materials can shift the reaction into the forward direction. Therefore, biodiesel production with higher methanol to coconut fatty acid molar ratio can gained higher efficiency of mixing (referred to higher FFA conversion) than the lower ratio.

Since the start of the reaction to 10 min of reaction with molar ratio of 9:1, the mostly fatty acid was converted into FAME, which result in the acid value was reduced into the lower level (6.80) and the FFA conversion was reached at high level (96.75%). After that, acid value and FFA conversion were rather constant (since 6.54 to 5.10 and 96.88 to 97.56%, by order). It means the reaction was got into equilibrium state.

Moreover, water produced by reaction might be inhibiting the conversion of FFA into FAME. When the esterification reaction was preceded and water was produced more from condensation of coconut fatty acid and methanol, catalysis of sulfuric acid was continuously diminished and water inhibited the FAME formation [30].

However, the reaction with molar ratio 6:1 also reached at over 90% of FFA conversion (92.75%) and it used fewer methanols. In consequence, the methanol to coconut fatty acid molar ratio at 6:1can be introduced as the proper molar ratio for biodiesel production from coconut fatty acid and methanol with acid catalyzed esterification.

Correlations in terms of acid value biodiesel produced from coconut fatty acid in this work and biodiesel produced from coconut oil established by Nakpong, P. and Wootthikanokkhan, S. who worked on biodiesel production process from high free fatty acid coconut oil by using the magnetic stirrer are shown in Figure 4.14.



(a) (b)

Figure 4.14 Comparison of acid value at 60 min of reaction of (a) biodiesel produced from coconut fatty acid in this work and (b) biodiesel produced from coconut oil with mechanical stirrer established by Nakpong, P. and Wootthikanokkhan, S. [10]

These graphs confirm that at higher ratios of methanol to coconut fatty acid, the fatty acid was reduced and changed into FAME more than at the lower ratios for both of mixing methods, static mixing and mechanical mixing. Moreover, they also reveal that static mixer also used retention time to reach the FFA conversion in high level less than mechanical mixer for all molar ratio of methanol to coconut fatty acid.

4.4 Effect of Temperature on Continuous Biodiesel Production

Figures 4.15 and 4.16 show the acid value and FFA conversion of biodiesel produced from pilot-scale experiment with SMX mixer at temperatures of 50, 60 and 70 ^{o}C. The results reveal that from the start of the reaction to 10 min of reaction, FFAs were changed into FAME with the nearby conversion for all temperature level (91.39%, 92.75% and 93.23% for 50, 60 and 70 ^{o}C, respectively). However, all FFA conversions were higher than 90%.

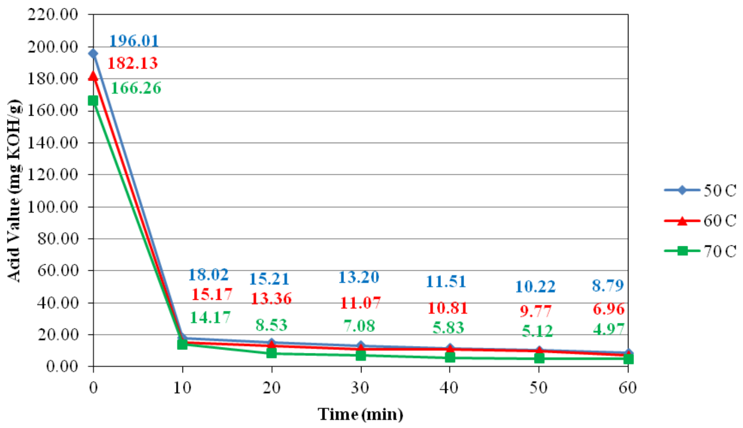


Figure 4.15 Acid value of biodiesel produced from different molar ratios

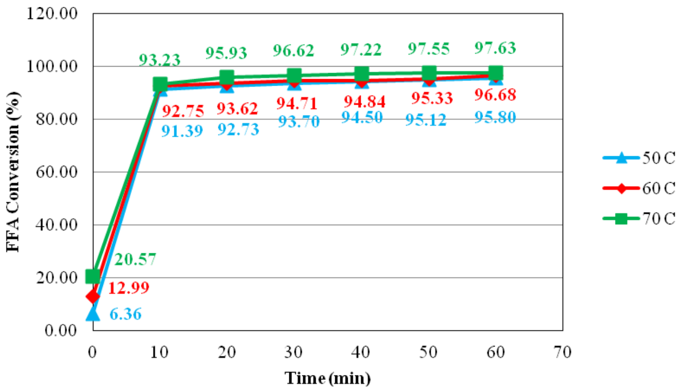
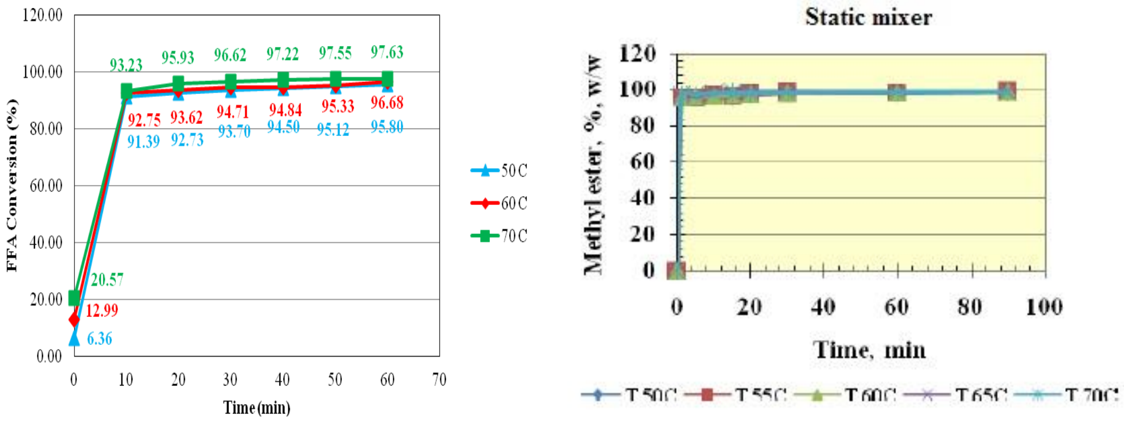


Figure 4.16 FFA conversion of biodiesel production produced from different temperature levels

The temperature was not a relevant operation parameter that could influence the yield of the product in the reaction. Increasing the temperature did not have a significant effect on FAME yield on esterification with methanol [31]. However, at 50 ^{o}C was the lowest temperature, which can reached FFA conversion more than 90%.

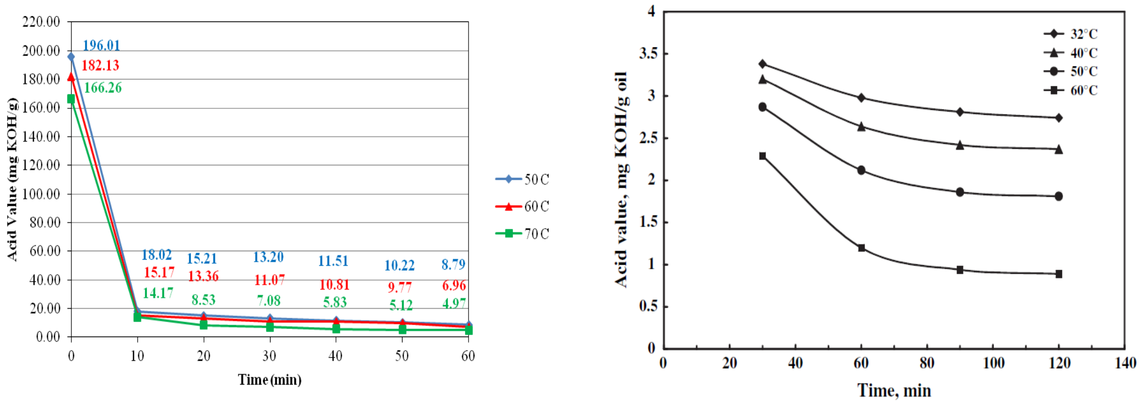
Figure 4.17 is also comparison of FFA conversion in different temperature levels between this research and previous work from Alamsyah, R. et al. It confirms about the temperature had low significant in order to increase the FFA conversion of biodiesel production by using static mixer for both of production reactions, transesterification and esterification, because static mixer can provide high FFA conversion level since the early step of the reaction for all temperature level for both methods.



(a) (b)

Figure 4.17 FFA conversions comparison at different temperature levels between (a) this work and (b) work from Alamsyah, R., et al. [6]

Moreover, the acid value comparison at different temperature levels between biodiesel produced from coconut fatty acid in this experiment and biodiesel produced from coconut oil with mechanical stirrer was studied by Nakpong, P. and Wootthikanokkhan, S. are shown in Figure 4.18.



(a) (b)

Figure 4.18 Acid values comparison at different temperature levels between (a) this work and (b) work from Nakpong, P. and Wootthikanokkhan, S. [10]

It shows that the static mixer had greater efficiency to reduce the acid value of the coconut feedstock for all temperature levels than did the mechanical stirrer due to its benefits in mixing application *i.e.* generate small methanol droplet size and increase the interfacial of methanol to react with fatty acid that mention in the previous chapter.

4.5 GC Analysis Results

The chromatogram of the biodiesel sample, which was produced by the SMX mixer at the methanol to coconut fatty acid molar ratio of 3:1 at 50 ^{o}C, is shown in Figure 4.19. It shows the relationship between the retention time of methyl ester and the area or quantity of that methyl ester. The chromatogram consisted of 6 peaks. Each peak referred to each methyl ester that was constituent of this coconut biodiesel. Main components in this sample were n-hexane that was used as solvent, methyl laurate, methyl myristate, methyl plamitate and methyl oleate.

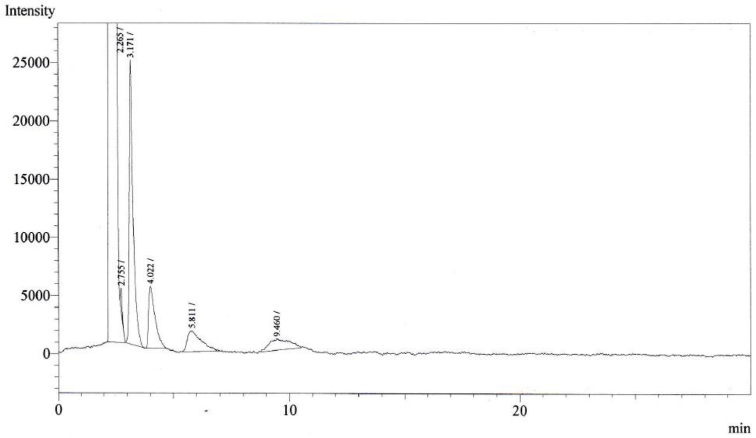


Figure 4.19 Chromatogram of coconut biodiesel sample, which produce with the SMX mixer at the methanol to coconut fatty acid molar ratio of 6:1 at 50 ^{o}C

The chromatogram between sample, standard methyl ester (methyl laurate, methyl myristate, methyl plamitate and methyl oleate) and solvent (n-hexane) can reveal that the first at retention time of 2.265 min was the n-hexane peak. The peak with the retention time of 3.171 min was methyl laurate. It was 53.51% of all methyl esters that were the constituent of coconut biodiesel, while methyl myristate (at 4.002 min), methyl plamitate (at 5.811 min) and methyl oleate (at 9.299 min) peaks had 19.83, 13.94 and 11.20%, respectively. These results are related to the amount of composition of coconut fatty acid, so it can used to confirm that the mostly of coconut fatty acid was converted into FAME via esterification with SMX mixer.

CHAPTER 5
CONCLUSION

The effects of static mixers on circulation acid catalyzed esterification in biodiesel production from coconut fatty acid and methanol were investigated. In order to determine the mixer type, SMX and Kenics mixers (represent as static mixers) and a plain pipe were used to produce biodiesel in pilot-scale. The results were compared with mechanical stirring in laboratory-scale (account for mechanical mixer in batch-scale). The FFA conversion comparison results revealed that static mixer had greater effect in order to convert fatty acid into FAME with higher FFA conversion and less reaction time. The SMX mixer, motionless mixer with complex series of eight cross-bars mixing elements, can reached the highest FFA conversion (88.40%), when compared with the other mixers, at the conditions molar ratio of methanol to coconut fatty acid of 3:1, temperature of 60 ^{o}C, and catalyst (sulfuric acid) concentration (compare with coconut fatty acid) of 0.7%v/v. Moreover, the suitable conditions for coconut biodiesel production by esterification, which it can provided FFA conversion over 90%, were methanol to coconut fatty acid molar ratio of 6:1 with reaction temperature of 50 ^{o}C in 10 min of reaction. These results exhibited that static mixer can overcome the challenges of biodiesel production due to it can shift the reaction into the forward direction and it can also operated in continuous process. The static mixer has no moving parts, and also requires a small space and low installation cost. Therefore, static mixer is promising to introduce to use in continuous biodiesel production process because of its benefits, *i.e.* it has lower energy and maintenance requirements.

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APPENDIXES

The acid value analysis of raw coconut fatty acid is shown in Table A-1. Moreover, the FFA conversion analysis of biodiesel samples for optimization of mixer type, methanol to coconut fatty acid molar ratio and temperature of reaction are given in Tables A-2, A-3 and A-4, respectively.

Table A-1 Acid value analysis results of raw coconut fatty acid

Data	**KOH**	**Coconut fatty acid**
Weight (g)	1.4523	2.0044
Volume (mL)	250	-
Concentration (N)	0.10	-
V_{KOH} (mL)	-	74.80
Acid value	-	209.32

Table A-2 Acid value analysis results of raw coconut fatty acid that produced with methanol and coconut fatty acid molar ratio of 3:1 at reaction temperature of 60 ^{o}C

Mixer type	**Time**	**KOH concentration (N)**	**Sample weight (g)**	**V_{KOH} (mL)**	**Acid value**	**FFA conversion (%)**
Kenics mixer	0	0.10	2.0406	65.97	181.37	13.35
	10		2.0108	20.97	58.50	72.05
	20		2.0021	15.15	42.44	79.72
	30		2.0037	13.97	39.11	81.32
	40		2.0045	12.80	35.82	82.89
	50		2.0122	12.06	33.61	83.94
	60		2.0025	11.14	31.21	85.09
SMX mixer	0	0.10	2.0090	66.05	187.08	10.63
	10		2.0055	15.10	42.84	79.53
	20		2.0094	11.35	32.14	84.65
	30		2.0054	10.15	28.80	86.24
	40		2.0043	9.70	27.54	86.84
	50		2.0036	9.00	25.56	87.79
	60		2.0041	8.55	24.28	88.40
Plain pipe	0	0.10	2.0012	65.20	185.39	11.43
	10		2.0023	27.00	76.73	63.34
	20		2.0006	24.10	68.55	67.25
	30		2.0011	23.50	66.82	68.08
	40		2.0039	21.35	60.62	71.04
	50		2.0035	20.60	58.51	72.05
	60		2.0066	20.50	58.13	72.23
Mechanical stirring	0	0.10	2.0033	64.20	182.35	12.88
	10		2.0055	27.70	78.59	62.45
	20		2.0005	23.30	66.27	68.34
	30		2.0043	20.50	58.20	72.20
	40		2.0057	19.20	54.47	73.98
	50		2.0048	18.50	52.51	74.92
	60		2.0046	18.30	51.95	75.18

Table A-3 Acid value analysis results of raw coconut fatty acid produced with SMX mixer and methanol reaction temperature of 60 ^{o}C

Molar ratio	**Time**	**KOH concentration (N)**	**Sample weight (g)**	**V_{KOH} (mL)**	**Acid value**	**FFA conversion (%)**
3:1	0	0.10	2.0090	66.05	187.08	10.63
	10		2.0055	15.10	42.84	79.53
	20		2.0094	11.35	32.14	84.65
	30		2.0054	10.15	28.80	86.24
	40		2.0043	9.70	27.54	86.84
	50		2.0036	9.00	25.56	87.79
	60		2.0041	8.55	24.28	88.40
6:1	0	0.10	2.0058	64.20	182.13	12.99
	10		2.0063	5.35	15.17	92.75
	20		2.0019	4.70	13.36	93.62
	30		2.0051	3.90	11.07	94.71
	40		2.0005	3.80	10.81	94.84
	50		2.0085	3.45	9.77	95.33
	60		2.0041	2.45	6.96	96.68
9:1	0	0.10	2.0095	65.40	185.19	11.53
	10		2.0077	2.40	6.80	96.75
	20		2.0010	2.30	6.54	96.88
	30		2.0028	2.20	6.25	97.01
	40		2.0051	2.00	5.68	97.29
	50		2.0031	1.95	5.54	97.35
	60		2.0074	1.80	5.10	97.56

Table A-4 Acid value analysis results of raw coconut fatty acid produced with SMX mixer methanol and coconut fatty acid molar ratio of 6:1

Temp (^oC)	**Time**	**KOH concentration (N)**	**Sample weight (g)**	**V_{KOH} (mL)**	**Acid value**	**FFA conversion (%)**
50	0	0.10	2.0074	69.15	196.01	6.36
	10		2.0054	6.35	18.02	91.39
	20		2.0013	5.35	15.21	92.73
	30		2.0052	4.65	13.20	93.70
	40		2.0026	4.05	11.51	94.50
	50		2.0047	3.60	10.22	95.12
	60		2.0072	3.10	8.79	95.80
60	0	0.10	2.0058	64.20	182.13	12.99
	10		2.0063	5.35	15.17	92.75
	20		2.0019	4.70	13.36	93.62
	30		2.0051	3.90	11.07	94.71
	40		2.0005	3.80	10.81	94.84
	50		2.0085	3.45	9.77	95.33
	60		2.0041	2.45	6.96	96.68
70	0	0.10	2.0021	58.50	166.26	20.57
	10		2.0083	5.00	14.17	93.23
	20		2.0021	3.00	8.53	95.93
	30		2.0081	2.50	7.08	96.62
	40		2.0020	2.05	5.83	97.22
	50		2.0004	1.80	5.12	97.55
	60		2.0032	1.75	4.97	97.63

The chromatogram of solvent (n-hexane) and standard methyl esters of methyl laurate, methyl myristate, methyl plamitate, and methyl oleate are shown in Figures A-1, A-2, A-3, A-4 and A-5, respectively.

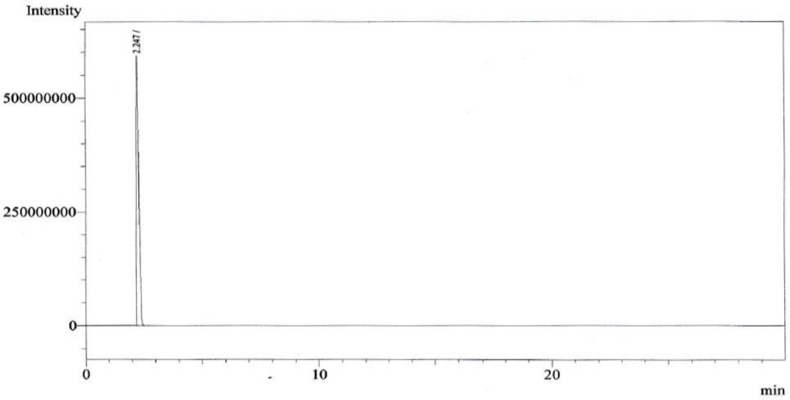

Figure A-1 Chromatogram of n-hexane

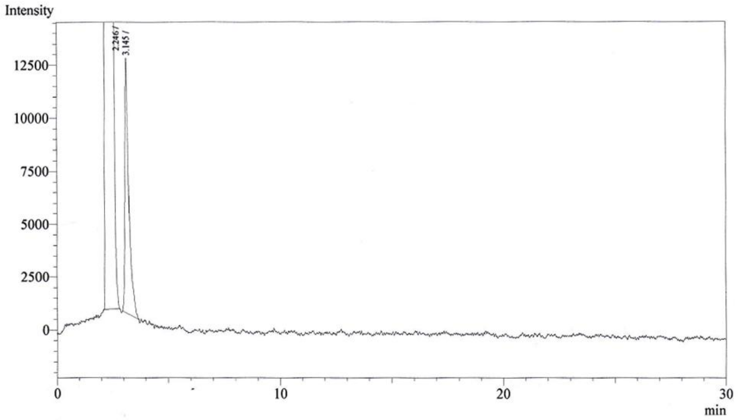

Figure A-2 Chromatogram of methyl laurate

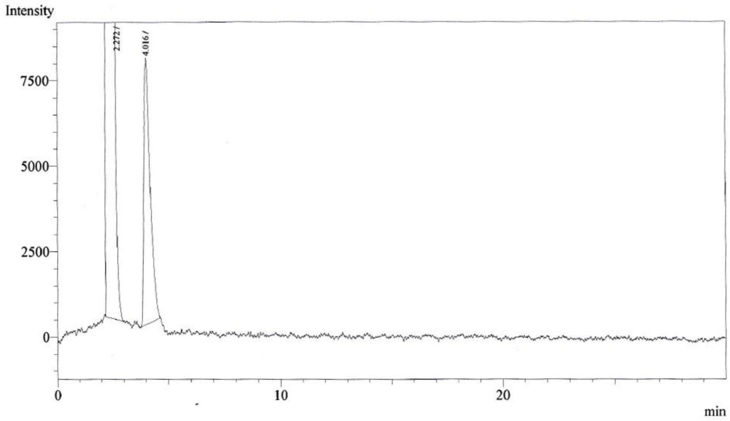

Figure A-3 Chromatogram of methyl myristate

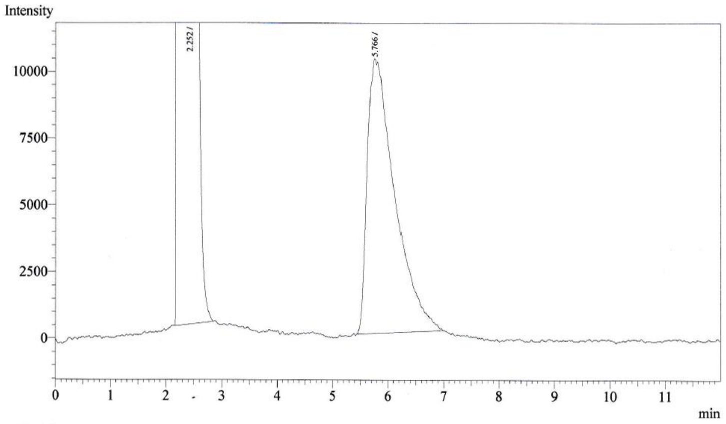

Figure A-4 Chromatogram of methyl plamitate

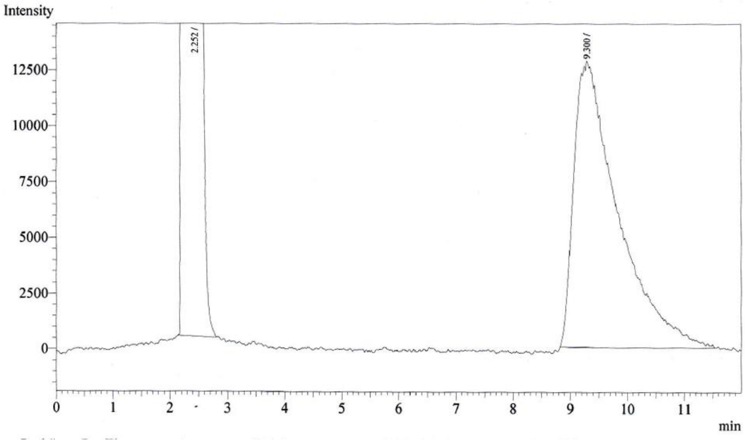

Figure A-5 Chromatogram of methyl oleate