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Enhancement of Biodiesel Production Reaction with Static Mixer

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Doctoral Dissertation

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Technical terms definition

Biodiesel : Mono-alkyl esters of long chain fatty acids derived from renewable lipid feedstock such as vegetable oils or animal fats.

Conventional mixer (Mechanical mixer) : A propeller type of mixer, usually utilized for mixing and blending of chemical. In biodiesel production, usually more than one set of propeller blades are utilized for creating sufficient turbulent.

Esterification reaction : A reaction between alcohols and carboxylic acids to form esters.

Fatty Acid Methyl Ester : Esters of fatty acids, which is another name for biodiesel.

Heterogeneous catalyst : A catalyst where the phase of the catalyst is different from the phase of the reactants.

Homogeneous catalyst : A catalyst where the catalyst is in the same phase as the reactants.

Static mixer : Static mixer are principally identified by their lack of moving parts. The mixer contains internal vanes or mixing elements that bring about sudden changes in the velocity patterns as well as momentum reversals. The purpose of the elements is to redistribute fluid in the directions transverse to the main flow, i.e. in the radial and tangential directions.

Transesterification reaction : A reaction between triglyceride lipid fat molecules and an alcohol to replace the alkoxy group form an ester.

Nomenclature

Chapter 3

a	specific surface area	$[m^2/m^3]$
C_0	initial triglyceride concentrations	[g/ml]
C_1	integration constant	[-]
C_A	actual triglyceride concentrations	[g/ml]
C_B	concentrations of methanol	[g/ml]
C_R	concentrations of FAME	[g/ml]
C_S	concentrations of glycerol	[g/ml]
d_{32}	Sauter-mean droplet diameter	[μm]
d_{av}	average diameter	[μm]
d_i	the diameter of droplets	[μm]
k	reaction rate constant	[ml/(g·min)]
k_c	mass transfer coefficient	[m/min]
$\vec{k}$	reaction rate constant for forward reactions	[ml/(g·min)]
$\overleftarrow{k}$	reaction rate constants for backward reactions	[ml/(g·min)]
M	initial molar ratio of TG to methanol	[-]
n	reaction order	[-]
n_i	number of droplets with the diameter of d_i	[-]
r_A	reaction rate	[g/(ml·min)]
x_A	conversion degree of triglyceride	[-]
φ	the holdup of alcoholic phase	[-]

Chapter 4

A	frequency factor	$[min^{-1}]$
C	Exact concentration of the standard volumetric potassium hydroxide used	[mol/l]
E	acidity removed	[mg KOH/g]
FFA_0	initial concentration of FFA	[mg KOH/g]
K_1	kinetic constants for the forward reactions	$[min^{-1}]$
K_2	kinetic constants for the backward reactions	[g/(mg·min)]
R	molar gas constant = 0.00813	[kJ/(mol·k)]
R^2	coefficient of determination	[-]
T	reaction temperature	[K]

V	Volume of standard volumetric potassium hydroxide used	[ml]
W_{oil}	Mass of the test sample	[g]
[FFA]	concentration of FFA	[mg KOH/g oil]
ΔE	activation energy	[kJ/mol]

Chapter 5

C_s	total number of sites	$[m^{-2}]$
k	kinetic constant for the surface reaction	$[s^{-1}]$
K_1	adsorption coefficients	[ml/g]
C_A	concentrations of the reactants A	[g/ml]
C_B	concentrations of the reactants B	[g/ml]

Abbreviation

AN	Acid number
DG	Diglycerides
FAME	Fatty Acid Methyl Ester
FFA	Free fatty acids
MG	Monoglycerides
TG	Triglyceride

Chapter 1

Introduction

1.1 Background of Biodiesel

1.1.1 Definition

Biodiesel is defined by American Society for Testing and Materials (ASTM) as mono-alkyl esters of long chain fatty acids derived from renewable lipid feedstock such as vegetable oils or animal fats. It is known as one of the alternative or renewable fuels, which is a substitute for regular petroleum fuel [1].

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1.1.2 Role of biodiesel

Prior to biodiesel, biofuel was developed by Rudolph Diesel, the inventor of compression ignition (CI) engine in 1900. Peanut oil was used as a fuel to run the diesel engine. At that time, plenty of crude oil was available and was refined enough to run the diesel engines. Therefore, vegetable oils were ignored as a fuel source [2].

But during the past decades, worldwide petroleum consumption has steadily increased, with the realization that crude oil is limited and poses threat to humans' health from emissions of exhaust gases. Due to these limitations of fossil fuels, there are many concerns on fluctuation of the petroleum price and increasing environmental problems, which caused a great demand for alternative sources of petroleum-based fuel. Vegetable oil has been reconsidered its feasibility as a fuel. However, due to high viscosity and low volatility, its long-term use has many problems such as deposition, ring sticking and injector choking in engines. Hence, upgrading of the vegetable oil was expected to improve the quality of the fuel and make it compatible with engines. This upgrading is to lower the viscosity of vegetable oils with chemical and thermal processes and to produce the petroleum-like fuel or known as biodiesel [3].

Some advantages of this alternative fuel is that it is biodegradable and has lower toxicity than the petroleum diesel fuel with a life cycle analysis of biodiesel showing that overall CO_2 emission can be reduced by 78% compared with petroleum-based diesel fuels, also no pollutant particulates and almost none sulfur contaminants. It also reduces most exhausts emissions such as carbon monoxide, sulfur dioxide and unburned hydrocarbons. Unfortunately, most emission tests have shown a slight increase in oxides of nitrogen (NOx). However with higher flash point, it leads to safer handling and storage. Another advantage is the excellent lubricity, when added to regular diesel fuel in an amount equal to 1–2%, it can convert fuel with poor

lubricating properties, such as modern ultra-low-sulfur diesel fuel, into an acceptable fuel [4].

Biodiesel can be utilized as B100 (neat) or blended in any proportion with petroleum diesel to create a biodiesel blend. For example, a blend of 20 % biodiesel with 80 % petroleum diesel, by volume, is termed “B20”. Just like petroleum diesel, biodiesel operates in the compression ignition engine, and essentially requires very little or no engine modifications because the biodiesel already has similar properties with these of petroleum fuel. Blending biodiesel with petroleum diesel improved lubricity and reduced emissions of petroleum diesel.

The global biodiesel utilization grew considerably in the past decades. However, petroleum diesel still is the most used fuel worldwide, since the cost of biodiesel is the main obstacle to make it competitive in the fuel market. The main production cost is from the feedstock itself as shown in Figure 1.1, which makes the price of crude petroleum oil still lower than that of refined vegetable oil [5]. Consequently, many efforts and researches are focusing on developing technologies capable of using lower-cost feedstock such as waste cooking oils or wastes from animal.

Disadvantages of using biodiesel produced from agricultural crops involve additional land use, whose environmental effects are inevitable. Even modest usages of biodiesel would consume almost all cropland in some countries in Europe. If the same thing is to happen all over the world, the impact on global food supply could be a major concern, and could make some countries being net importers of food products, from their current status of net exporters.

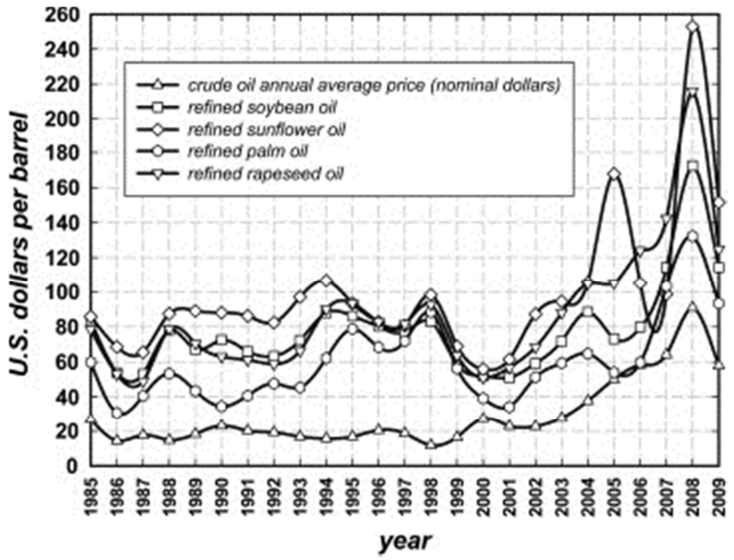

Fig. 1.1 Prices of some refined vegetable oil varieties.

The use of biofuel in the land based transport is still low in most countries. And most of the largest biodiesel consumers are belonging to developed countries such as

the European Union with France, Germany, and Italy being the largest consumers within Europe, followed by Brazil and the United States.

Although biodiesel cannot entirely replace petroleum-based diesel fuel, there are some reasons that can support the biodiesel development. First, biodiesel provides a market for excess production of vegetable oils and animal fats and it also decreases, although will not eliminate, the country's dependence on imported petroleum [4].

Therefore, the opportunities for the future for biodiesel include improvements in the conversion technology, expanding the amount of available feedstock, and adding value to the glycerol byproduct.

1.1.3 Biodiesel Production

There are many processes for biodiesel production, with the main objective of reducing the viscosity of the raw oil which is one of the major obstacles for long-term utilization of vegetable oil in diesel engines. The well-known technologies are the thermal process or pyrolysis, which resulted in production of low value materials and sometimes resulted in more production of gasoline instead of diesel. Other processes such as blending and microemulsification of vegetable oils reduced the viscosity but still posed few problems. These problems were namely carbon deposition and lubricating oil contamination.

Hence, the chemical process by transesterification reaction as shown in Figure 1.2 is the most investigated method and has been paid attention by scientists for a long time since 1853 [6-9]. The transesterification reaction is said to be the most suitable process for reducing the viscosity. It is the reaction between triglycerides (TG), which is the main component in the vegetable oil, and alcohol compound. Main product is a mixture of Fatty Acid Methyl Ester (FAME) of long-chain fatty acids such as palmitic, stearic, or oleic acids with glycerol being produced as a co-product. There are several variables that have effects on the product yield in the transesterification reaction. They are the molar ratio of alcohol to raw oil, the reaction temperature, the type and the concentration of catalyst, the mixing mechanism, and the raw oil itself [10].

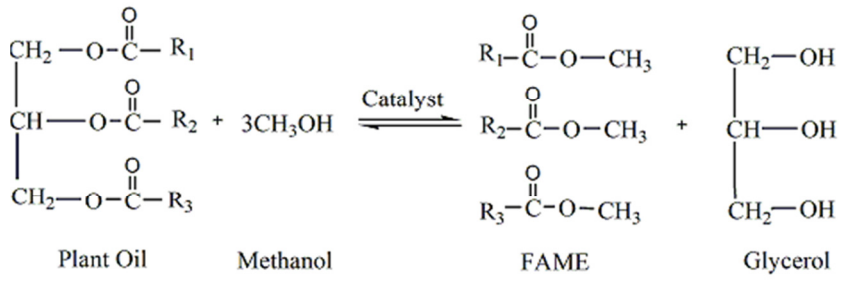

Fig. 1.2 Transesterification reaction

The transesterification consists of a number of consecutive, reversible reactions.

Figure 1.3 shows the transesterification reaction of triglyceride to methyl esters. The first step is the conversion of the triglycerides to diglycerides, followed by the conversion of the diglycerides into monoglycerides, and finally monoglycerides into glycerol, yielding one methyl ester molecule from each glyceride at each step [11, 12]. The reactions are reversible, although the equilibrium lies towards the production of fatty acid esters and glycerol. The reaction mechanism for alkali-catalyzed transesterification was formulated as three steps [13]. The first step is an attack on the carbonyl carbon atom of the triglyceride molecule by the anion of the alcohol (methoxide ion) to form a tetrahedral intermediate.

In the second step, the tetrahedral intermediate reacts with an alcohol (methanol) to regenerate the anion of the alcohol (methoxide ion). In the last step, rearrangement of the tetrahedral intermediate results in the formation of a fatty acid ester and a diglyceride. When catalysts were mixed with alcohol, the actual catalyst, alkoxide group is formed [14]. A small amount of water, generated in the reaction, may cause soap formation during the transesterification [15].

$$Triglycerides\ (TG) + R'OH \overset{Catalyst}{\Longleftrightarrow} Diglycerides\ (DG) + R'COOR_1$$

$$Diglycerides\ (DG) + R'OH \overset{Catalyst}{\Longleftrightarrow} Monoglycerides\ (MG) + R'COOR_2$$

$$Monoglycerides\ (MG) + R'OH \overset{Catalyst}{\Longleftrightarrow} Glycerol + R'COOR_3$$

Fig. 1.3 Transesterification reaction mechanism

Since the transesterification reaction is reversible, excess alcohol is required to shift the reaction equilibrium to the products side. The stoichiometric transesterification requires 3 mol of the alcohol per mole of the triglyceride to yield 3 mol of the fatty esters and 1 mol of the glycerol. However the transesterification reaction is an equilibrium reaction in which a large excess of alcohol is required to drive the reaction close to completion in a forward direction. The molar ratio of 6:1 or higher generally gives the maximum yield.

Including the conventional alkali-catalyzed traneseterification, there are three categories of catalysts that can be used for biodiesel production: alkalis, acids, and enzymes [16-18]. Compare with enzyme catalysts, the alkali and acid catalysts are more commonly used in biodiesel production. The alkali and acid catalysts include homogeneous and heterogeneous catalysts. Due to the low cost of raw materials, sodium hydroxide (NaOH) and potassium hydroxide (KOH) are usually utillized as alkali homogeneous catalysts and alkali-catalyzed transesterification is most commonly used commercially [19-26] .

The acid catalyst is normally utilized with nonedible oils, crude vegetable oils, and used cooking oils which typically contain more than 1% free fatty acids (FFA), and

animal fats contain more than 5% FFA. Since the alkaline catalyst reacts with the high free fatty acid feedstock and produce soap and water which is a hindrance for the transesterification reaction. In this case, an acid catalyst such as sulfuric acid is used to esterify the free fatty acids to methyl esters. The drawbacks with the acid esterification are the water formation and longer reaction duration due to lower catalyst activity compared to the alkali catalyst. However, when producing biodiesel from the high free fatty raw material, the alkaline-acid catalyst two-step process is mostly utilized [27-30]. The first step is the acid-catalyzed esterification process, converts the free fatty acids to methyl esters, reducing the acid value of the oil and in the second step the methyl esters are converted from triglycerides by an alkali-catalyzed transesterification process.

Enzyme catalysts have become more attractive recently since it can avoid soap formation and the purification process is simple to accomplish. However, they are less often used commercially because of the longer reaction times and higher cost. To reduce the cost, some researchers developed new biocatalysts in recent years. An example is so called whole cell biocatalysts which are immobilized within biomass support particles. An advantage is that no purification is necessary for using these biocatalysts [31-33].

In addition, solid heterogeneous catalysts can stimulatingly catalyze both transesterification and esterification reactions so there is no need for the pre-esterification step, also these catalysts are particularly useful for those feedstock with high free fatty acid content [34]. However, with the use of a solid catalyst, the reaction proceeds at a slower rate because the reaction mixture constitutes a three-phase system, which due to diffusion reasons, inhibits the reaction [35, 36].

The alcohol materials that can be used in the transesterification process include methanol, ethanol, propanol, butanol, and amyl alcohol. Among these alcohols, methanol and ethanol are used most frequently. Methanol is especially conventionally utilized because of its lower cost and its physical and chemical advantages. Some researchers reported that methanol can react with triglycerides quickly and the alkali catalyst is easily dissolved in it. However, due to its low boiling point, there is a large explosion risk associated with methanol vapors which are colorless and odorless. Both methanol and methoxide are extremely hazardous materials that should be handled carefully. It should be ensured that one is not exposed to these chemicals during biodiesel production [37].

Biodiesels are characterized by their viscosity, density, cetane number, cloud and pour points, distillation range, flash point, ash content, sulfur content, carbon residue, acid value, copper corrosion, and higher heating value (HHV). However, the most important parameters affecting the ester yield during the transesterification reaction are still the molar ratio of alcohol to vegetable oil and the reaction temperature. The viscosity values of vegetable oil methyl esters decrease sharply after the

transesterification. The flash point values of vegetable oil methyl esters are significantly lower than those of vegetable oils. There is also high regression between the density and the viscosity values of vegetable oil methyl esters [6].

The EN 14214 shown in Table 1.1 is an international standard that describes the minimum requirements and test methods for biodiesel.

Table 1.1 International standard (EN 14214) requirements for biodiesel

Property	**Units**	**lower limit**	**upper limit**	**Test-Method**
Ester content	% (m/m)	96,5	-	EN 14103
Density at 15°C	kg/m³	860	900	EN ISO 3675 / EN ISO 12185 / EN12185.
Viscosity at 40°C	mm²/s	3,5	5,0	EN ISO 3104 / EN 14105
Flash point	°C	> 101	-	EN ISO 2719 / EN ISO 3679.
Sulfur content	mg/kg	-	10	- EN ISO 20846 / EN ISO 20884.
Carbon residue remnant (at 10% distillation remnant)	% (m/m)	-	0,3	EN ISO 10370
Cetane number	-	51,0	-	EN ISO 5165
Sulfated ash content	% (m/m)	-	0,02	ISO 3987
Water content	mg/kg	-	500	EN ISO 12937
Total contamination	mg/kg	-	24	EN 12662
Copper band corrosion (3 hours at 50 °C)	rating	Class 1	Class 1	EN ISO 2160
Oxidation stability, 110°C	hours	6	-	EN 15751 / EN 14112
Acid value	mg KOH/g	-	0,5	EN 14104
Iodine value	-	-	120	EN 14111
Linolenic Acid Methylester	% (m/m)	-	12	EN 14103
Polyunsaturated (>= 4 Double bonds) Methylester	% (m/m)	-	1	EN 14103
Methanol content	% (m/m)	-	0,2	EN 14110
Monoglyceride content	% (m/m)	-	0,8	EN 14105
Diglyceride content	% (m/m)	-	0,2	EN 14105
Triglyceride content	% (m/m)	-	0,2	EN 14105
Free Glycerine	% (m/m)	-	0,02	EN 14105 / EN 14106
Total Glycerine	% (m/m)	-	0,25	EN 14105
Group I metals (Na+K)	mg/kg	-	5	EN 14108 / EN 14109 / EN 14538
Group II metals (Ca+Mg)	mg/kg	-	5	EN 14538
Phosphorus content	mg/kg	-	4	EN14107

1.1.4 Analytical Method

The analytical method in this research followed the standard EN 14103, Fat and oil derivatives – Fatty Acid Methyl Ester Determination of ester and liolenic acid methyl ester content. In EN 14103, the result for the fatty acid methyl ester content is expressed as a mass fraction in percent using methyl heptadecanoate (C_{17}) as the internal standard. Total ester content and Linolenic acid methyl ester content could be analyzed by this method. The details of the preparation and the calculation of this method are shown in Appendix A.

1.2 Statement of problem

Even though biodiesel has many advantages, there are still many challenges that need to be overcome in biodiesel production. One of the major obstacles in the commercialization of biodiesel fuel is its high production cost, mainly from high cost of vegetable oil. As stated in section 1.1.2 that the use of cheap and non-edible vegetable oils, waste cooking oil, animal fats, and non-conventional oil such as microalgae as raw feedstock, is an effective way to reduce the cost of biodiesel [38].

The other challenges are high running cost coming from the chemicals utilization, energy consumption for a long reaction time, the purification processes, and the mass transfer limitation. The mass transfer is limited because oils and alcohol are immiscible due to the low solubility of short-chain alcohols [39] and the limitation of the conventional mechanical mixing [40-43] and since the transesterification reaction is known to be a reversible reaction so there is a possibility of the backward reaction which results in the product reduction.

To overcome this mass transfer limitation, using catalyst supports or process intensification technologies is one of the possible solutions. The intensity of mixing has a strong influence on the reaction rate which has been investigated and reported in many studies, because oils and methanol are not completely miscible and the mixing efficiency was stated as one of the most important factors affecting the yield of the transesterification and esterification reactions [44-53].

Many technologies of the mixer in reactors have been developed for process intensification, such as the ultrasonic, the micro wave technology, the micro-channel, the oscillatory flow, the cavitation, and the static mixers. These technologies can enhance the reaction rate, reduce the molar ratio of alcohol to oil and the energy input by intensification of the mass transfer and the heat transfer, thus achieving the continuous reaction in the reactor. Some of these technologies have already been commercialized successfully [54-59].

The low frequency ultrasonic irradiation is widely used in industry for

emulsification of immiscible liquids. Previously, productions of biodiesel from vegetable oils with short chain alcohols under the ultrasonic irradiation were investigated. The results showed that the low frequency ultrasound is an efficient, time saving and economically functional technology, offering a lot of advantages over the classical procedures. Ultrasounds can be a valuable tool for the transesterification, aiming to prepare the biodiesel fuel at the industrial scale [60-62].

In parallel with the ultrasonic technology, the microwave technology has also been developed for the biodiesel synthesis. Because the mixture of vegetable oil and methanol contains both polar and ionic components, the microwave irradiation can play an active role in heating reactants to the required temperature quickly and efficiently. In the presence of a variety of catalysts, yields greater than 97% were achieved with the reaction time of less than 2 minutes. Other studies showed that the preparation of biodiesel using the microwave heating proved to be more energy efficient than the conventional synthesis as well [63-66].

1.3 Biodiesel production using the static mixer

A Static mixer is a mixer that consists of specially designed motionless geometric elements enclosed within a tubular pipe or a column as shown in Figure 1.4 and create effective radial mixing of two immiscible liquids as they flow through the mixer. Recently, they have been used in continuous biodiesel synthesis in combination with other equipment [50, 67]. The power input to the mixing process is a result of pressure loss through the mixer. static mixer mostly is applied in polymer processing, or in the chemical, pharmaceutical, petroleum, waste treatment, and food processing industries [68].

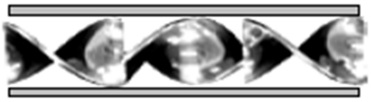

Fig. 1.4 Static mixer

In developing the continuous biodiesel production process, many researchers observed inline static mixers are performing effectively as a pre-mixer which followed by a high-shear mixer, in addition to its function as a reactant mixer and a heat exchanger [50, 57, 69]. A limited number of preliminary works investigated the utilization of static mixers in biodiesel production processes [55, 67]. The utilization of static mixers for dispersing two immiscible liquids are for liquid–liquid extraction, metal extraction, emulsification processes, and some liquid–liquid reactions [70, 71].

A work by Thompson [55] used a stand-alone closed-loop static mixer system as a continuous-flow reactor to produce biodiesel from canola oil with methanol when

sodium hydroxide was used as catalyst. Also, Boucher et al. [72] reported a reactor/separator design involving a static mixer for continuous biodiesel production and product separation. Pretreated waste canola oil and the solution of potassium hydroxide in methanol flow into a static mixer, which was exploited as an injector into a reaction chamber with no moving parts. Emulsified reactants were released into the chamber from the mixer with decreasing bulk velocity and separated into two phases under laminar flow conditions in the main body of the reactor.

1.3.1 Application of static mixer in other processes

In-line pipeline mixers are dedicated to the task of ensuring uniformity across the cross-section of the flow. Typically they are used after two streams have been brought together. The mixer may be *dynamic*, with a rotating element within the flow or it may be *static* or *motionless*, making use of fixed deflectors to bring about inter-change of streamlines. Some types of dynamic mixers are described in Perry & Green (1997). Static mixers add extra pressure drop to the line in which they are located, so they are using the energy of the stream itself to bring about mixing. Several varieties of static mixers are on the market. Godfrey (1985) compares the pressure drop and the effectiveness of various offerings. One can choose between a device with high effectiveness and high pressure gradient and a device with less effectiveness per unit of length but lower pressure gradient. Unfortunately, some mixers have low effectiveness and high pressure gradient. Relative to dynamic mixers, static mixers have the great advantage of having no external drive and requiring no seals [73].

There are few examples of static mixers utilized in many industrial applications for mixing of miscible liquids. The most investigated mixer for liquid–liquid dispersion in turbulent flow in the literature is the classical Kenics helical mixer [74-77]. Emulsification using the Sulzer SMX mixer has been studied not only in laminar flow but also in turbulent regime [78-81]. Results about liquid–liquid dispersion are also reported in some literatures using the SMV mixer, the Lightnin Series 50 and the High Efficiency Vortex mixer [82-84].

In the liquid-liquid immiscible systems, static mixers are well suited for co-current extraction processes. They are competitive application with conventional mechanically agitated systems such as rotating disc columns or stirred tanks. A major advantage is their resistance to flooding, even when the phases have similar densities. The aim is to form drops that are small enough to provide high interfacial area but large enough to avoid formation of an emulsion, and static mixers are well suited to this purpose. Baker (1991) reported industrial applications for amine washing, caustic washing, water washing of organics and extraction of hydrogen sulfide from petroleum fractions using diethanolamine.

Recently, static mixers have been used for co-current extractions with

supercritical carbon dioxide, for example to carry out fractionation of lipids in order to separate squalene from triglycerides and diacylglyceryethers [85]. Co-current extraction of caffeine from supercritical CO_2 with water using static mixers has been proposed to replace countercurrent packed columns. Motionless mixers are also used to enhance liquid–liquid reactions. Examples are largely proprietary, but see the contribution of Chamayou et al. (1996) [71] on the production of Amiodarone, a widely used anti-arrhythmic drug.

Static mixers can also be used in the classical, countercurrent mode for liquid–liquid extractions. Jancic et al. (1983) and Streiff and Jancic (1984) [86, 87] studied their application to several test systems: kerosene–water, butanol–succinic acid–water, toluene–acetone–water and carbon tetrachloride–propionic acid–water. They concluded that inserting static mixers reduces coalescence and requires a lower residence time than conventional devices, even with high liquid flow rates. Other applications of static mixers with liquid–liquid systems are reported by Merchuk et al. (1980) for copper extraction, and by Le Coze et al. (1995) [88, 89] for indium extraction

1.3.2 Advantage of static mixers

As stated in the previous sections that static mixers are very effective in mixing liquids that are not readily miscible under normal conditions. Since a static mixer performs a series of mechanism to mix reactants, namely dividing, rotating, channeling, or diverting the flow before recombining it as shown in Figure 1.5 [43]. It creates additional turbulence to enhance mixing. Static mixer has been used to intensify physical and chemical processes in liquids, particularly the processes of gas and solid dissolution.

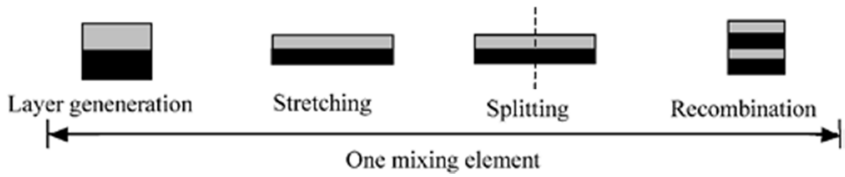

Fig. 1.5 Mechanism of the static mixer

Another advantage of static mixers is that as the motionless mixers, they typically require less energy consumptions than conventional mechanical agitation. The only energy cost represented by static mixers comes from the external pumping power needed to propel materials through the mixer. Static mixer also reduced maintenance requirements because there are no moving parts. The energy of the flow stream itself is utilized to create mixing. Moreover, there are small space requirements, less construction materials, narrow residence time distributions, and enhanced heat transfer. The advantages of static mixers compare with conventional continuous stirred-tank reactors (CSTR) are shown in Table 1.2

Table 1.2 Potential advantages of static mixers compare with conventional mechanically stirred vessels.

Static mixer	CSTR
Small space requirement	Large space requirement
Low equipment cost	High equipment cost
No power required except pumping	High power consumption
No moving parts except pump	Agitator drive and seals
Small flanges to seal	Small flanges plus one large flange to seal
Short residence times	Long residence times
Approaches plug flow	Exponential distribution of residence times
Good mixing at low shear rates	Locally high shear rates candamage sensitive materials
Fast product grade changes	Product grade changes may generate waste
Self-cleaning, interchangeable mixers or disposable mixers	Large vessels to be cleaned

Many researches also showed that static mixers have effective results when applied to the transesterification process for biodiesel reaction with the possibility of narrow residence time distributions [70, 90-92]. That is why the utilization of static mixers for continuous processes is an attractive alternative to conventional mechanical agitation devices since it can deliver similar or sometimes better performances but can be achieved at lower cost.

1.4 Research objectives

As stated in previous sections, many developments of biodiesel production in present days are focusing on reducing the cost arising from the chemical utilization, energy consumption, purification processes, and the cost of raw materials. One possible method is to develop a continuous production system which has the potential to reduce the production costs and energy requirement. In our work, the main target is to study the performance of a static mixer in different biodiesel production processes to optimize the capability of developing this static mixer into continuous biodiesel production system or in the bigger scale biodiesel production.

First we studied the application of static mixers to conventional alkali-catalyzed transeseterification to investigate whether the static mixer could enhance the reaction kinetics and the conversion efficiency compared with the conventional mechanical stirrers, by increasing the contact surface area between the raw oil and methanol. Then, in order to compare the performance of static mixers, it was applied with another two biodiesel production process which are acid-catalyzed esterification reaction, and heterogeneous catalyst packed-bed column with the transesterfication reaction, to

represent different results of the static mixer from the fast reaction to the slow reaction, respectively.

In order to understand the mechanism of enhancement of the transesterification reaction by the static mixer, the kinetics or the mechanism of these three reactions were also investigated to explain the reason how the enhancement occurred or why the static mixer could not enhance the reaction in some cases.

1.5 Thesis outline

This thesis will be presented in 6 chapters, discussing mainly the topics concerning the comparison of the static mixer and the conventional mechanical stirrer in biodiesel production process.

In the current Chapter 1, the background of biodiesel and the details of the production reaction and its main parameters were explained. Previous works were discussed to present the problem of the conventional biodiesel production processes and stated the challenges in the development of biodiesel production. These challenges lead to the utilization of the static mixer in this research and the application and advantage of this static mixer are also explained in this chapter.

In Chapter 2, the comparative studies on the conventional mixer and the static mixer under the batch process were studied. Both the conventional mechanical stirrer and the static mixer were used to produce biodiesel under the alkali-catalyzed transesterification reaction and investigated the potential of reaction enhancement by the static mixer.

Chapter 3 explained the mechanism of the reaction enhancement by the static mixer from the results in chapter 2. The mechanism is investigated by comparing droplet size measurement and the reaction rate coefficient. There are three operating stages in the reaction that need to be considered, the slow initial mass transfer stage, then the fast chemical controlled stage, and the final slow equilibrium stage.

Chapter 4 presented the enhancement of the acid-catalyzed pretreatment process for high free fatty acids oil by the static mixer and its mechanism or kinetics. In chapters 2 and 3, the reaction enhancement of the static mixer occurred under the fast alkali-catalyzed process. Therefore, in this chapter, the acid catalyst which has a lower catalytic activity was utilized to investigate the performance of the static mixer even at a slower reaction rate.

In Chapter 5, the heterogeneous catalysts were utilized with the transesterification reaction. Many researches are focusing on a continuous production system with the use of the heterogeneous catalyst, which can reduce the production costs and energy requirement. However, the heterogeneous catalyst has even lower catalyst activity

when compared with the homogeneous ones. So the static mixer is also applied to investigate the possibility of reaction enhancement since there is a possibility that the agitation intensity may not be the main factor that can control the reaction rate.

In the last Chapter 6, the thesis was finalized by conclusion in this chapter. Recommendations for future works are also proposed in this chapter.

Chapter 2

Comparative studies on conventional mixer and static mixer under batch process

2.1 Introduction

As mentioned in previous chapter, introduction of the static mixer technology into the biodiesel production can overcome the limitation of the conventional mechanical stirrer by which the oil and alcohol form two immiscible phases [58].

In this chapter, we investigate the effectiveness of the static mixer to verify that it can obtain better Fatty Acid Methyl Ester(FAME) yields under various conditions. The other main factors in biodiesel production process or the transesterification reaction are the molar ratio of methanol, the catalyst concentration, and the reaction time. In this chapter, each factor and the raw material were varied and the product yields were compared between the conventional mixer and the static mixer to optimize the biodiesel fuel production reaction for maximizing the yield.

This chapter is only focusing on to explore the possibilities of using static mixers as a mixing device for the transesterification reaction and thereby to enhance the reaction rate. Therefore, the mechanism or the explanations of this enhancement will be investigated and discussed by applying this static mixer to other reaction in biodiesel production processes in later chapters.

2.2 Material and experimental procedures

Raw materials in this chapter were canola oil purchased from local market and waste cooking oil received from Best Trading Co. Ltd. in Atsugi city, Japan. Canola oil is one of the vegetable oils that can be utilized for biodiesel production [93-96]. Waste cooking oil is also well known for its low-cost and as renewable resources but the main difficulties of waste cooking oil are its high free fatty acid value, water content, and other contaminants. Methanol was utilized as the reactant and potassium hydroxide (KOH) was used as the catalyst in the transesterification reaction.

The conventional reaction for biodiesel production is the transesterification which

is also called as alcoholysis reaction as shown in Figure 2.1.This reaction is the reaction between triglycerides molecules in the plant oil and methanol or other alcohols, the catalysts is also required in this reaction and alkaline catalyst is mostly utilized due to the short reaction time even though this reaction can also be catalyzed by acid, enzyme, or heterogeneous catalysts. The main product of this reaction is Fatty Acid Methyl Esters (FAME) or as known as Biodiesel after the purification process and the by-product of this reaction is glycerol which can be recycled and utilized as an industrial chemical after the extraction.

In the conventional biodiesel production, an excess mole ratio between methanol and plant oil, at least 6:1, is required to shift the equilibrium to the products side and give maximum conversion efficiency to the fatty acid methyl ester even though the stoichiometric value is only 3:1 [12, 97, 98].

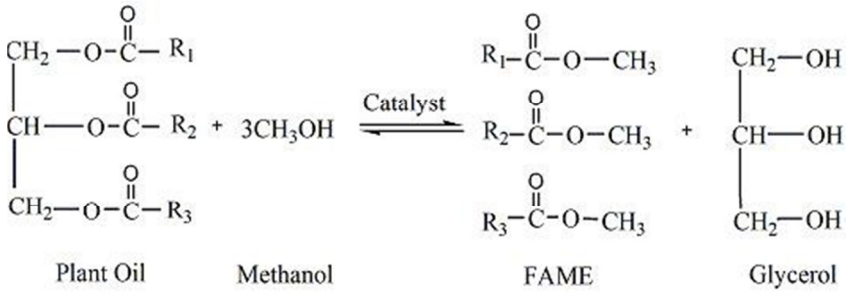

Fig. 2.1 Transesterification Reaction

Two types of mixers were utilized under the concept of this transesterification reaction. These mixers are the conventional mechanical mixer and the static mixer.

2.2.1 Conventional Mixer

For a conventional mixer, a stirring apparatus shown in Figure 2.2 was utilized. Catalyst KOH was mixed with methanol before added to raw oil. The mixed solution was stirred with NISSIN company`s SW-RS7770 magnetic stirrer at the speed of 600 rpm and a water bath with the maximum capacity of 3L was utilized for heating. The capacity of each batch experiment was fixed at 500ml per batch.

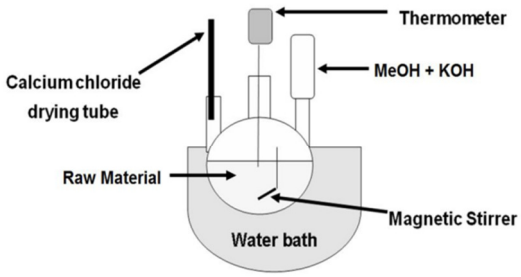

Fig. 2.2 Conventional mixing apparatus

2.2.2 Static Mixer

For another method of mixing, the static mixer, a helical type static mixer, as shown in Figure 2.3, was utilized. The length of the pipe is 26 cm, with 0.8 cm inner diameter. The static mixer consisted of 20 elements and each element had 1.2 cm length and 0.8 cm diameter with 1 mm gap between the elements and the pipe exit at both ends of the pipe. The components were mixed through the static mixer in 2-3 seconds with the maximum volumetric flow rate of 0.12 L/s, and the superficial velocity of 2.4 m/s. After this static mixing, the emulsified product yield was monitored for 30 minutes. The capacity of each batch experiment was fixed at 1L per batch.

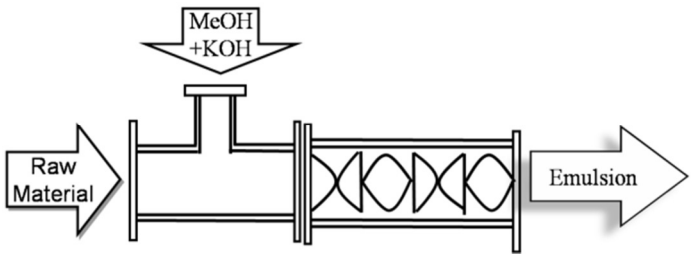

Fig. 2.3 Static mixer

The device utilized in this chapter as a static mixer, which can also be called as emulsification device, is an instrument equipped by a pump and pipes which connected to two inlets of raw material and methanol and potassium hydroxide mixture and in the other end of the pipe is the static mixer. This static mixer equipment is shown in Figure 2.4 and a product of this mixer is shown in Figure 2.5. The product appears to be a emulsified homogeneous-like mixture as shown in the picture.

Fig. 2.4 Static mixer (or emulsification) device

Fig. 2.5 Emulsified mixture of biodiesel

2.2.3 Experimental parameters and analysis

In biodiesel production, the main parameters are the molar ratio of methanol and the concentration of catalyst KOH. Experiments in this chapter were conducted at the room temperature to slow down the reaction speed to make the effects of changing the molar ratio of methanol and the catalyst concentration more apparent. Experimental conditions are shown in Table 2.1.

Table 2.1 Experimental conditions

MOLAR RATIO OF METHANOL	KOH (%WT)
3.3	0.6
	1.2
	1.8
4.3	0.6
	1.2
	1.8
6	0.6
	1.2
	1.8

Each experiment was repeated under the same conditions for at least 2-3 times to ensure the repeatability of the procedure.

Samples were taken at 0, 0.5, 1, 1.5, 2, 3, 4, 5, 7, 10, 15, 20, 25, and 30 minutes respectively. The volume of each sample is fixed at 1ml per sample, so totally 14ml of samples were taken during each batch of the experiment. For the conventional stirring method, the reaction starting time was just after methanol was completely added to the raw oil and the rotation of the magnetic stirrer started. On the other hand, the reaction starting time of the static mixing method was just after the reactants were

mixed or emulsified.

After samples were taken, hydrochloric acid was quickly mixed with samples to stop the reaction. Then they were centrifuged to separate the upper FAME layer and only the components in this layer were analyzed. Products were analyzed by a gas chromatography, using the equipment of GC-2010 (Shimadzu Co., Japan) with the flame ionization detector, following the EN 14103 standard. The capillary column is the ultra-alloy column with the length of 15 m, the inner diameter of 0.25 mm, and the film thickness of 0.1 μm. Helium is utilized as a carrier gas at the flow rate of 2 mL/min. The injector temperature was 250˚C and the oven temperature was 200˚C. Methyl heptadecanoate was used as the internal standard.

2.3 Results and Discussion

2.3.1 Effect of the reaction time

To compare the results of the static mixer and the conventional mixer, first we investigated the time change of the FAME yield. The results are shown in Figures 2.6-2.8 for canola oil and in Figures 2.9-2.11 for waste cooking oil at different catalyst concentrations. Only the results with 6:1 molar ratio of methanol were compared since it is the recommended molar ratio for the transesterification reaction.

As shown in these figures, in the first stage of the reaction (0-10 min), the static mixer provided a higher reaction rate than the conventional mixer. While the FAME yield for the conventional mixer slowly became stable, the FAME yield for the static mixer was almost stable form the starting point. However, these figures show that with a low concentration of catalyst, even though the reaction rate for the static mixer was still higher than the conventional mixer, the FAME yield obtainable was rather low.

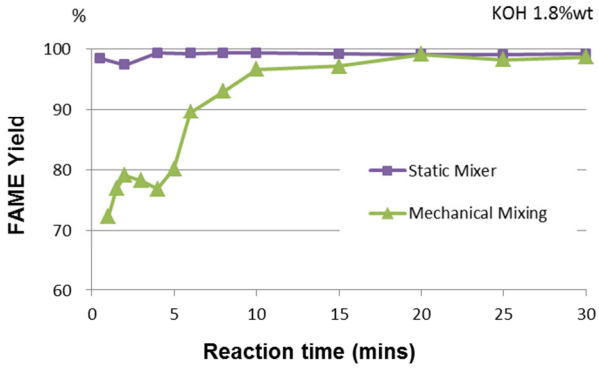

Fig.2.6 Time change of the FAME yield with 6 molar ratio of methanol, 1.8% KOH concentration, for (■) static mixer, and (▲) conventional mixer (canola oil).

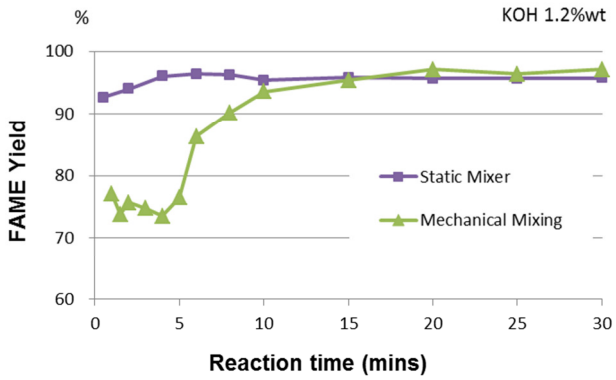

Fig. 2.7 Time change of the FAME yield with 6 molar ratio of methanol, 1.2% KOH concentration, for (■) static mixer, and (▲) conventional mixer (canola oil).

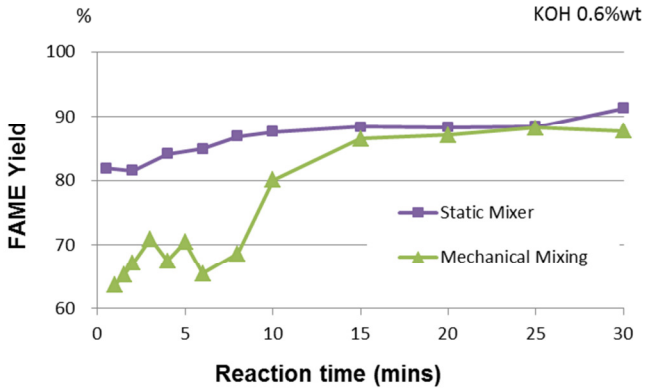

Fig. 2.8 Time change of the FAME yield with 6 molar ratio of methanol, 0.6% KOH concentration, for (■) static mixer, and (▲) conventional mixer (canola oil).

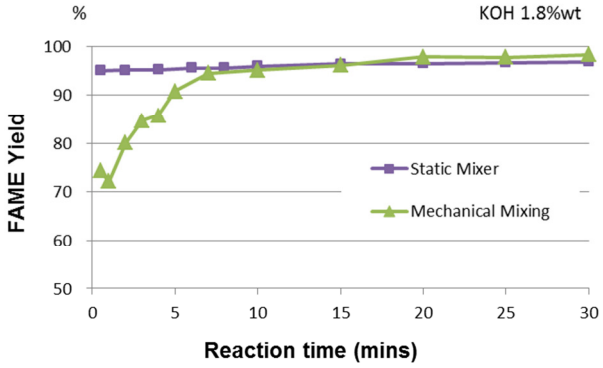

Fig. 2.9 Time change of the FAME yield with 6 molar ratio of methanol, 1.8% KOH concentration, for (●) static mixer, and (■) conventional mixer (waste cooking oil).

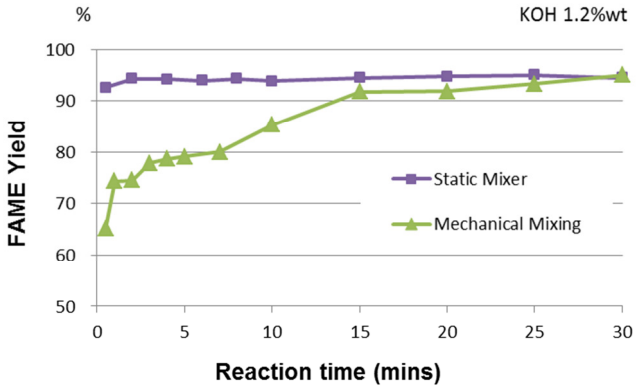

Fig. 2.10 Time change of the FAME yield with 6 molar ratio of methanol, 1.2% KOH concentration, for (●) static mixer, and (■) conventional mixer (waste cooking oil).

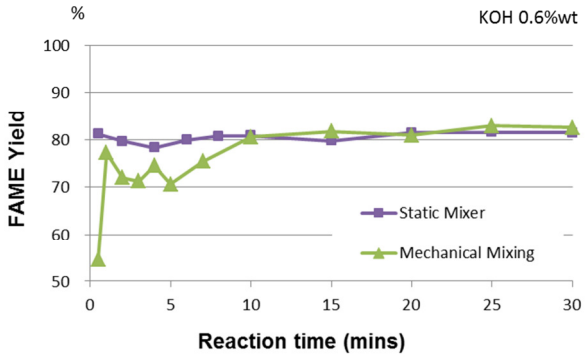

Fig.2.11 Time change of the FAME yield with 6 molar ratio of methanol, 0.6% KOH concentration, for (●) static mixer, and (■) conventional mixer (waste cooking oil).

2.3.2 Effect of the molar ratio of methanol

As shown in Table 2.1, molar ratios of methanol that were examined are 3.3:1, 4.3:1, and 6:1. The FAME yield for the static mixer and the conventional mixer are shown in Figures 2.12-2.15. Figures 2.12-2.13 and 2.14-2.15 are the results of canola oil and of waste cooking oil, respectively. The FAME yields for both mixers are compared after 5 and 30 minutes from the start of the reaction, which correspond to the initial stage and the final stage of the reaction, respectively. The variations of concentration of catalyst are 1.8%wt, 1.2%wt, and 0.6%wt of raw materials.

The results show that at the end of the reaction, the FAME yield for both mixers are similar, but the yield difference between the initial and the final stages for the static mixer is very small. As stated above, the FAME yield for the static mixer already reached the stable state just after the start of the reaction. On the contrary, the results of the conventional mixer showed that the FAME yield significantly increased after 30 minutes from the start of the reaction. It can be said that the static mixer can achieve higher FAME yield than the conventional mixer at any molar ratios of methanol.

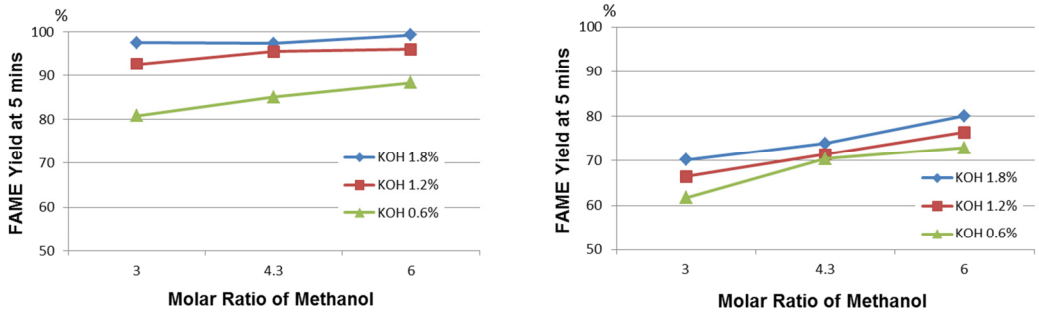

Fig. 2.12 Effect of the molar ratio of methanol on the FAME yield for canola oil under 3 different KOH concentrations after 5 minutes from the start of the reaction. Left: static mixer, Right: conventional mixer

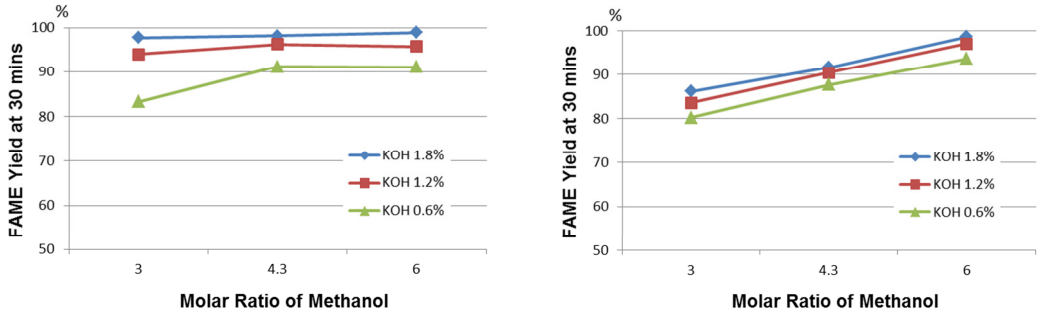

Fig. 2.13 Effect of the molar ratio of methanol on the FAME yield for canola oil under 3 different KOH concentrations after 30 minutes from the start of the reaction. Left: static mixer, Right: conventional mixer

Figures 2.14 and 2.15 below show the results of waste cooking oil. Even though the compositions and characteristics of waste cooking oil are different from canola oil, the reaction enhancement by the static mixer can be observed also.

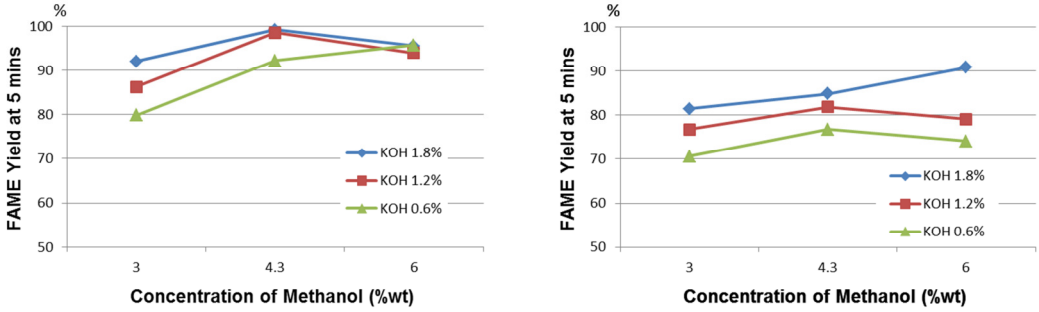

Fig. 2.14 Effect of the molar ratio of methanol on the FAME yield for waste cooking oil under 3 different KOH concentrations after 5 minutes from the start of the reaction. Left: static mixer, Right: conventional mixer.

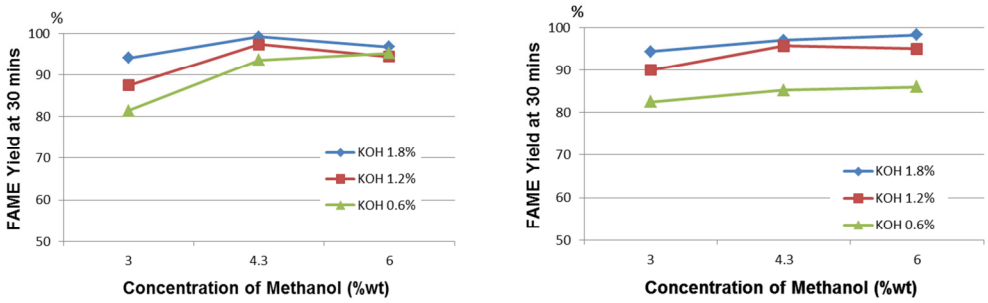

Fig. 2.15 Effect of the molar ratio of methanol on the FAME yield for waste cooking oil under 3 different KOH concentrations after 30 minutes from the start of the reaction. Left: static mixer, Right: conventional mixer

2.3.3 Effect of the catalyst concentration

As shown in Table 2.1, concentrations of KOH catalyst that were examined were 0.6wt%, 1.2wt% and 1.8wt%. The results for the static mixer and the conventional mixer are shown in Figures 2.16-2.19. The FAME yields are compared for the initial stage (5 minutes) and the final stage (30 minutes) of the reaction. The variations of the molar ratio of methanol were 3.3:1, 4.3:1, and 6:1.

The effect of the catalyst concentration shows the same trend as the effect of the molar ratio of methanol. It shows that the FAME yields for the static mixer after 5 minutes and 30 minutes from the start of the reaction have a very small difference. These results also illustrate that the static mixer can acquire higher reaction rate than the conventional mixer under any concentrations of catalyst for both canola oil and waste cooking oil.

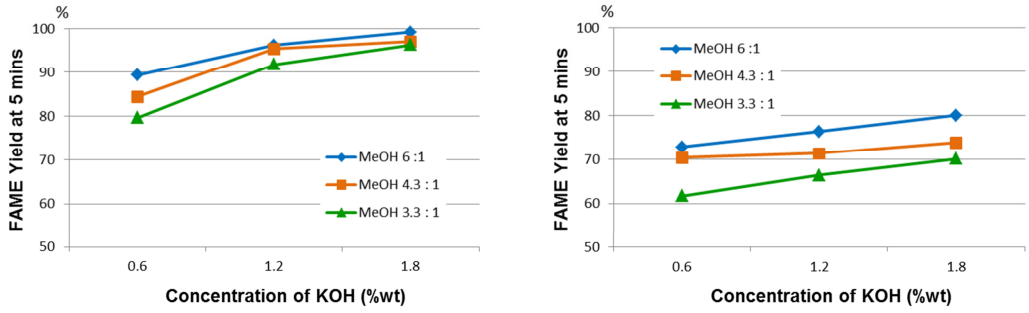

Fig. 2.16 Effect of the catalyst concentration on the FAME yield for canola oil under 3 different molar ratios of MeOH after 5 minutes from the start of the reaction. Left: static mixer, Right: conventional mixer

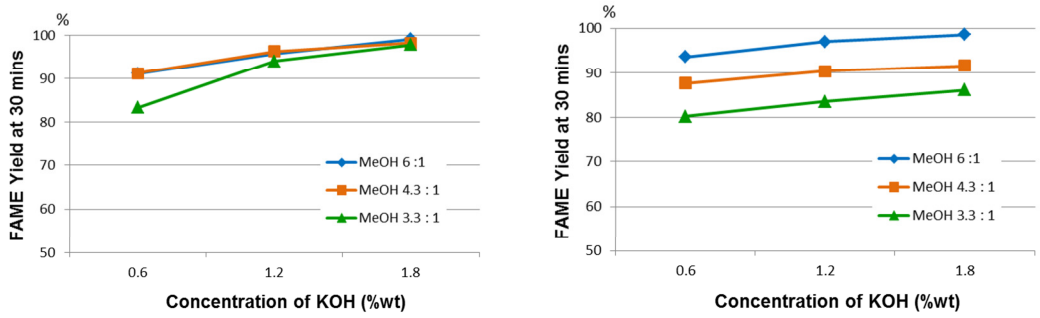

Fig. 2.17 Effect of the catalyst concentration on the FAME yield for canola oil under 3 different molar ratios of MeOH after 30 minutes from the start of the reaction. Left: static mixer, Right: conventional mixer

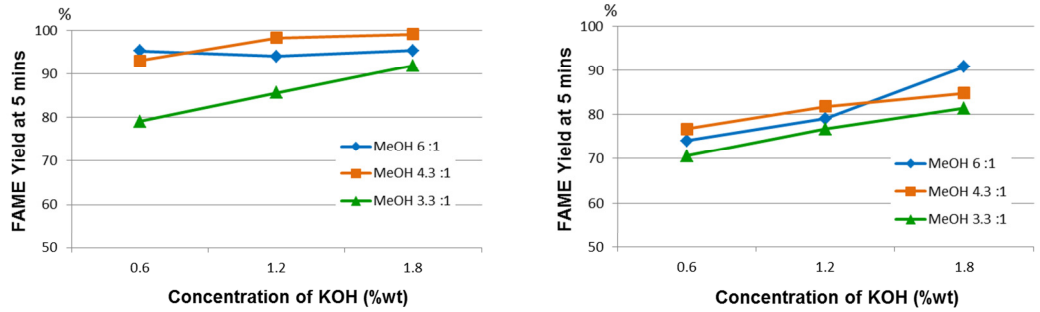

Fig. 2.18 Effect of the catalyst concentration on the FAME yield for waste cooking oil under 3 different molar ratios of MeOH after 5 minutes from the start of the reaction. Left: static mixer, Right: conventional mixer

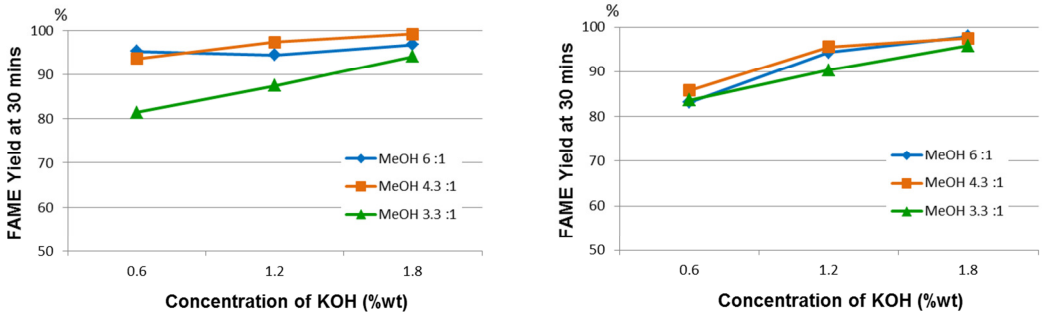

Fig. 2.19 Effect of the catalyst concentration on the FAME yield for waste cooking oil under 3 different molar ratios of MeOH after 30 minutes from the start of the reaction. Left: static mixer, Right: conventional mixer

2.4 Conclusion

The following conclusions are derived from results of the static mixer and the conventional mechanical mixer in biodiesel production with the transesterification reaction from canola oil and waste cooking oil in this chapter.

Experimental results indicated that with the use of the static mixer, the reaction time required for getting high enough fatty acid methyl ether yields is much shorter than the conventional mixer. This shows that the mixing of the static mixer is more effective than the conventional mixer.

With the same conditions of the molar ratio of methanol and the catalyst concentration, the static mixer can achieve higher FAME yield than the conventional mixer. This reaction enhancement of the static mixer can be achieved for both canola oil and waste cooking oil which have different characteristics. There is a possibility that we can reduce the amount of methanol and catalyst that are needed for the transesterification reaction to obtain optimum fatty acid methyl ether conversion.

As for the possibility of the application of this static mixer for the operation scale, we studied the mechanism of this enhancement of alkali-catalyzed for transesterification reaction in the next chapter 3 to explain why or how higher product yield can be achieved, in order to find the possibility of applying the same enhancement to the bigger scale process or other similar reactions.

Chapter 3

Mechanism studies on enhancement of biodiesel production with alkali catalyst by static mixer

3.1 Introduction

In chapter 2, the effectiveness of the static mixer is shown and the results show that the product yield can be enhanced by this mixer. So in this chapter we are focusing on the mechanism of this enhancement to find the relationship between the effect of the static mixer and the reaction rate. The main objective is to study the kinetics of the transesterification process by comparing the reaction kinetics for both the static mixing and the conventional mixing methods.

Many researchers have studied the variables affecting the vegetable oil transesterification reaction. Some did study on the kinetics of this reaction, and reported that the intensity of mixing has a strong influence on the reaction rate [12, 44, 46-48, 50, 51, 53]. So this chapter will focus on the effect of the static mixer on the reaction rate since the results in the previous chapter 2 showed that the product yield can be promoted by the use of the static mixer and we assumed that this promotion is the result from the enhanced reaction rate.

This chapter included two steps for kinetic studies, first is the measurement of droplet sizes of methanol in the raw oil which lead to the second step of the kinetic calculation. There are three operating stages in kinetics studies and the detailed explanation will be shown in the kinetic calculation in the section 3.2.

For the chemical reaction kinetics, there are three main operating stages which controlled the rate of the reaction. First is the slow initial mass transfer stage or the diffusion-controlled (or diffusion-limited) stage, followed by the second chemical-controlled (or reaction-controlled) stage, and the last one is the equilibrium stage where the reaction ends [51, 53, 99].

In many studies, the first mass transfer stage is known to be negligible when the agitation intensity is high enough. The agitation is more significant during the initial

slow mass transfer stage than after triggering the reaction. In the second stage, the agitation is not so necessary since the reaction rate could not be enhanced by further agitation [47]. However, in our study we are also studying the first mass transfer stage by investigating the droplet sizes of methanol and distribution during the reaction, and to analyze the surface area of the reactants during the vigorous agitation.

For the transeterification reaction, many researchers reported the reaction order differently. Most of them suggested that the forward and backward reactions of the transesterification should follow a pseudo-first- and second-order kinetics respectively. Some says that kinetics for the forward reaction consisted of a combination of second-order consecutive and fourth order shunt reactions, or suggests a pseudo-second-order model for the initial stages of the reaction, but only for the forward reaction. These differences are based on the type and amount of reactants, or the different conditions of the transesterfication process. So with our own results of the reaction kinetics, we also calculated and analyzed the reaction order which is the most suitable to explain the mechanism of this biodiesel production by the static mixer.

Lastly, the results in this chapter will represent that the agitation by the static mixer has an effect on the reaction rate by increasing the surface area of the reaction. Therefore, this relationship was evaluated to find that whether the surface area is the sole factor that causes the reaction rate enhancement or not.

3.2 Kinetics Calculation

Just like in chapter 2, the reactions are conducted by using canola oil, methanol, and potassium hydroxide as the main reactants and the catalyst respectively. And the mixing instruments are the same water bath stirrer and the static mixer with the same reaction conditions.

In the introduction, it is already mentioned that there are 3 operating stages in kinetics studies. First is the slow initial diffusion-controlled stage, followed by the second chemical-controlled stage, and the last is the equilibrium stage.

The first diffusion-controlled stage is the phase where the rate of reaction is affected by stirring or agitation. Diffusion-controlled reactions are reactions that occur so quickly that the reaction rate is the rate of transport of the reactants through the reaction solution [100]. The process of this stage can be considered as the diffusion of reactants until they encounter each other. The formation of products from the activated complex is much faster than the diffusion of reactants and thus the rate is controlled by the collision frequency or the surface area of the reactants.

As soon as the reactants encounter each other, they react with each other

according to the stoichiometry and form the products. In this phase, the significance of the agitation begins to drop and the reaction is driven by the reacting reactants solely, and from this point, the reaction moves to the chemical-controlled stage. In this study, we are mainly focusing on the transesterifcation reaction between canola oil and methanol.

The final equilibrium stage is a state where the concentrations of products and reactants are unchanged over time. For the transesterification reaction, this means that the fatty acids methyl esters and glycerol already formed and the tri-glyceride, di-glyceride, including mono-glyceride already fully or mostly depleted.

3.2.1 Diffusion-controlled stage

Even though in most of kinetic studies, the initial mass transfer stage is shown to be negligible since it can be shorten by a strong agitation and/or the increase of the reaction temperature. However, for studying reaction kinetics, we have to assume that the transesterification reaction starts to occur in the initial mass transfer stage and the chemical reaction controls overall process kinetics, so the droplet sizes of methanol were analyzed to represent the effect of the agitation to the droplet sizes and the surface area.

The droplet sizes of products during 30 minutes of the reaction were measured by a digital microscope from the time zero to the time of the reaction finish for both processes. After the sample was taken, it was immediately analyzed by the microscope. Photos of the molecules were taken and diameters of droplets can be calculated by the functions of microscope. The Sauter-mean droplet diameter (d_{32}) is calculated using Equation (1) where d_i is the diameter of a droplet and n_i is the number of droplets with the diameter of d_i.

$$d_{32} = \frac{\sum n_i d_i^{\,3}}{\sum n_i d_i^{\,2}} \qquad (1)$$

The mean diameter was calculated from the average diameter of all the droplet sizes as shown in Equation (2)

$$d_{av} = \frac{\sum n_i d_i}{\sum n_i} \qquad (2)$$

For this kinetic studies, a kinetic model proposed by Olivera S. Stamenkovic who studied on kinetics of the transesterification reaction under the room temperature was utilized [101]. Using this assumption of the reaction system, the rate constants for the forward and backward reactions were calculated and compared between the two conventional mixers and the static mixer.

According to this work, methanol disperses in oil heterogeneously in the early period of the reaction and the reaction is influenced by a diffusion law speed. Thus the

reaction kinetics can be expressed by Equation (3).

$$-r_A = -\frac{dC_A}{d_t} = k_c a(C_A - C_{A,S}) \quad (3)$$

Where r_A is the reaction rate, k_c is the mass transfer coefficient, a is the specific surface area of the oil and methanol interface, C_A and $C_{A,s}$ represent the triglyceride (TG) concentrations in the oil phase and in the interfacial area, and t is the reaction time.

The specific interfacial area, a, was calculated from the Sauter-mean drop diameter, d_{32}, and the holdup of alcoholic phase, φ:

$$a = \frac{6\varphi}{d_{32}} \quad (4)$$

Since a chemical reaction is much faster in the fast chemical kinetic controlled stage than in the slow mass transfer controlled stage, we can assume that $C_{A,S} \to 0$ and TG concentration is related to the conversion degree of TG (x_A) as shown in Equation (5). Then Equation (3) can be transformed into Equation (6) as follows.

$$C_A = C_{A0}(1 - x_A) \quad (5)$$

$$\frac{dx_A}{d_t} = k_c a(1 - x_A) \quad (6)$$

Considering that the equation is a linear equation, the value of the mass transfer coefficient can be calculated by Equation (7) as the slope of Equation (6).

$$\int_0^{x_A} \frac{dx_A}{a(1-x_A)} = k_c t \quad (7)$$

3.2.2 Chemical-controlled stage

After the first stage, methanol droplets become smaller and the surface area of the oil and methanol interface increases. The reaction becomes pseudo-homogenous and kinetic controlled. Then the mass transfer becomes faster than the chemical reaction. The reaction rate in this stage is shown by Equation (8).

$$-r_A = -\frac{dC_A}{dt} = kc_A^2 \quad (8)$$

where, k is the reaction rate constant for the irreversible pseudo-second-order reaction. Then we utilize x_A in place of C_A as follows;

$$-\frac{dx_A}{dt} = kC_{A0}(1 - x_A)^2 \quad (9)$$

After integrating Equation (9), the result is as follows;

$$\frac{1}{1-x_A} = kC_{A0}t + C_1 \quad (10)$$

C_1 represents the linear interception and the reaction rate can be calculated from the linear relationship between $\frac{1}{1-X_A}$ and the reaction time.

3.2.3 Equilibrium stage

It is assumed that when the reaction is near the equilibrium stage, the forward and backward reactions follow the second-order overall kinetics. Then the reaction rate in this phase can be expressed by Equation (10).

$$-r_A = -\frac{dC_A}{dt} = \vec{k}C_A C_B - \overleftarrow{k}C_R C_S \quad (11)$$

where, $\vec{k}$ and $\overleftarrow{k}$ are the reaction rate constants for forward and backward reactions. C_B, C_R and C_S are concentrations of methanol, FAME, and glycerol, respectively. The initial concentration of methanol is C_{B0} while those for FAME and glycerol are zero. Then $C_B = C_{B0} - 3C_{A0}x_A$, $C_R = 3C_{A0}x_A$ and $C_S = C_{A0}x_A$. Therefore, this equation can be expressed as follows;

$$\frac{dx_A}{dt} = \vec{k}(1 - x_A)(C_{B0} - 3C_{A0}x_A) - 3\overleftarrow{k}C_{A0}x_A^2 \quad (12)$$

Then,

$$\frac{dx_A}{3M(1-K)x_A^2 - (1+3M)x_A + 1} = \vec{k}C_{B0}dt \quad (13)$$

where, $K = \frac{\overleftarrow{k}}{\vec{k}}$, and $M = \frac{C_{A0}}{C_{B0}}$

When Equation (11) is integrated, the result is shown as follows;

$$\ln\frac{[6M(1-K)x_A - (1+3M) - \sqrt{-\Delta}]}{[6M(1-K)x_A - (1+3M) + \sqrt{-\Delta}]} = f(x_A) = \vec{k}C_{B0}t\sqrt{-\Delta} + C_2 \quad (14)$$

where, $\Delta = 4 \cdot 3M(1-K) - (1+3M)^2 < 0$, then we get the value of K as,

$$K = \frac{3Mx_{Ae}^2 - (1+3M)x_{Ae} + 1}{3Mx_{Ae}^2} \quad (15)$$

3.2.4 Reaction order calculation

To find the reaction order suitable for this research results, Equation (16) is utilized to find the *n* or the reaction order and find the expected conversion.

$$X = 1 - [1 - (1 - n)C_0{}^{n-1}kt]^{\frac{1}{1-n}} \quad (16)$$

where *X* is triglyceride conversion; C_0 is the initial concentration of triglyceride, *k* is the reaction rate constant, and *t* is the reaction time.

The calculation is done by assuming *n* to get the minimum coefficient of determination (R^2) between actual *X* and calculated *X*

3.2.5 Influence of surface area on reaction rate coefficient

With the droplet size results from section 3.2.1 and the reaction rate constant from section 3.2.2, we evaluated this relationship by comparing the difference of the enhanced surface area and the enhanced reaction rate constants between the two mixers or the magnification factor. The transesterification reaction is assumed to be a non-homogeneous reaction since there are two phases of oil and methanol formed during the reaction.

Then the surface area is assumed to have the dominant effect on the reaction rate constant since the reaction proceeds on the surface of methanol bubbles. If the surface area changed, the global reaction rate should follow this change. The surface area should also directly affects the reaction rate constant and the magnification factor of the two mixers should remain constant at any reaction time. The results are shown and compared in the next section 3.3.5.

3.3 Results and Discussion

3.3.1 Diffusion-controlled stage

The Sauter-mean and the mean droplet diameter of methanol in oil for both mixing methods are compared at 0.5, 3, 10, and 30 minutes of the reaction time as shown in Table 3.1, and droplet size distributions are compared in Figure 3.1. Also the particle size images are shown in Figures 3.2 and 3.3.

Table 3.1 Results of Sauter-mean drop diameter (d_{32}) and mean diameter (d_{av})

	STATIC MIXER		CONVENTIONAL MIXER	
Time (min)	d_{32} (μm)	d_{av} (μm)	d_{32} (μm)	d_{av} (μm)
0.5	4.36	3.74	22.64	16.60
3	4.22	3.63	16.82	10.86
10	7.38	4.80	17.66	11.14
30	9.72	6.49	15.17	9.97

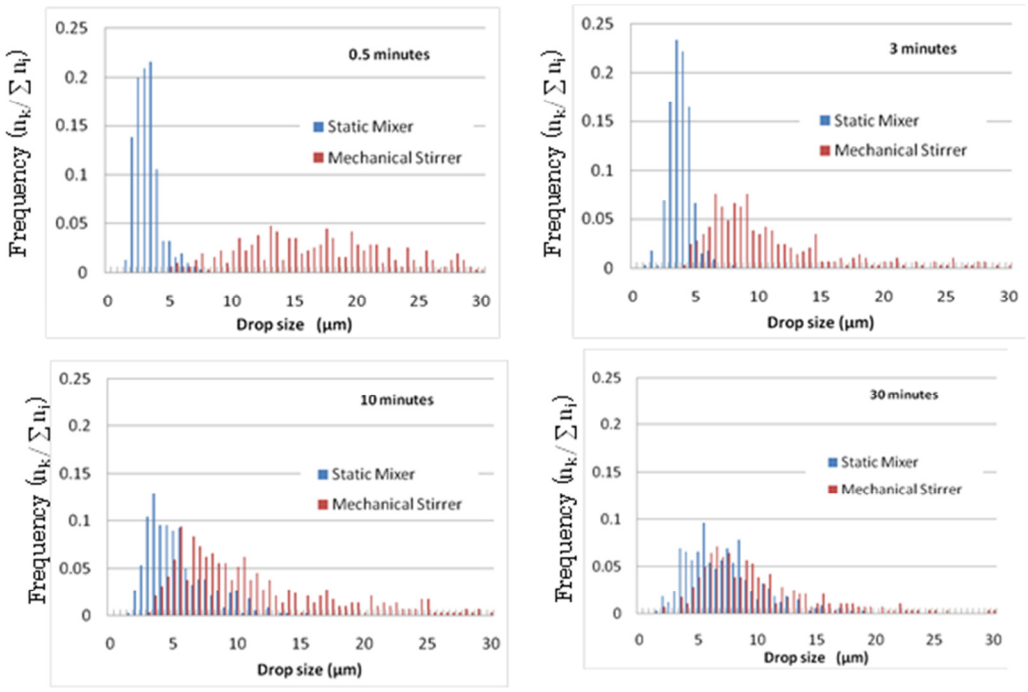

Fig. 3.1 Droplet size distribution

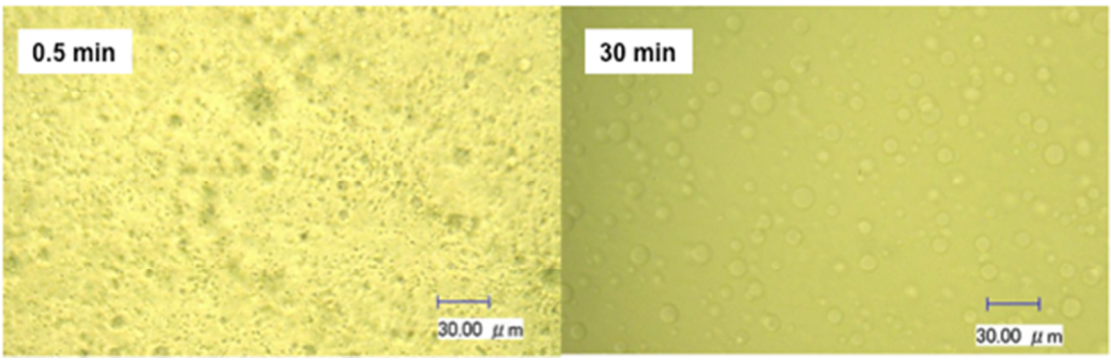

Fig. 3.2 Methanol droplet images for the static mixer at the reaction time of 0.5 and 30 minutes

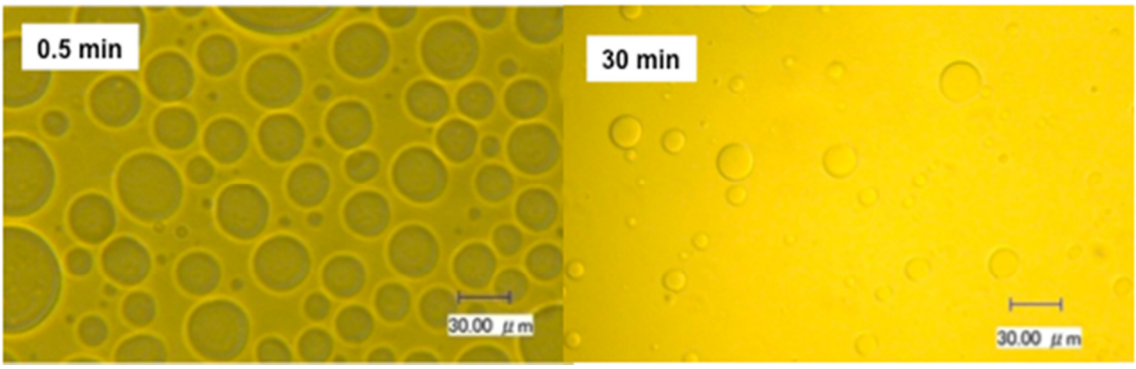

Fig. 3.3 Methanol droplet images for the mechanical mixer at the reaction time of 0.5 and 30 minutes

Figure 3.1 show that the static mixer generates smaller droplet sizes than the mechanical mixer in the early stage of the reaction. In the case of the static mixer, about 90% of droplets are less than 5 μm. On the other hand, in the case of the mechanical mixer, there is a significant change in droplet size distribution between 0.5 minutes and 3 minutes of the reaction but the change became smaller after that. It can be said that the static mixer can generate fine particles of methanol in oil at the start of the reaction. At 0.5 minutes, immediately after the reaction starts, the droplet size for the mechanical mixer is 5 times larger than that for the static mixer.

As time passes, the droplet size for the mechanical mixer becomes smaller while that for the static mixer becomes larger. At 30 minutes of the reaction, the droplet size for the mechanical mixer became smaller but it cannot be said that droplets dispersed uniformly as shown in Figure 3.3. The droplet size after 30 minutes of the reaction time for the mechanical mixer is much larger, less uniform, and various sizes distribution can be seen when compared with the static mixer shown in Figure 3.2. Therefore, the static mixer with more uniform droplet size distribution can promote the reaction.

In the case of the static mixer, it can be said that a high yield of FAME can be immediately obtained just after the reagents are mixed and the initial mass transfer stage can be ignored. On the other hand, as can be seen from the Sauter-mean droplet diameter at 30 minutes after the start of the reaction shown in Table 3.1, the difference of droplet sizes for both mixing methods became less significant because the droplet diameter gradually increases due to the coalesce of droplets during this time passage in the case of the static mixer.

From Equation (6), the mass transfer coefficient (k_c) of the initial mass transfer stage for each reaction condition is calculated and shown in Table 3.2. From the droplet size distribution result, we are able to confirm that the static mixer has a potential to significantly increase the interface surface area between oil and methanol compared with the mechanical mixer. Table 3.2 shows that mass transfer coefficients for the static mixer are much larger than those of the mechanical mixer.

Table 3.2 Mass transfer coefficient $k_c \times 10^5$ (m/min)

METHANOL (MOLAR RATIO TO OIL)	KOH (%WT)	STATIC MIXER	MECHANICAL MIXER
6	1.8	1.867	0.655
	1.2	0.597	0.446
	0.6	0.270	0.225
4.3	1.8	1.268	0.416
	1.2	0.276	0.230
	0.6	0.097	0.063

3.3.2 Chemical-controlled stage

When droplets of methanol are small enough, the reaction is considered to be pseudo-homogenous. Small amount of FAME began to form and the forward reaction rate of the rate-determining phase is larger than the backward reaction rate due to the excess amount of methanol.

From Equation (9), the value of the reaction rate constant (k) for each condition is calculated and shown in Table 3.3, Figure 3.4 and 3.5.

Table 3.3 Reaction rate constant, k (ml/g·min)

METHANOL (MOLAR RATIO TO OIL)	KOH (%WT)	STATIC MIXER	MECHANICAL MIXER
6	1.8	1.576	0.967
	1.2	0.996	0.549
	0.6	0.361	0.231
4.3	1.8	1.357	0.446
	1.2	0.296	0.353
	0.6	0.104	0.068

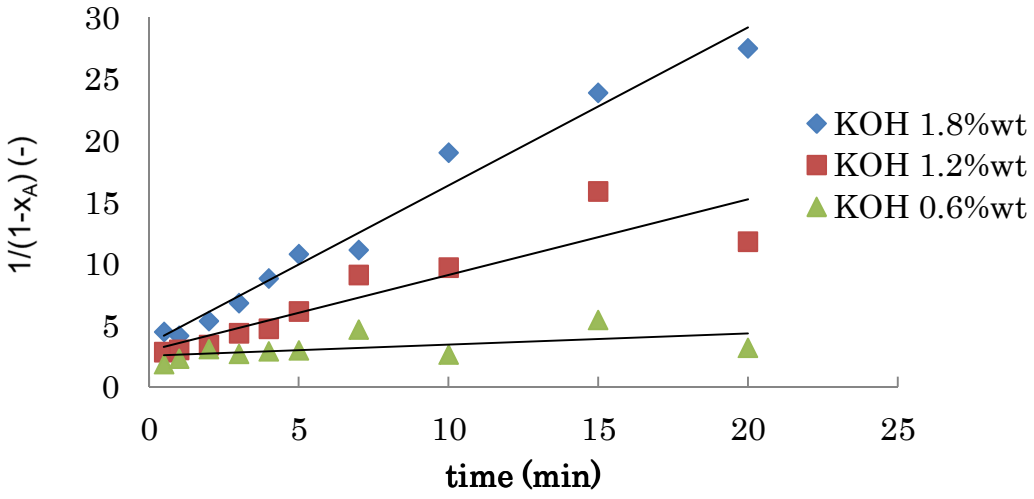

Fig. 3.4 Kinetic controlled regime for the static mixer

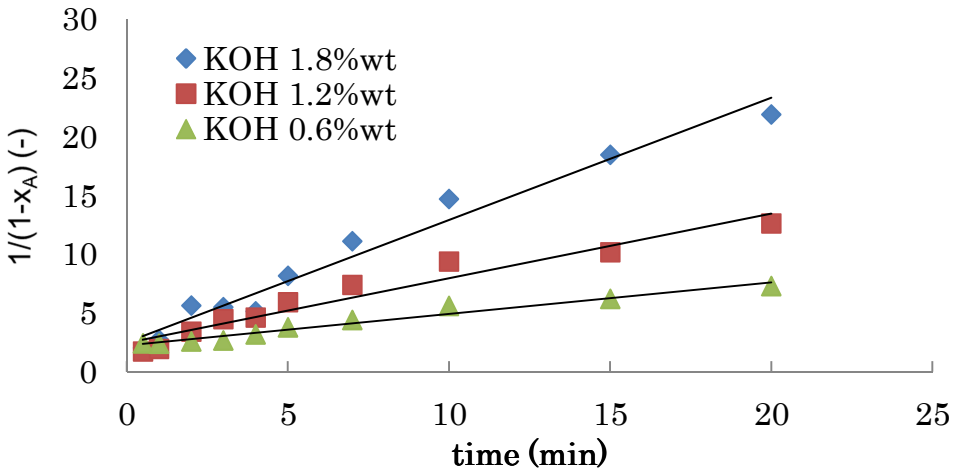

Fig. 3.5 Kinetic controlled regime for the mechanical mixer

The reaction rate constants for the static mixer are larger than those of the mechanical mixer, since the droplet size distribution of the mechanical mixer has a smaller change compared with the static mixer in the first stage of the reaction as shown in Figure 3.1. The effect of the agitation intensity on the reaction rate is limited. This means that even the agitation intensity is increased, it will not affect the reaction rate or decrease the particle sizes furthermore. However, since the interface surface area between oil and methanol increased rapidly by the static mixer, it has significant impact on the reaction rate. As in the kinetic-controlled stage is the slowest phase that controlled the whole reaction and started when raw materials begin to react with each other. So the increased surface area enabled raw materials to collide and react more, which accelerated the reaction itself.

3.3.3 Equilibrium stage

After passing a sufficient reaction time, the reaction becomes close to the

equilibrium with the substantial backward reaction as a secondary reaction. In the last equilibrium stage, the values of $\vec{k}$ and $\overleftarrow{k}$ for the static mixer and the mechanical mixer are determined by Equation (13) and shown in Tables 3.4 and 3.5 respectively. The values of $\vec{k}$ and $\overleftarrow{k}$ for the static mixer is much smaller than those for the mechanical mixer, indicating that the reaction already reached the equilibrium state after 30 minutes. From these results, it can be said that it is possible to complete the transesterification reaction for FAME production in a shorter reaction time by employing the static mixing.

Table 3.4 $\vec{k}$ and $\overleftarrow{k}$ values for the static mixer

Methanol (molar ratio to oil)	KOH (%wt)	$\vec{k} \times 10^{-2}$ (m^3mol^{-1} min^{-1})	$\overleftarrow{k} \times 10^{-3}$ (m^3mol^{-1} min^{-1})
6	1.8	0.413	0.039
	1.2	1.098	0.368
	0.6	1.143	0.787
4.3	1.8	1.892	0.179
	1.2	2.130	0.713
	0.6	2.447	1.092

Table 3.5 $\vec{k}$ and $\overleftarrow{k}$ values for the mechanical stirrer

Methanol (molar ratio to oil)	KOH (%wt)	$\vec{k} \times 10^{-2}$ (m^3mol^{-1} min^{-1})	$\overleftarrow{k} \times 10^{-3}$ (m^3mol^{-1} min^{-1})
6	1.8	0.660	0.116
	1.2	2.277	0.746
	0.6	5.991	4.082
4.3	1.8	3.456	0.326
	1.2	3.975	0.996
	0.6	3.978	3.002

3.3.4 Reaction order analysis

From Equation (16) after assuming minimum reaction order n = 2.4 into the equation, we get the calculated reaction rate constant k = 2.876. Figure 3.6 shows the reaction model plotted from the new reaction order and the parity plot comparing the calculated and measured conversion is presented in Figure 3.7.

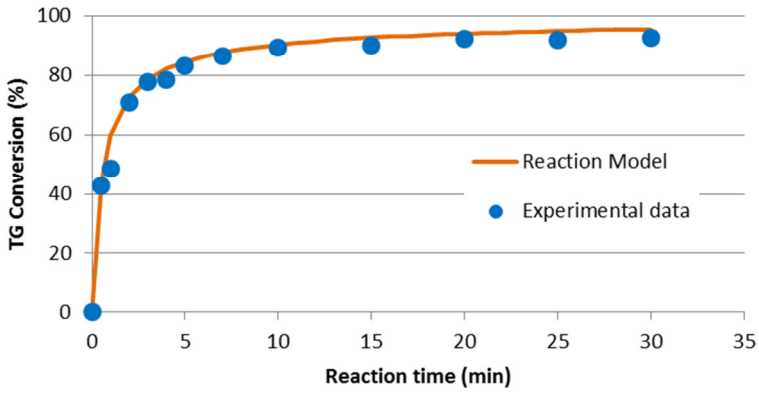

Fig. 3.6 Reaction model from the new calculated reaction order

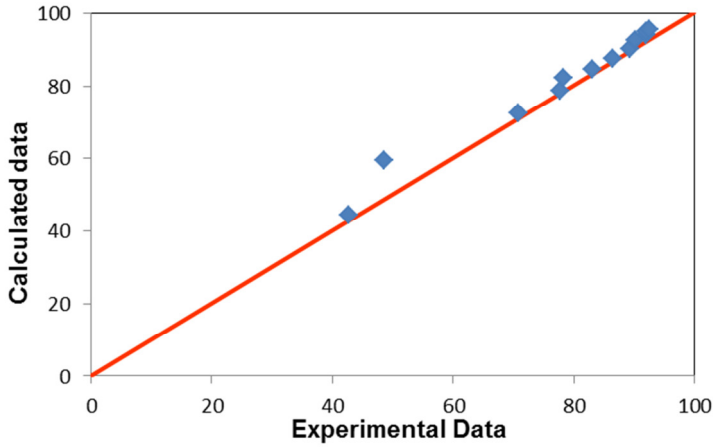

Fig. 3.7 Parity plot comparing the calculated and measured conversion

From the calculated data, it is shown that the new reaction order which is suitable for our reaction conditions is 2.4 which has the optimum accuracy and is different from the other researchers who assumed the reaction order as pseudo-first-order reaction, second-order reaction, pseudo-second-order reaction, or up until fourth-order reaction. This indicated that even the transesterification should be the first-order reaction which has the constant reaction rate since it has only two reactants, the reaction rate changed according to time change and the reaction rate constant becomes different at each point of time which causes the reaction order to be higher than the first-order.

3.3.5 Influence of surface area on reaction rate coefficient

According to Table 3.1 which indicated the diameter of the methanol molecules in the reaction, the specific surface area were calculated from this diameter and shown in Table 3.6 below. The magnification factor of the specific area is shown in Figure 3.8

Table 3.6 Specific surface area comparison of static mixer and conventional mixer

	STATIC MIXER		CONVENTIONAL MIXER	
Time (min)	d_{32} (µm)	Specific surface area (m^2/m^3)	d_{32} (µm)	Specific surface area (m^2/m^3)
0.5	4.36	7,013,441	22.64	1,349,879
3	4.22	7,238,366	16.82	1,817,208
10	7.38	4,141,336	17.66	1,730,374
30	9.72	3,142,723	15.17	2,014,800

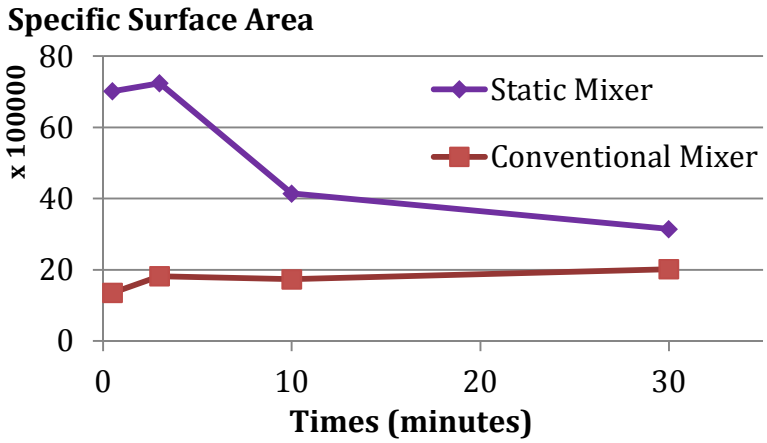

Figure 3.8 Specific surface areas for static mixer and conventional mixer

Also from Table 3.3 which compared the reaction rate constant for each mixer, we calculate the reaction rate constant at each point of time and show the results in Table 3.7 for the static mixer, and Table 3.8 shows the result of the conventional mixer. Then the graph or each catalyst concentration is plotted and shown in Figures 3.9 to 3.11 to calculate the magnification factor.

Table 3.7 Reaction rate constant at specific time for the static mixer at each catalyst concentration

TIME (MIN)	CATALYST CONCENTRATION		
	KOH 1.8%	KOH 1.2%	KOH 0.6%
0.5	3.872	2.199	1.076
3	0.230	0.182	0.056
10	0.125	0.056	0.012
30	0.0169	0.0004	0.2440

Table 3.8 Reaction rate constant at specific time for the conventional mixer at each catalyst concentration

TIME (MIN)	CATALYST CONCENTRATION		
	KOH 1.8%	KOH 1.2%	KOH 0.6%
0.5	1.513	1.111	1.150
3	0.151	0.113	0.153
10	0.063	0.042	0.044
30	0.018	0.012	0.030

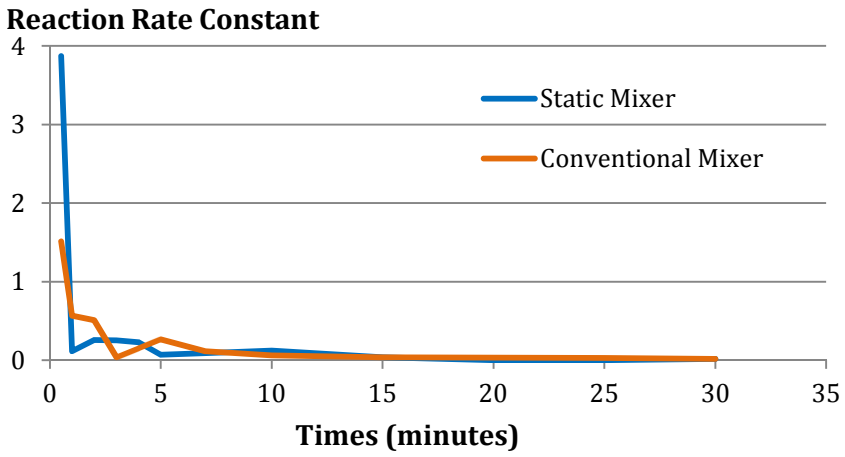

Figure 3.9 Reaction rate constant for both mixers at 1.8% catalyst concentration

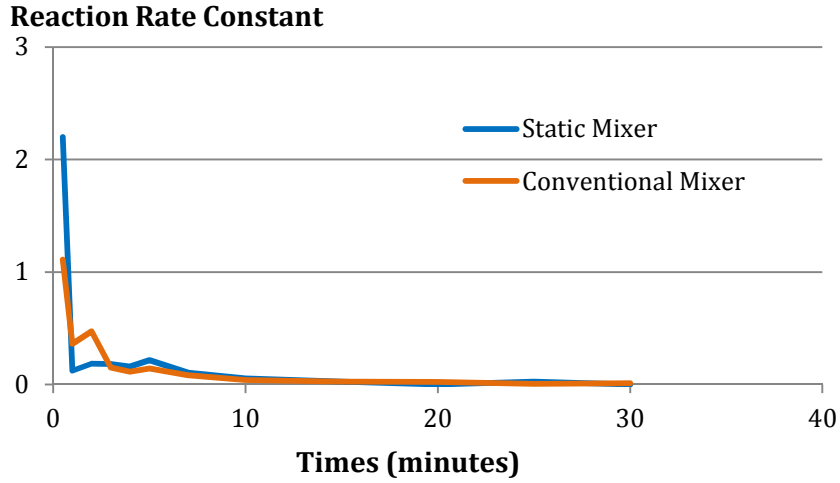

Figure 3.10 Reaction rate constant for both mixers at 1.2% catalyst concentration

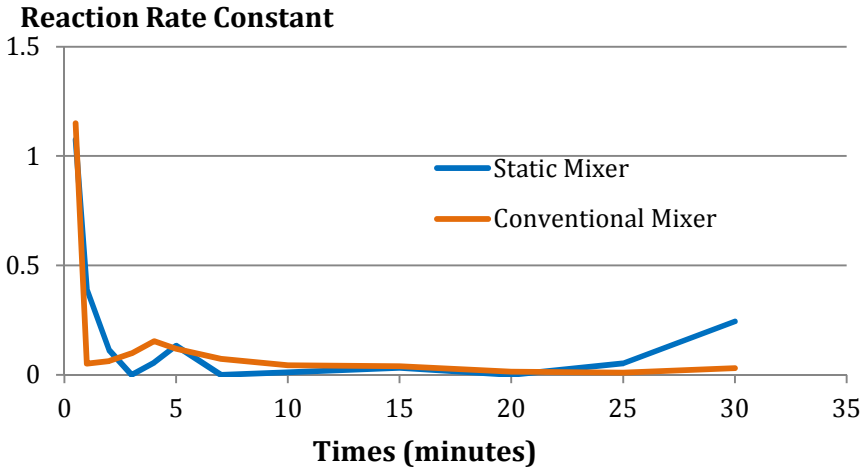

Figure 3.11 Reaction rate constant for both mixers at 0.6% catalyst concentration

From Figures 3.9-3.11, we can see that there is better reaction rate enhancement if higher concentration of the catalyst was utilized. With the assumption that higher catalyst concentration might promote the reaction rate enhancement by the static mixer, the graph shown in Figures 3.9 to 3.11 was compared to investigate the difference of magnification factor between these two factors in Table 3.9.

Table 3.9 Magnification factor comparison of the specific surface area and reaction rate constant

TIME (MIN)	MAGNIFICATION FACTOR			
	Specific surface area	Reaction rate constant		
		KOH 1.8%	KOH 1.2%	KOH 0.6%
0.5	5.196	2.559	1.978	0.936
3	3.983	1.516	1.417	0.364
10	2.393	1.975	1.329	0.265
30	1.560	0.924	0.039	0.084

From Table 3.9, it is shown that the magnification of the surface area is much higher than the magnification of the reaction rate constant at the same point of time and the magnification factor decreased as time passed. The cause of these differences and the decrease of magnification factors are the change of the droplet size or the surface area. For the conventional mixer, the specific surface area remained constant throughout the reaction but the specific surface area for the static mixer decreases as time passes which results in the decrease of the magnification factor and the reaction rate constant.

From section 3.2.5, we assumed that the effect of the surface area on the reaction rate constant is dominant, so the magnification factor of the surface area and the reaction rate constant of both mixers should be the same, but the results showed a large difference which means that the surface area has limitation effect on the reaction rate constant even it is dominant. There might be other factors also having the effect on the time dependent change of the reaction rate constant and has the negative effect to reduce the function of the static mixer. For example, the assumption in this calculation is based on that on the bubbles surface, the concentration of methanol is the same. If the size of the bubbles become larger, the concentration or density of methanol might decrease and causes the negative effect that decreases the reaction rate constant.

3.4 Conclusion

For possible acceleration of the transesterification reaction in biodiesel production, a static mixer was compared with a mechanical mixer. More fine, uniform, and smaller methanol droplets can be generated in raw oil with the use of the static mixer. This resulted in the increase of the interface surface area between raw oil and methanol and greater yield of FAME product in the initial stage of the reaction. The static mixer demonstrated much larger value of the reaction rate than the mechanical mixer which means that the static mixer can accelerate the transesterification reaction significantly. However, the static mixer gave effects on the reaction only in the initial stage of the reaction.

The reaction order suitable for this results explanation is in higher order than the ones proposed by other researchers, which means that the reaction mechanism changed following the time change since the catalyst also promoted the reaction rate proportionally. The study of the influence of the surface area on the reaction rate constant also showed that the surface area has limited effect on the reaction rate constant even though it is the dominant parameter. There might be other factors which also have the negative effects on the reaction rate enhancement.

In this chapter, the reaction enhancement effect of the static mixer under the alkali-catalyzed transesterification reaction is investigated, but in order to study the feasibility of the static mixer, the enhancement by this static mixer will be investigated further with the other process utilizing acid catalyst and heterogeneous catalyst which will be presented in the next chapter 4 and chapter 5, respectively.

Chapter 4

Mechanism studies on reaction enhancement of pretreatment process with acid catalyst by static mixer

4.1 Introduction

Even though the transesterification reaction in biodiesel production can be promoted by many types of catalysts, the acid catalyzed transesterification process is not very popular compared with the alkaline catalyzed process due to the slower reaction. Also, the acid catalyst has a lower activity and requires higher reaction temperature than for the alkaline catalyzed reaction. Moreover, a longer reaction time makes the process impractical and uneconomical. On the other hand, the advantage of using an acid catalyzed transesterification is the tolerance towards the presence of high free fatty acids or FFAs in the feedstock. In fact, acid catalysts can produce biodiesel from low cost feedstock with FFA greater than 1% [16, 102-105].

Due to the slower reaction by the acid catalyst, biodiesel production from feedstock with high free fatty acids normally requires two steps; first is to use an acid catalyst for the esterification reaction to reduce the amount of free fatty acids in the feedstock and then followed by an alkaline catalyst for the transesterification reaction to perform a two-step biodiesel production process. The esterification reaction is presented in Equation (1), which is the reaction between the free fatty acid in the oil with methanol and the products are water and Methyl Ester which is the same product as the transesterification reaction.

$$\underset{\text{(Free Fatty Acid)}}{RCOOH} + \underset{\text{(Methanol)}}{CH_3OH} \longrightarrow \underset{\text{(Methyl ester)}}{RCOOCH_3} + H_2O \quad (1)$$

Up to now, the conventional mechanical mixing method is commonly utilized for both esterification and transesterification reactions. In this chapter, the conventional mixing method is utilized for esterification first, in order to investigate reaction parameters such as the molar ratio of methanol to oil, the catalyst

concentration, the reaction temperature and the reaction time and also their effects on the reduction of the acid value.

Then the results are compared with the result using the static mixer to investigate the effect of the mixing method on the acid value reduction. The previous chapters proved that the mixing intensity of the static mixer has strong influence on the transesterification reaction and able to increase the reaction rate. Therefore, in this chapter, we would like to test that whether the fine small droplets of methanol created by the static mixer will lead to better performance of the acid reduction compare with the conventional mixing method.

4.2 Experimental procedures and calculation

In this chapter, Jatropha oil was utilized as raw material. The oil was obtained from the Kasetsart University, Thailand. For the esterification reaction, 99.8% solution of methanol, and 98% solution of H_2SO_4 acid were purchased from Wako Pure Chemicals Industries Ltd, Japan. For the titration to check the acid value, 0.1mol/L potassium hydroxide ethanolic solution, diethyl ether super dehydrated solution and 99.5% solution of ethanol were also purchased from Wako Pure Chemicals Industries Ltd, Japan and 10g/L phenolphthalein solution was purchased from Kanto Chemical co. Inc, Japan.

4.2.1 Acid catalyst esterification reaction

To avoid the experimental errors, the Jatropha oil must be free of water and other impurities. Initially, the oil was heated up to 105^0C for 1h to remove water by evaporation. Then the acid catalyzed pretreatment was conducted by the conventional mixing method.

The experiments were performed at different operating conditions including five molar ratios of methanol to oil, five different catalyst concentrations, and three different reaction temperatures as shown in Table 4.1.

Table 4.1 Experimental conditions

MOLAR RATIO OF METHANOL TO OIL	H_2SO_4 (%WT)	REACTION TEMPERATURES
1.1 : 1	0.5	20^0C
0.9 : 1	0.75	40^0C
0.8 : 1	1	60^0C
0.7 : 1	1.25	
0.6 : 1	1.5	

A stirring apparatus shown in Figure 4.1, which is the same one used for the transeseterification reaction in Chapter 2. Required amount of methanol and H_2SO_4 acid were mixed separately and then added to the preheated oil. The mixed solution was stirred with NISSIN company`s SW-RS7770 magnetic stirrer at the speed of 600 rpm constantly and a water bath with the maximum capacity of 3L was utilized for heating continuously for 30 minutes.

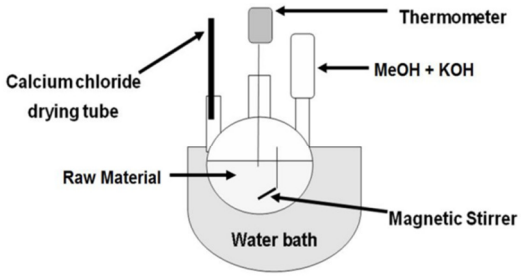

Fig. 4.1 Conventional mixing apparatus

After the reaction, the reaction mixture was then poured to a separation funnel and was allowed to settle overnight. The excess methanol and water are in the top layer and are removed. The oil with lower content of FFA settled at the bottom layer. The bottom layer of oil was collected and the titration method was utilized to check the acid value of the treated oil

4.2.2 Acid value analysis

The acid value (also known as neutralization number or acid number) is the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize one gram of chemical substance. The acid number is a measure of the amount of carboxylic acid groups in a chemical compound, such as a fatty acid, or in a mixture of compounds. A known amount of sample was dissolved in organic solvent and was titrated with a solution of potassium hydroxide with known concentration (0.1M) and with phenolphthalein as a color indicator.

The acid number is used to quantify the amount of acid present. It is the quantity of base, expressed in milligrams of potassium hydroxide that is required to neutralize the acidic constituents in 1 g of sample. The acid value of the reaction mixture after the acid catalyzed pretreatment was determined by the acid base titration technique (DIN EN14104). The acid value was reported as shown in equation (2)

$$AN = V \times C \times \frac{56.1}{W_{oil}} \qquad (2)$$

Where,

AN = Acid number

V = Volume (ml) of standard volumetric potassium hydroxide used

C = Exact concentration (moles per L) of the standard volumetric potassium hydroxide used

56.1 = Molecular weight of potassium hydroxide

W_{oil} = Mass (g) of the test sample

4.2.3 Utilization of static mixer for acid value reduction

Instead of the same static mixer utilized in chapter 2, the experiment was conducted by using an emulsification pump purchased from SPG Technology Company. The emulsification pump is shown in Figure 4.2 and the mechanism of this pump is that it contained a filter which is able to disperse a small droplet of methanol into the oil phase on the other size of the filter as shown in Figure 4.3.

Fig. 4.2 Emulsification pump apparatus

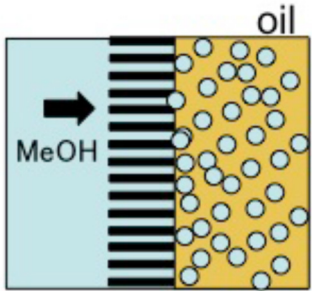

Fig. 4.3 Emulsification pump mechanism

The mechanism of this emulsification pump is the same as the static mixer in the point of creating small droplets of methanol. Thus, yield between these two mixers was tested and compared by transesterification reaction as shown in Figure 4.4 to check the possibility of utilizing the emulsification pump instead of the static mixer as a smaller lab scale apparatus. This result showed that, the product yield of the static mixer and the emulsification pump is similar. Therefore, it is possible to use the emulsification pump as a representative for the static mixer.

Required amount of oil were put into the small bottle of the pump, then the mixture of methanol and H_2SO_4 acid were mixed to the oil by the injector connected to the pump. This will form an emulsion solution, where small droplets of methanol-H_2SO_4 were uniformly dispersed in the oil. The injector was pumped continuously for 1 hour to complete the reaction time.

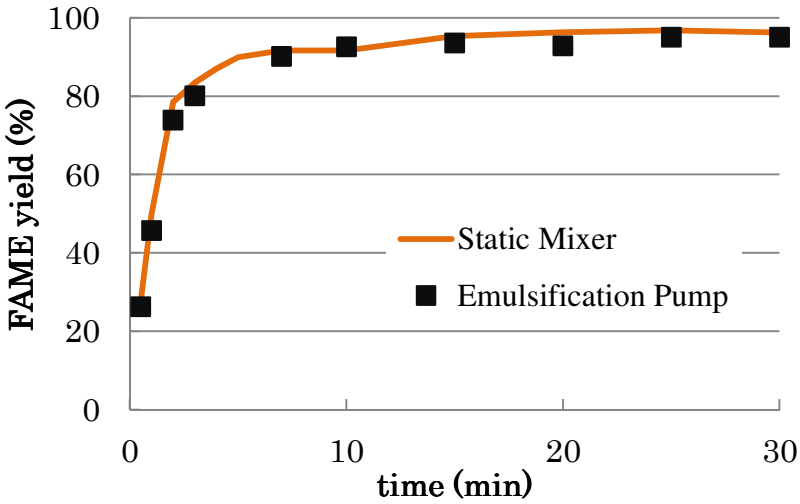

Fig. 4.4 Comparison of the actual static mixer and the emulsification pump

4.2.4 Kinetic calculations

There are some studies on the esterification reaction that focusing on the kinetic study since it has been only recently that the kinetics of the esterification reaction received attention [106-108]. Kocsisová et al. was working on the concentrated fatty

acid at the atmospheric pressure and a continuous feed of methanol to the system [109]. The reactor temperature was set at 60 °C above the boiling point of the alcohol, thus effectively removing the water formed during the reaction, and consequently obtaining higher conversion values. Under these conditions, a first-order reaction was found.

Nevertheless, in the figures shown in the work of Kocsisová et al., it is indicated that even though a pseudo first order model reasonably adjusts the experimental results, the model does not fully represent the real system. Dussadee et al. studied kinetic of myristic acid esterification with methanol in the presence of triglycerides over sulfated zirconia prepared by solvent-free method as a catalyst and reported a pseudo-homogeneous second order reversible model [110]. There is also several reports on the kinetic of FFA esterification in presence of triglyceride using different heterogeneous acid catalysts and a pseudo-homogeneous second order reversible (PH) model was realizable and applied for several esterification reactions of FFA in the presence of triglyceride.

The kinetic model used in this chapter relied on the following assumptions:

(a) The esterification reaction was a reversible heterogeneous process the rate of which under the operating conditions used was controlled by the chemical reaction.

(b) The rate of the non-catalyzed reaction was negligible relative to the catalyzed reaction.

(c) The chemical reaction occurred in the oil phase.

(d) The methanol/oil mole ratio used was high enough for the methanol concentration to remain constant throughout the process.

Under these conditions, the reaction was assumed to be pseudo-homogeneous, first-order in the forward direction and second-order in the backward direction, and hence to conform to the following kinetic law:

$$-\frac{\mathrm{d[FFA]}}{\mathrm{dt}} = \mathrm{K_1[FFA]} - \mathrm{K_2[FAME][water]} \qquad (3)$$

where [FFA] denotes the concentration of FFA in mg KOH/g oil (i.e. the acid value); [FAME] and [water] are the concentrations of FAME and water, respectively, formed during the reaction, both also referred to 1 g of oil; and K_1 and K_2 are the kinetic constants for the forward and backward reactions, respectively. If [FAME] and [water] are assumed to be zero at the start (t = 0), and FFA = FFA_0 - E (E being the acidity removed),

then, according to Carberry [111], we get Equation (4) as follow;

$$-\frac{\mathrm{dE}}{\mathrm{dt}} = \mathrm{K_1(FFA_0 - E)} - \mathrm{K_2}E^2 \qquad (4)$$

where FFA_0 is the initial concentration of FFA.

Integration of Equation (4) yields

$$2 \cdot K_2 \cdot \propto \cdot t = \ln \frac{[FFA_0 + E \cdot (\beta - \frac{1}{2})]}{[FFA_0 - E \cdot (\beta + \frac{1}{2})]} \quad (5)$$

Where;

$$\propto = \sqrt{\left(\frac{K^2}{4}\right) + K \cdot FFA_0} \quad (6)$$

$$\beta = \frac{\alpha}{K} \qquad \text{and} \qquad K = \frac{K_1}{K_2} \quad (7)$$

K_1 and K_2 were determined by trial and error, using variable β values until a plot of the right-hand side of Equation (5) consisting of a straight line with a negligible intercept was obtained.

The influence of the temperature on the specific reaction rate was determined by fitting K_1 and K_2 to the Arrhenius equation,

$$K = A \cdot \exp[\frac{-\Delta E}{RT}] \quad (8)$$

using plots of ln K as a function of the reciprocal temperature as shown in Equation (9).

$$\ln K = \ln A - \frac{\Delta E}{RT} \quad (9)$$

Where both the frequency factor A, and the activation energy ΔE (kJ/mol), were obtained by nonlinear regression and R is the molar gas constant (0.00813 kJ/(mol·k).

4.3 Results and Discussion

4.3.1 Effect of the mixing method on the reduction of the acid value

In order to compare the result of the two mixing methods, the acid value was calculated by varying the concentrations of methanol and catalyst and the result of the acid value for both mixers are shown in Figure 4.5 for the conventional mixer and Figure 4.6 for the static mixer (emulsification pump).

From these figures, it can be observed that the increase of the catalyst concentration could reduce the acid value because the ester formation rate increased along with the catalyst concentration. However, in the case of the conventional mixer, at a lower catalyst concentration of 0.5%w/w, the acid value could not be reduced below 2mgKOH/1g oil even when the methanol to oil molar ratio was 1:1, while the static mixer showed better catalyst activity at the same catalyst concentration so that the acid value could be reduced nearly to 2mgKOH/1g oil when the methanol to oil

molar ratio was 1:1.

From Figure 4.6, it is shown that 0.75% catalyst concentration was sufficient to reduce the acid value less than 2mgKOH/1goil for the static mixer case with only 0.8:1 methanol ratio. And for both mixers, when the catalyst amount was 1.25% and 1.5%, the results were almost the same, showing that there is an upper limit of the catalyst concentration above which there will be no significant differences in acid value reduction. From the results, the optimum catalyst concentration for the conventional mixing method should be 1.25%, and 1% catalyst concentration should be the optimum value for the static mixing method.

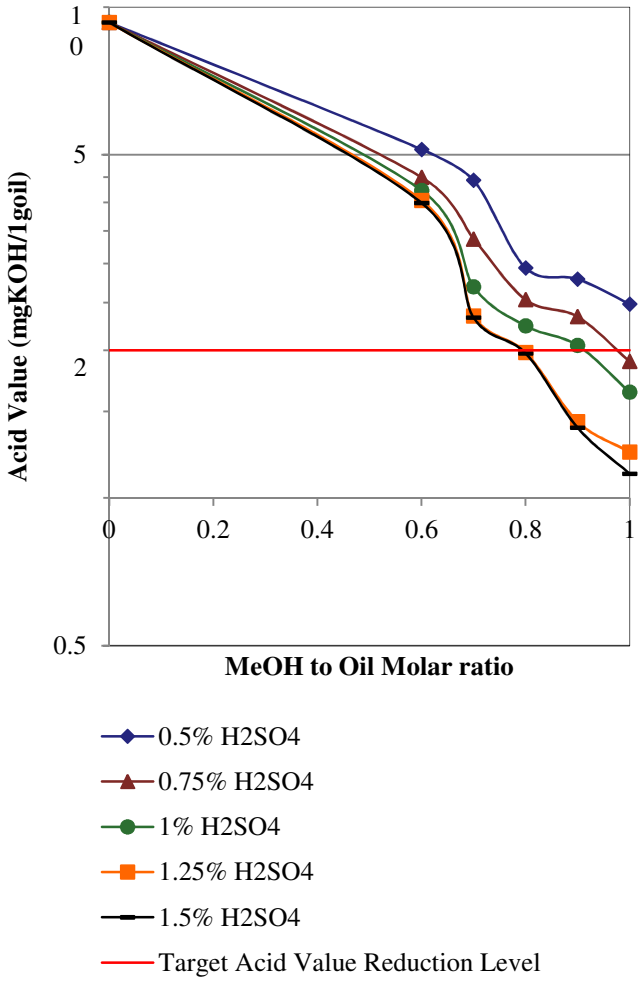

Fig. 4.5 The effect of the catalyst concentration and the methanol to oil molar ratio on the reduction of the acid value by conventional mixing

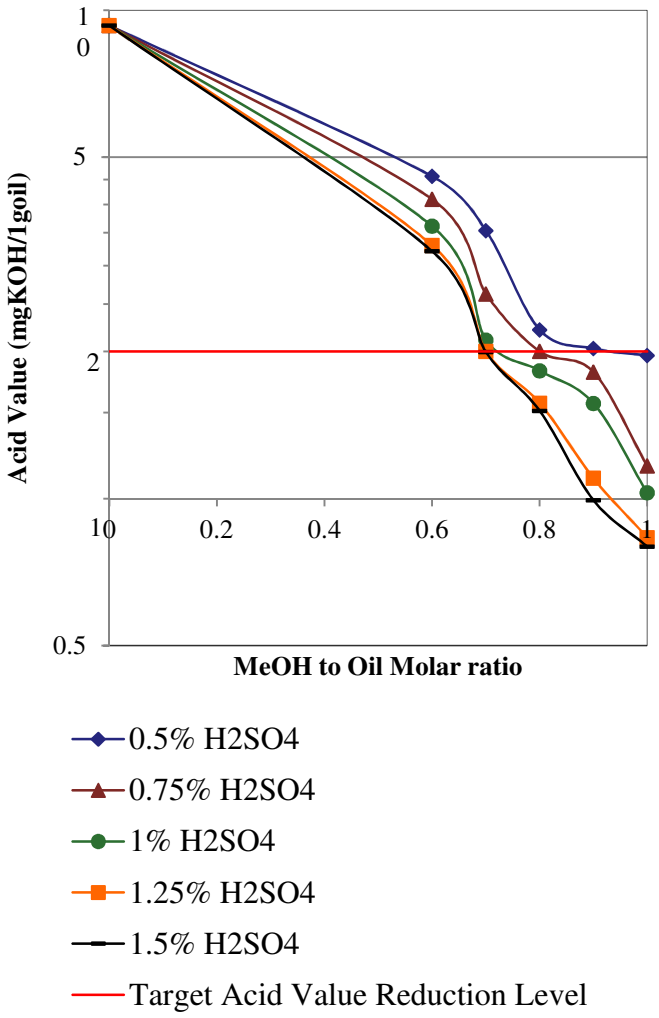

Fig. 4.6 The effect of the catalyst concentration and the methanol to oil molar ratio on the reduction of the acid value by the static mixer

4.3.2 Reaction kinetics

Based on Equation (5), Figure 4.7 and 4.8 shows the fitting of the experimental data obtained at the methanol/oil molar ratio of 1:1, the catalyst concentration of 0.75% and the temperature of 60^0C. Similar plots were constructed under all other experimental conditions. Then the parity plot to compare the calculated data to the experimental data are shown is Figure 4.9 and 4.10 for conventional mixer and static mixer respectively.

As expected, K_1 increased with increasing the methanol/oil molar ratio and the catalyst concentration; on the other hand, K_2 was negligible irrespective of the catalyst concentration, which indicates that the hydrolysis reaction hardly took place. Based on the small value of K_2, some researchers have proposed fitting experimental data to a first-order kinetic law [106, 108, 112-114]. The results of calculated K_1 and K_2 are as shown in the following table 4.2

Table 4.2 Kinetic constants for forward and backward reaction

MIXER	K_1 (FORWARD)	K_2 (BACKWARD)
Conventional mixer	0.0289	0.0003
Static mixer	0.0384	0.0004

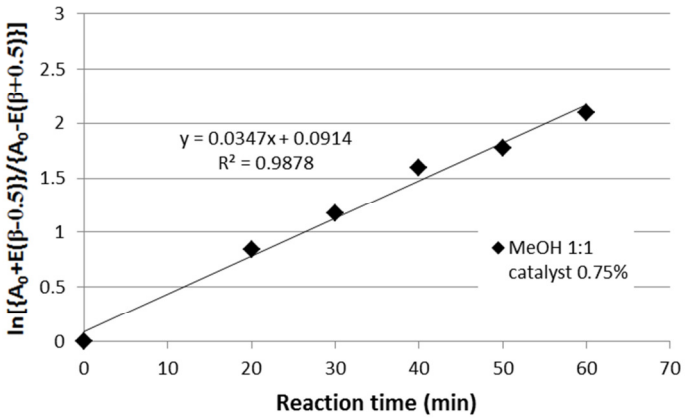

Fig. 4.7 Determination of kinetic constants at the methanol/oil molar ratio of 1:1, the catalyst concentration of 0.75% for at 60^0C temperature for conventional mixing

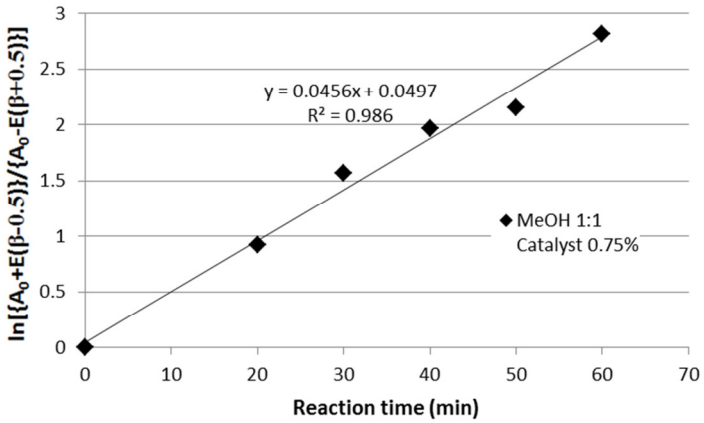

Fig. 4.8 Determination of kinetic constants at the methanol/oil molar ratio of 1:1, the catalyst concentration of 0.75% for at 60^0C temperature for static mixing

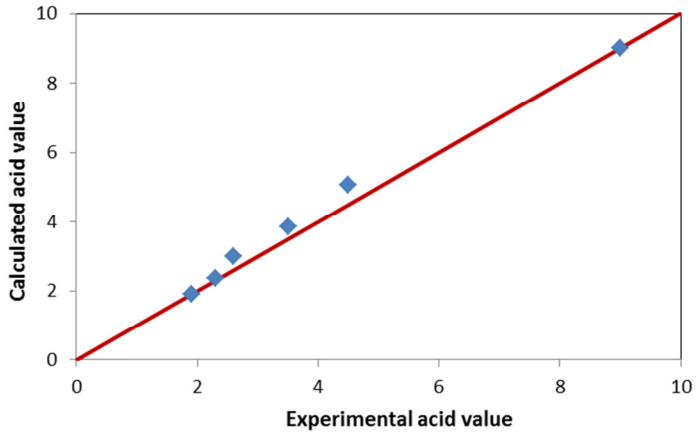

Fig. 4.9 Comparison of acid value of experimental and calculated data for conventional mixing

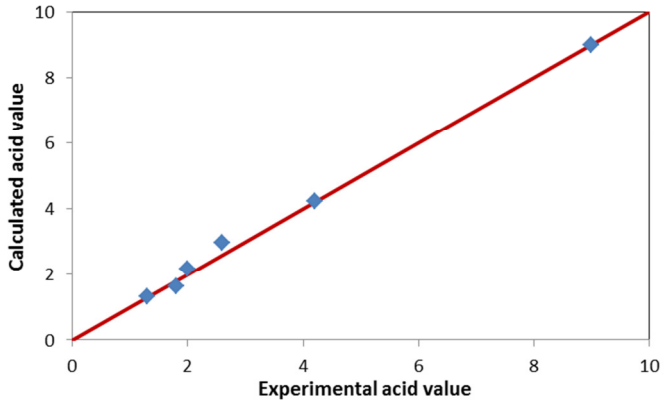

Fig. 4.10 Comparison of acid value of experimental and calculated data for conventional mixing

In order to plot the Arrhenius equation from Equation (8), first the effect of the temperature was investigated for both the conventional mixer and the static mixer. The results are shown in Figures 4.11 and 4.12 for the conventional mixer and the static mixer, respectively.

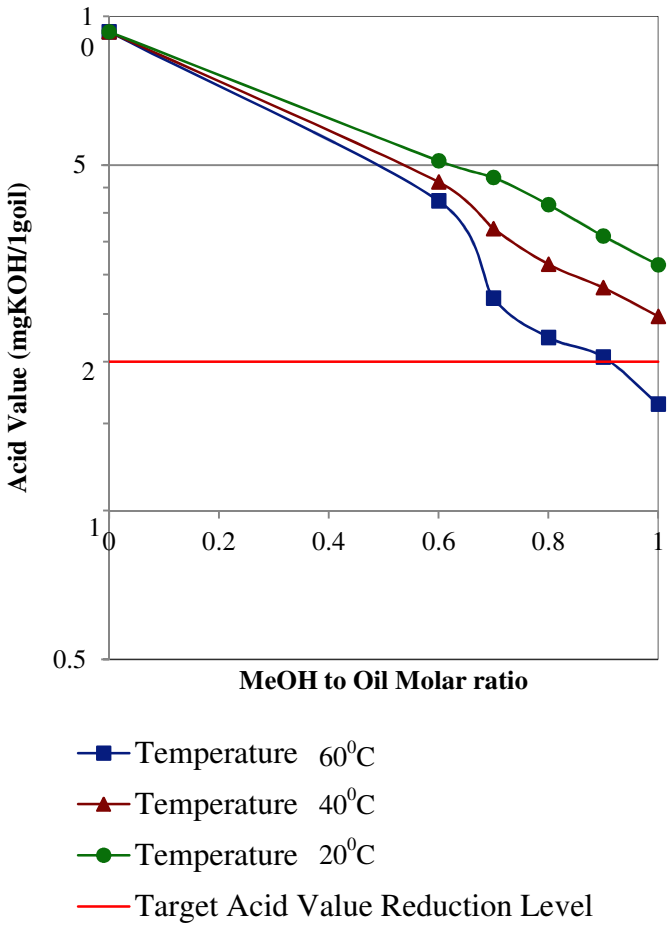

Fig. 4.11 The effect of the reaction temperature on the reduction of the acid value by the conventional mixing

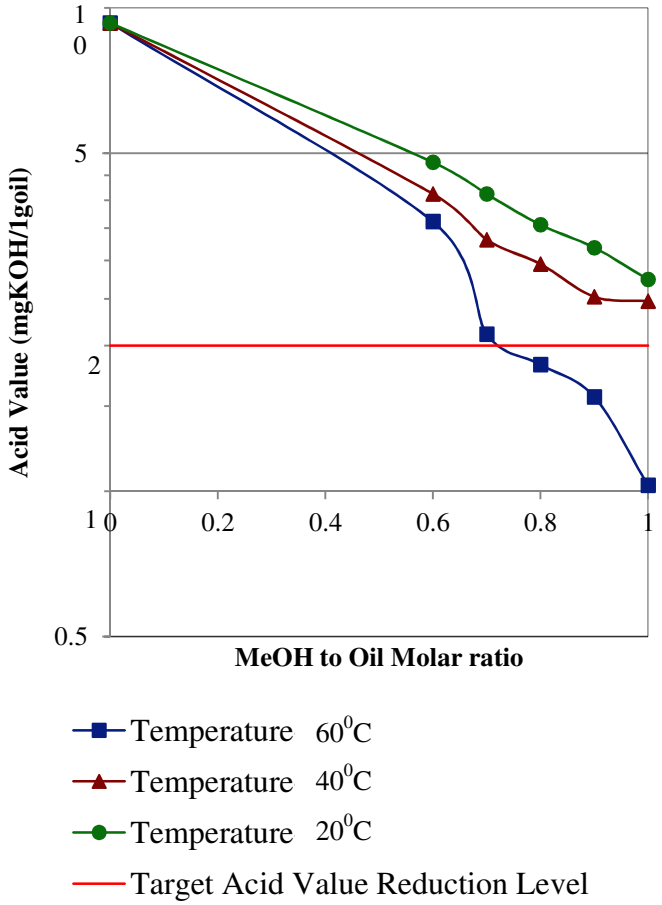

Fig. 4.12 The effect of the reaction temperature on the reduction of the acid value by the static mixing

From Figures 4.11 and 4.12, we got the Arrhenius plot from Equation (9) for each mixer as shown in Figures 4.13 and 4.16 below.

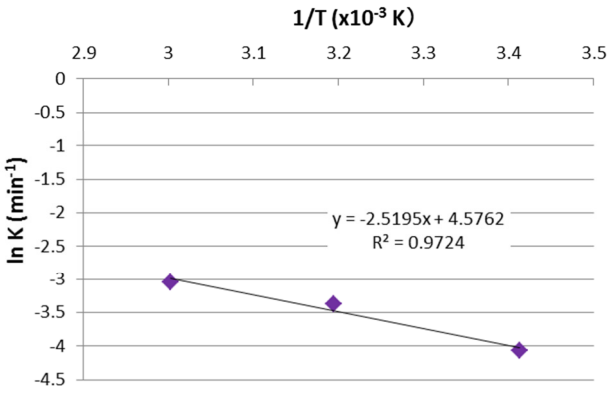

Fig. 4.13 Reaction rate constant for forward reaction in the Arrhenius plot for the conventional mixer

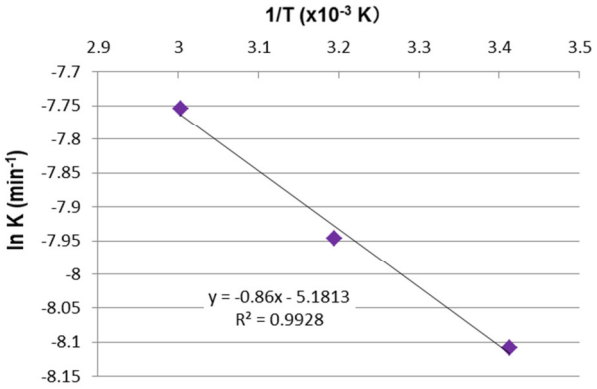

Fig. 4.14 Reaction rate constant for reverse reaction in the Arrhenius plot for the conventional mixer

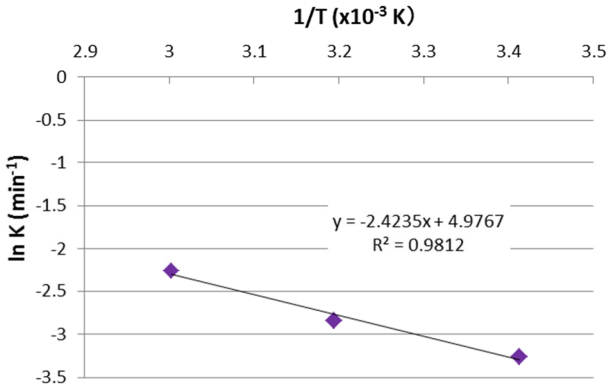

Fig. 4.15 Reaction rate constant for forward reaction in the Arrhenius plot for the static mixer

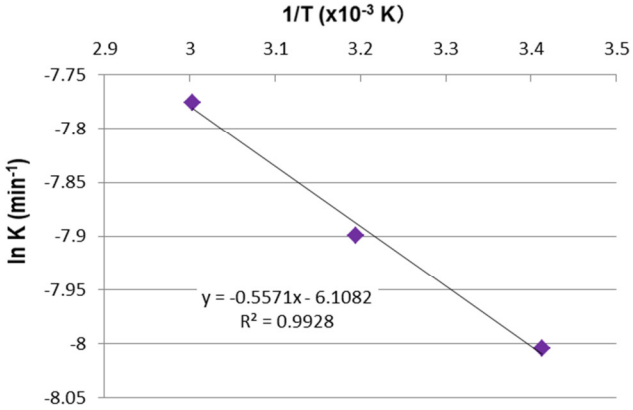

Fig. 4.16 Reaction rate constant for reverse reaction in the Arrhenius plot for the static mixer

Finally, the frequency factor A and the activation energy ΔE for each mixer were calculated and shown in Table 4.2. The results showed that the activation energy for the forward reaction is slightly decreased with the utilization of the static mixer and the frequency factor of static mixer is higher than conventional mixer.

Table 4.3 Activation energy and frequency factor for the esterification reaction by the conventional mixer and the static mixer

	A (min^{-1})	ΔE (kJ/mol)	R^2
K_1 (conventional mixer)	97.148	0.020	*0.972*
K_2 (conventional mixer)	0.006	0.007	*0.993*
K_1 (static mixer)	144.996	0.020	*0.981*
K_2 (static mixer)	*0.002*	*0.005*	*0.993*

4.4 Conclusion

From the result in this chapter, it can be concluded that the static mixing method has a high potential for accelerating the esterification reaction compared with the conventional mixing method. Also the test results prove that the esterification reaction is strongly influenced by the reaction parameters such as; the methanol to oil molar ratio, the catalyst concentration and the reaction time by the static mixing method.

Therefore, the optimum condition for each mixing method are the methanol to oil molar ratio of 0.8:1 for the static mixer and 1:1 for the conventional mixer, the catalyst concentration of 0.75% for the static mixer and 1% for the conventional mixer. Then the reaction temperature of 60^0C and the reaction time of 1h were required to reduce the acid value of Jatropha oil from 9.3 to less than the target value of 2mg KOH/1g oil.

The results of kinetic studies also showed that the static mixer could enhance the forward reaction and the activation energy was slightly decreased which might be the reason of this enhancement.

Until this chapter, the comparison of the conventional mixer and the static was investigated with the homogenous catalyst for both alkali and acid catalyst. The comparison of these two mixers will be carried on to the biodiesel production with heterogeneous catalyst in the next chapter.

Chapter 5

Mechanism studies on enhancement of biodiesel production with heterogeneous catalyst by static mixer

5.1 Introduction

One of the factors that is important for cost reduction in biodiesel production is the catalyst. The catalyst presence is necessary to increase the reaction rate and the transesterification reaction yield since non-catalytic transesterification reaction is slow and normally needs high pressures and temperatures to be completed [115]. Conventional biodiesel production consists of a process that utilizes homogeneous catalysts such as sodium or potassium hydroxide which can achieve high conversion under mild conditions, simpler usage, and shorter reaction time, and the catalyst itself is cheap [2, 40].

However, homogeneous catalyst is only suitable when high purity feedstock are employed. If a raw material has an amount of free fatty acids (FFA) over 0.1–0.5 wt.%, undesirable saponification reactions will occurred [103, 116-118]. The soap formation consumes the catalyst and decreases the ester yields. Moreover, the soap formed during the reaction prevents glycerol separation from biodiesel which will make the process less efficient, and the separation and purification become more complicated [119]. During homogeneous catalytic transesterification, the glycerol produced is of low quality and requires lengthy process and distillation for purification. Another drawback of the homogeneous catalyst is its hygroscopic nature, hazardous for the environment as compared to heterogeneous catalyst [120].

From a large scale industrial production point of view, biodiesel manufacturing by homogeneously catalyzed transesterification reaction shows great disadvantages since production costs are high as the processes involve washing and purification steps in order to meet the stipulated biodiesel quality. The catalyst must be neutralized and removed from the reaction products whose process is quite difficult. Also, the products need thorough water washing and neutralization by respective acid or alkali, resulting in the need for high amounts of water in washing and generation of excess wastewater adding the extra process costs [121-123]. Therefore, the product biodiesel also must be dried to remove the remaining moisture content and the glycerol separation process also needs improvements. Correspondingly, any commercial

biodiesel plants must have the built-in capability in order to handle various different feedstock which may differ in free fatty acids contents, acid value, water contents, or other qualities.

Because of this, several studies have been carried out considering the technical aspects of different catalyst alternatives for biodiesel production. These limitations of homogeneous catalysts can be avoided by using a heterogeneous (or solid) catalyst. The heterogeneous catalytic transesterification is included in Green Technology due to the following attributes that the catalyst can be recycled, there is no or very less amount of waste water produced during the process, and separation of biodiesel from glycerol is much easier [124, 125]. After the transesterification reaction, it is relatively easy to separate the catalyst from biodiesel and glycerol so that the heterogeneous catalyst can overcome the problems of the purification since methanol or ethanol does not mix with solid heterogeneous catalyst, which would greatly simplify and economize the catalyst removal step[120].

The major drawback of heterogeneous catalysts in general lies their preparation and reaction conditions which is energy intensive resulting in the escalation of their production cost and their leaching aspect. For a catalyst to be truly heterogeneous in nature, it should not leach into the reaction medium and should be reused. In addition, the catalyst should have high selectivity for the desired product formation and should give high yield and conversion to biodiesel. Also, the formation of three phases together with oil and alcohol which leads to diffusion limitations thus decreases the rate of the reaction. So the transesterification reaction by a heterogeneous catalyst usually requires longer reaction time or even higher amount of alcohol and reaction temperature compares to the homogeneous ones.

Nevertheless, heterogeneous catalysts convert triglycerides into biodiesel slowly but produced biodiesel in a very feasible economic way due to the reusability of catalyst for both the batch and continuous processes. In general, the heterogeneous catalyzed biodiesel production processes have less number of unit operations, with simple product separation and purification steps and no neutralization process is required [126]. Many of the heterogeneous catalysts have been reported in recent papers to produce good yield and conversion of feedstock to biodiesel [127, 128].The effectiveness of the heterogeneous catalytic conversion depends on the activity of the solid catalyst used.

In the previous chapters, biodiesel production by the static mixer had been studied and the results showed that the static mixer could enhance reaction kinetics and the conversion efficiency than the conventional mechanical stirrer in the alkali-catalyzed transesterification reaction and the acid-catalyzed esterification reaction. The static mixer has better potential to deliver vigorous mixing and increases the surface in the reaction. With the possibility of developing the continuous reaction system, biodiesel production by the static mixer had been applied and studied with this heterogeneous

catalyst.

In this study, the feasibility study of combining the static mixer technology and the heterogeneous catalyst was investigated step by step. First, two types of catalyst were compared to each other to see the performance of the catalyst. Then the experiments were carried to change the reactor to the one that is suitable with the static mixer, by using a circulating column reactor filled with heterogeneous catalyst which can also perform the transeseterification reaction. After that the performance of the mixing method itself was investigated by utilizing this reactor. Then in the last part, the experiment was carried out in the bigger scale in order to optimize the potential of this mixing technology.

5.2 Material and Experimental procedures

Raw material utilized in this experiment is 100% canola oil purchased from the local market, methanol is utilized for reacting with canola oil. Two particular interests of the catalysts utilized in this study as heterogeneous catalysts are activated carbon-based catalyst and catalyst produced from biomass called bio-catalyst.

The procedure for comparing two catalysts and two types of mixing method is mainly divided into 3 steps as shown in Figure 5.1. The first step is the batch experiment with the objective of comparing the catalytic activity of the two mentioned catalysts. The second step is to compare the performance of the catalysts in two different reactors, the batch reactor and the circulating column reactor by using only conventional mixing method. The third step is focusing on comparing the mixers utilized in circulating column reactor, under two types of catalysts.

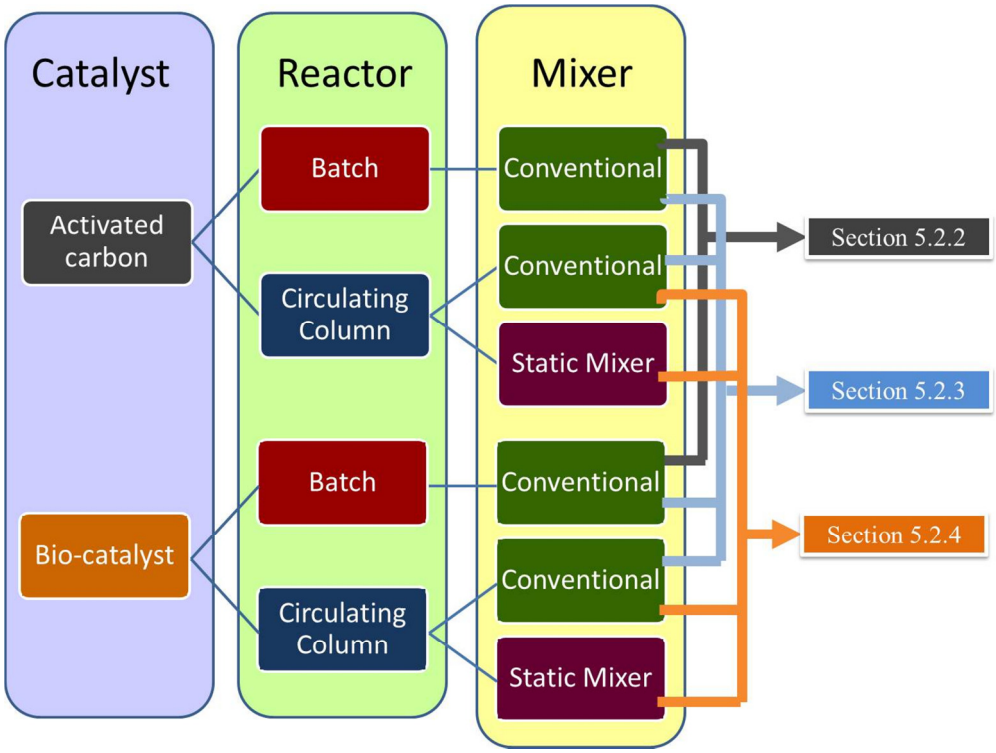

Fig. 5.1 Outline of experiments steps in chapter 5

The results of the performance comparison and kinetics evaluation will be shown for each step. There is one more experiment concerning the feasibility study of big-scale continuous reactor comparing two mixing methods with activated carbon as the catalyst in section 5.2.5.

5.2.1 Kinetics studies

In heterogeneous catalysis, two main reaction mechanisms have been widely proposed, namely Langmuir–Hinshelwood and Eley–Rideal [129-131]. In the Langmuir–Hinshelwood mechanism, the two reactants are adsorbed on the catalyst surface before the reaction takes places as shown in Figure 5.2, whereas in the Eley–Rideal mechanism, one reactant is adsorbed onto the surface first then reacts directly with the unadsorbed reactant, as shown in Figure 5.3. For the vast majority of surface catalytic reactions, it has been accepted that the Langmuir–Hinshelwood mechanism is preferred, while few reactions proceed via the Eley–Rideal mechanism.

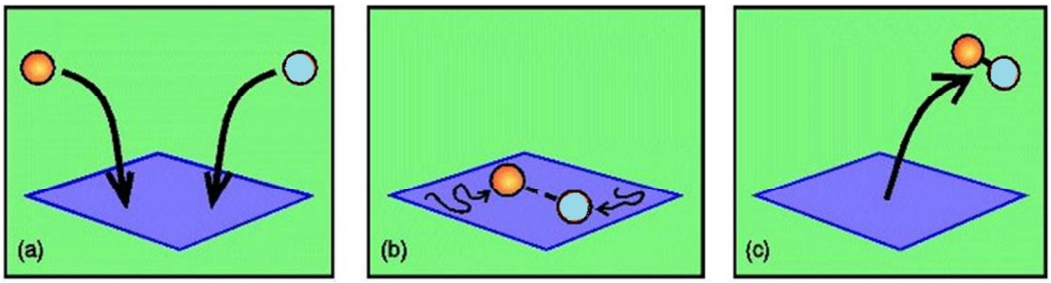

Fig. 5.2 Langmuir–Hinshelwood mechanism (a) Two atoms are adsorbed onto the surface (b) They diffuse across the surface and interact when they are close (c) A molecule is formed and desorbs

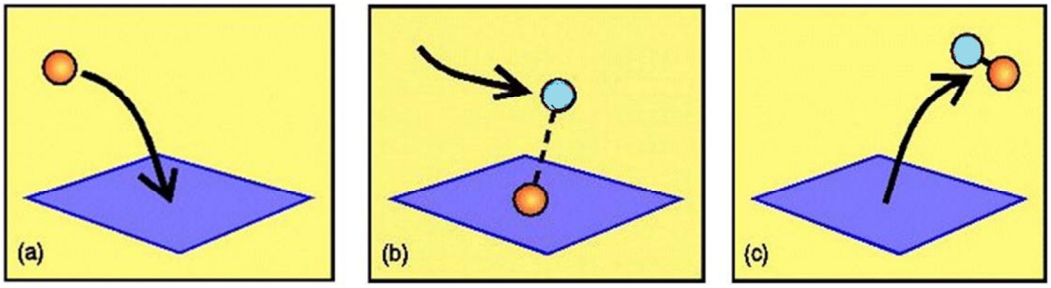

Fig. 5.3 Eley–Rideal mechanism (a) An atom is adsorbed onto the surface (b) Another atom passes to interact with the one on the surface (c) A molecule is formed and desorbs

Most of the works have been done on optimization of reaction conditions for biodiesel production by homogeneous and heterogeneous catalysts and kinetics of homogeneous base catalysts but very little information is available for kinetics of heterogeneous catalysts. Dossin et al. [131] reported the kinetic mechanism of production of biodiesel from rapeseed oil using MgO as a heterogeneous catalyst. Veljkovic et al. [132] studied the methanolysis of sunflower oil in the presence of the CaO catalyst and suggested the reaction mechanism to explain sigmoidal kinetics by incorporating the initial triglyceride mass transfer control region in the rate expression.

Lopez et al. [133] proposed the reaction mechanism of the esterification of acetic acid with methanol with different rate-determining steps on the tungstated zirconia catalyst and suggested the Eley–Rideal mechanism to describe the reaction with adsorption of carboxylic acid reacting with methanol. Abdoulmoumine [134] used impregnated zirconium oxide with sodium hydroxide for transesterification of soybean oil and found that the Langmuir-Hinshelwood kinetics is the most suitable and also found that the Eley–Rideal kinetics is followed by the supported Al_2O_3.

Chantrasa et al. [135] investigated the transesterification of tricaprylin and methanol using the solid base hydrotalcite catalyst in a well-mixed batch reactor and suggested the Eley–Rideal mechanism to explain the power law rate expression. Kapil et al. [129] found that the rate expression based on methanol adsorption as the rate

limiting in the Langmuir-Hinshelwood elementary mechanism is the most suitable for the transesterification reaction. Xiao et al. [136] carried out the transesterification reaction between palm oil and methanol catalyzed by the KF/Ca-Mg-Alhydrotalcite solid base catalyst in a packed bed reactor and suggested the surface reaction of triglyceride with adsorbed methanol as the rate determining step.

The equations of the Langmuir-Hinshelwood mechanism and the Eley–Rideal mechanism are as shown below in Equation (1) and (2) respectively.

$$r = kC_S^2 \frac{K_1 K_2 C_A C_B}{(1 + K_1 C_A + K_2 C_B)^2} \quad (1)$$

Where;

C_s is the total number of sites (occupied or not), m^{-2}
k is the kinetic constant for the surface reaction, s^{-1}
K_1 and K_2 are the Langmuir adsorption coefficients
C_A and C_B are the concentrations of the reactants A and B, *g/ml*

And the equation for the Eley–Rideal mechanism is as follows;

$$r = kC_S C_B \frac{K_1 C_A}{K_1 C_A + 1} \quad (2)$$

Where;

C_s is the total number of sites (occupied or not), m^{-2}
k is the kinetic constant for the surface reaction, s^{-1}
K_1 is the adsorption coefficients
C_A and C_B are the concentrations of the reactants A and B, *g/ml*

5.2.2 Comparison of two different catalysts with conventional mixing in a batch reactor

This experiment is focused on comparing the activity of two catalysts utilized as heterogeneous catalysts which are the activated carbon-based catalyst and the catalyst produced from biomass called bio-catalyst. The activated carbon-based catalyst shown in Figure 5.4 was provided by Prof. Arief Budiman from Gadjah Mada University, Indonesia. A carbon-based catalyst has a very low production cost but it has to be impregnated with Potassium Hydroxide (KOH) first as a pretreatment. However, it can initiate the transesterification reaction under relatively mild conditions compared with the other heterogeneous catalyst.

Fig. 5.4 Activated carbon-based catalyst

Another catalyst utilized in this study is a bio-catalyst imported by Hirai Corp., Inc. Japan from USA, which has a pretty high cost but has the ability to reduce the reaction temperature and requires less amount of reactants compared with the other catalyst. The picture of this catalyst is shown in Figure 5.5

Fig. 5.5 Bio-catalyst

For the batch experiment apparatus, a magnetic stirring apparatus shown in Figure 5.6 was utilized. Catalysts, methanol, and canola oil were put inside the flask before the reaction started. The mixed solution was stirred with NISSIN company`s SW-RS7770 magnetic stirrer at the speed of 600 rpm and a water bath with the maximum capacity of 3L was utilized for heating. These equipments are the same ones which were utilized in the previous chapter 3 and 4 for the batch process of the alkali-catalyzed and acid-catalyzed processes.

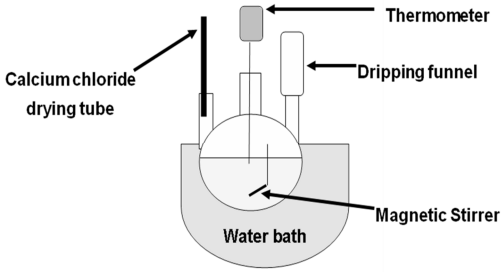

Fig. 5.6 Schematic diagram of the batch experiment

The experimental parameters for this batch experiment are shown in Table 5.1. The main parameters in this experiment are the molar ratio of methanol to canola oil, the catalyst concentration, and the reaction temperature which are different for each catalyst. After the reaction, the catalysts were analyzed by a scanning electron microscope (SEM) to see the change of the catalysts before and after the reaction.

Table 5.1 Experimental conditions for the batch experiment comparing two catalysts

TYPE OF CATALYST AND TEMPERATURE REQUIREMENT	MOLAR RATIO OF METHANOL TO OIL	CATALYST CONCENTRATION (%WT)
Activated carbon (60^0C)	10 : 1	10%
	8 : 1	5%
Bio catalyst ($30\text{-}35^0$C)	6 : 1	3%
	4 : 1	1%

5.2.3 Comparison of batch and circulating column reactors under conventional mixer testing for two catalysts

This experiment is focused on comparing the performance of each catalyst with different reactors. One of the reactors is the batch reactor utilized in the previous section 5.2.2 and the other reactor is the circulating column reactor shown in Figure 5.7. Only the conventional mechanical mixing by a magnetic stirrer can be utilized in this experiment since the static mixer is unable to operate with the heterogeneous catalyst in a batch reactor.

In the circulating column reactor apparatus shown in Figure 5.7, the column is filled with the catalysts to initiate the transesterification reaction. The reaction parameters are shown in Table 5.2 which are the type of the catalyst and the molar ratio of methanol to canola oil. The amount of the catalyst was fixed at 15g per batch. The solution of raw oil and methanol were mixed by the conventional stirrer before flowing into the packed bed reactor, then after the solution flew out of the column, the

sample was taken and the solution was re-cycled through the column to extend the reaction time.

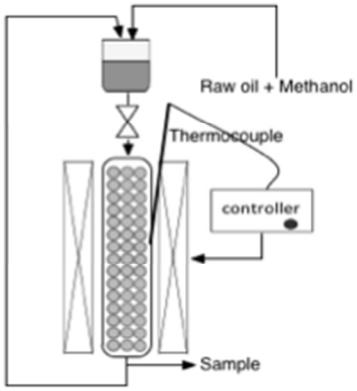

Fig. 5.7 Schematic diagram of the circulating column

For this circulating column, time zero was when the mixture of oil and methanol started to flow into the column. The retention time only considered the time the mixture is flowing inside the column and neglected the retention time in the feeding tank including the time taken for pumping the mixture from the product tank to the feeding tank.

Table 5.2 Experimental conditions for comparing batch and circulating column reactors

MIXING METHOD	TYPE OF CATALYST AND TEMPERATURE REQUIREMENT	MOLAR RATIO OF METHANOL TO OIL
Conventional mixing	Activated carbon (60^0C)	10 : 1
		8 : 1
	Bio catalyst ($30\text{-}35^0$C)	6 : 1
		4 : 1

5.2.4 Comparison of two mixing method with circulating column testing for two catalysts

The target of this experiment, which is the main objective of this chapter, is to investigate the performance of the conventional mixer and the static mixer with the heterogeneous catalyst. The mixer utilized in this experiment is the same conventional and static mixers utilized in the previous chapters 2-4. In order to confirm whether the static mixer can enhance the reaction when it is operated with the heterogeneous

catalyst, both the activated carbon and the bio-catalyst were utilized in the circulating column reactor.

Table 5.3 shows the parameters of this experiment which are the two types of mixers, the two catalysts, and the molar ratio of methanol to canola oil. The reactor utilized in this experiment is the same circulating reactor utilized in the previous section 5.2.3, the solutions of oil and methanol is mixed by either the conventional mixer or the static mixer before flowing through the column of catalysts.

Table 5.3 Experimental conditions for comparing two mixers in the circulating column reactor

MIXING METHOD	TYPE OF CATALYST AND TEMPERATURE REQUIREMENT	MOLAR RATIO OF METHANOL TO OIL
Conventional mixing	Activated carbon (60^0C)	10 : 1 8 : 1
Static mixing	Bio catalyst ($30\text{-}35^0$C)	6 : 1 4 : 1

5.2.5 Continuous column reactor experiment

In this experiment, the big-scale continuous column reactor is utilized as the apparatus in order to study the time dependency of the catalyst activity. This apparatus was provided by Prof. Arief Budiman from Gadjah Mada University. In this experiment, three molar ratios of methanol to canola oil were compared which are 8:1, 6:1, and 4:1. However, only the activated carbon catalyst was utilized and the experiment was done in Gadjah Mada University, Indonesia with the apparatus shown in Figure 5.8.

The apparatus is consists of the feeding system shown in Figure 5.8, the two-step catalyst packing column shown in Figure 5.10 which is heated to 60^0C by the hot water column attached outside, and the product container is shown in Figure 5.11. The flow rate of the feedstock is measured by counting the oil drops from the feeding system as shown in Figure 5.12.

After the apparatus was started, it was suggested that the reactor needed to be operated continuously for four hours in order to activate the catalyst. During this activation, the mixture of oil and methanol was flowing down the column continuously and after passing four hours, the sample was taken and the operating time was counted as the time zero (t=0). The results shown in the section 5.3.4 will be the results starting from this time zero.

Fig. 5.8 Continuous column reactor

Fig. 5.9 Feeding system for continuous column reactor

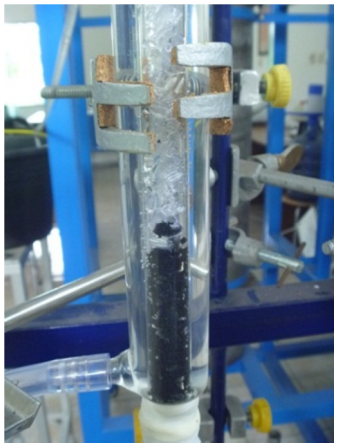

Fig. 5.10 Catalyst column with plastic packing to adjust the flow

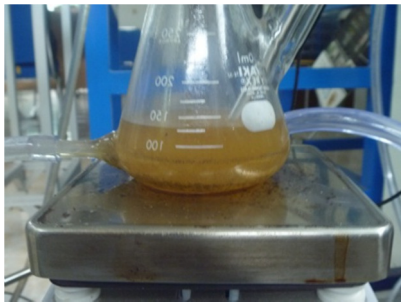

Fig. 5.11 Product storage and product extraction tube

Fig. 5.12 Adjusting the flow by counting the oil drops

5.3 Results and Discussion

For the reaction kinetics, we compare the results by utilizing both the Langmuir-Hinshelwood mechanism and the Eley–Rideal mechanism shown in equations (1) and (2), respectively, and compare the kinetic constant (k) of both catalysts. However, the results showed that both mechanisms could explain the mechanism of the reactions. Therefore, this chapter will focus on only the Eley–Rideal mechanism because it has less unknown factors compared with the Langmuir-Hinshelwood mechanism so that it is more suitable to use this model to compare with experimental results. All the results of the Langmuir-Hinshelwood mechanism will be presented in Appendix B.

According to the Eley–Rideal mechanism, it suggests that either oil or methanol molecule is adsorbed first on the catalyst before interacting with another molecule. Both phenomena were investigated by analyzing the kinetic and the results showed that the reaction could not be explained using this mechanism by assuming that methanol was adsorbed first while the assumption that oil was adsorbed first showed explainable results. This suggests that this kinetic study should be based on the assumption that the oil was adsorbed first into the catalyst but not methanol.

5.3.1 Comparison of two different catalysts with the conventional mixing under the batch reactor

First, the batch results of both the activated carbon catalyst and the bio-catalyst are compared to show the catalytic activity of both catalysts. Figure 5.13 shows the results of the activated carbon under four different molar ratio of methanol to raw oil at the 10% catalyst concentration, and Figure 5.14 shows the results of the catalyst concentration variation under the 10 molar ratio of methanol to raw oil.

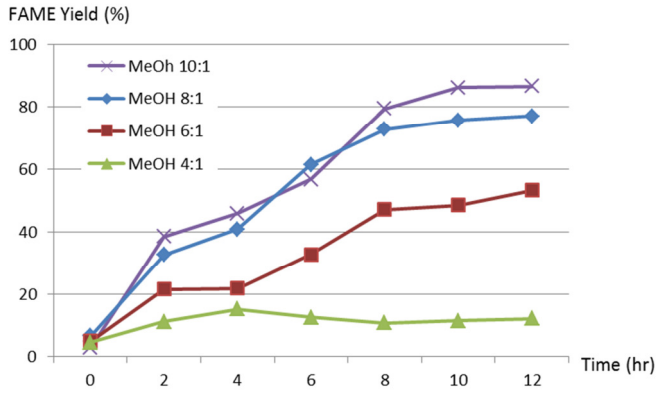

Fig. 5.13 Results by changing the methanol molar ratio to raw oil with the activated carbon as the catalyst

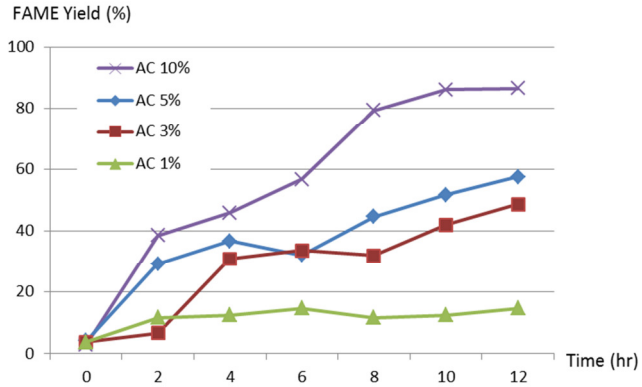

Fig. 5.14 Results by changing the catalyst concentration with the activated carbon as the catalyst

The results showed that the activated carbon has a low reactivity. Even at a high molar ratio of methanol to raw oil of 8 or 10, it still requires at least 10% concentration of the catalyst to reach the FAME yield higher than 80%.

For the bio-catalyst, the results of the changes of the methanol molar ratio to raw oil and the catalyst concentration are shown in Figures 5.15 and 5.16, respectively.

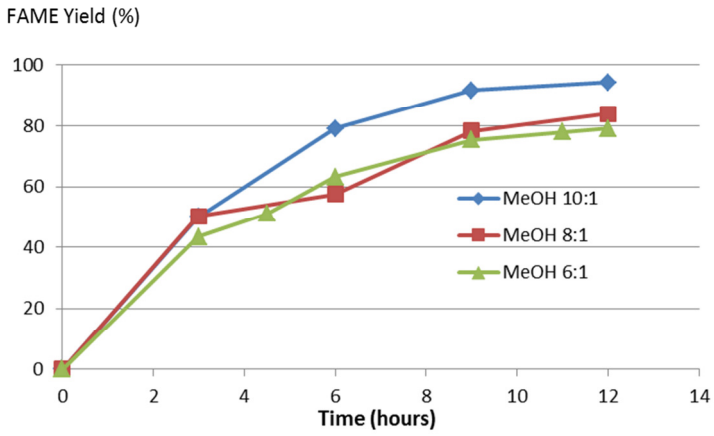

Fig. 5.15 Results by changing the methanol molar ratio to raw oil with the bio-catalyst as the catalyst

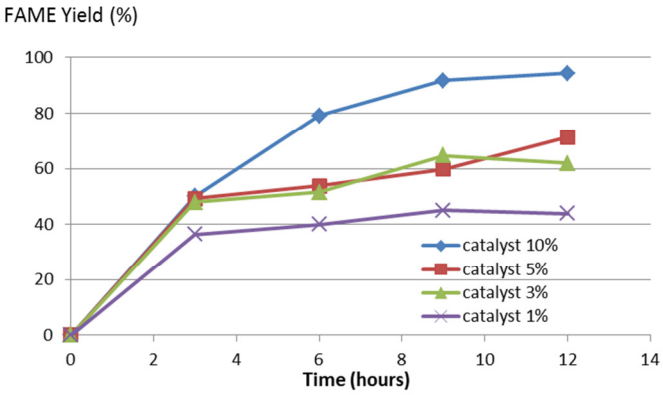

Fig. 5.16 Results by changing the catalyst concentration with the bio-catalyst as the catalyst

When comparing the batch results shown in Figures 5.13 to 5.16, the results showed that the bio-catalyst has a higher catalyst activity as shown in Figure 5.17 below which compares the results for both catalysts when changing the methanol molar ratio to raw oil.

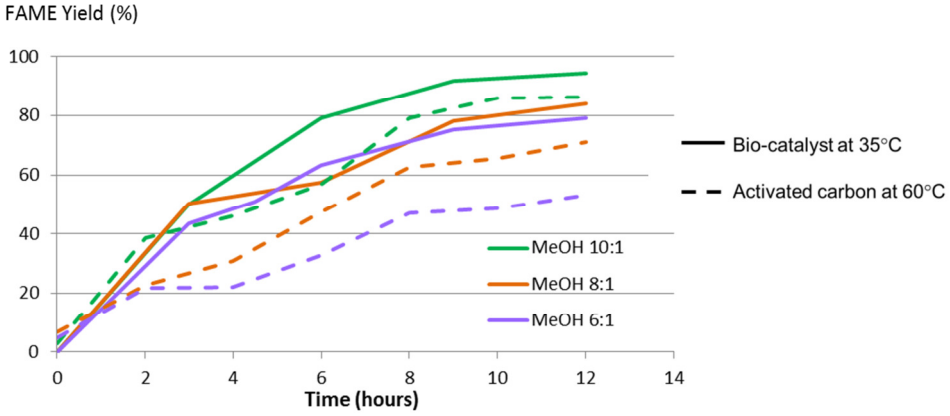

Fig. 5.17 Results of the bio-catalyst compared with the activated carbon

The results showed that the bio-catalyst has a faster reaction rate than the activated carbon. While the reaction of the activated carbon was operated under 60

degree Celsius, only 30-35 degree is required for the bio-catalyst. With only 6 or 8 molar ratio of methanol to raw oil for the bio-catalyst, it could obtain similar product yield to the activated carbon under the 10 molar ratio of methanol to raw oil. Therefore, the bio-catalyst can obtain higher product yield and faster reaction rate.

The reaction model and the parity plot of the activated carbon is shown in Figures 5.18 and 5.19, then also the reaction model and the parity plot of the bio-catalyst is shown in Figures 5.20 and 5.21. The kinetic constant of the activated carbon and the bio-catalyst are 0.08 and 0.16 respectively. This means that the bio-catalyst has a higher catalytic activity than the activated carbon. The root-mean-square error (RMSE) and the kinetic constant for both catalysts are shown in Table 5.4

Table 5.4 The root-mean-square error and the kinetic constant for the results of two catalysts in the batch reactor

MOLAR RATIO OF METHANOL	ACTIVATED CARBON CATALYST	BIO-CATALYST
10 : 1	7.399	6.489
8 : 1	7.971	6.850
6 : 1	8.698	8.225
Kinetic Constant (s^{-1})	0.08	0.16

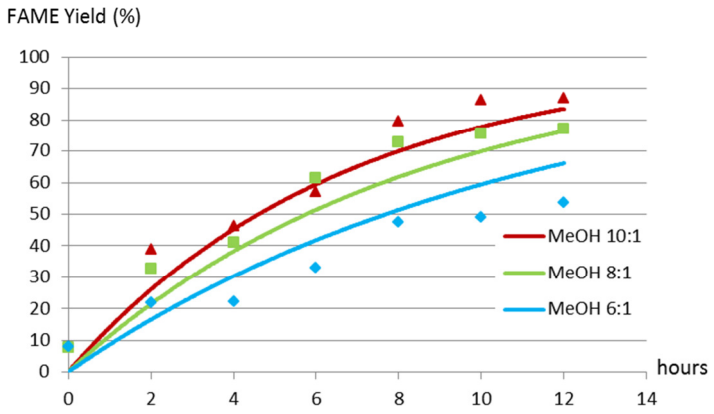

Fig. 5.18 Reaction model for the batch reactor with the activated carbon catalyst

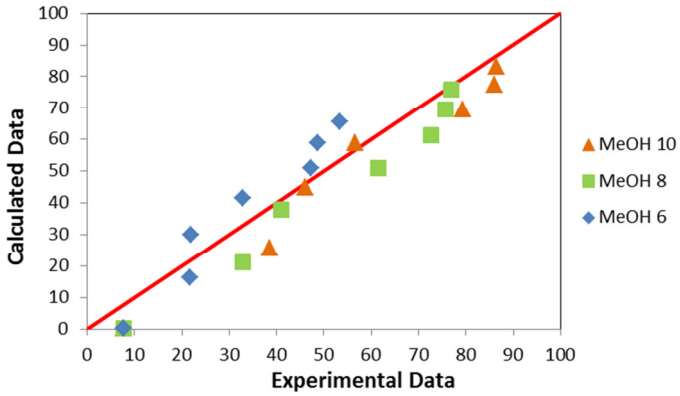

Fig. 5.19 Parity plot for the batch reactor with the activated carbon catalyst

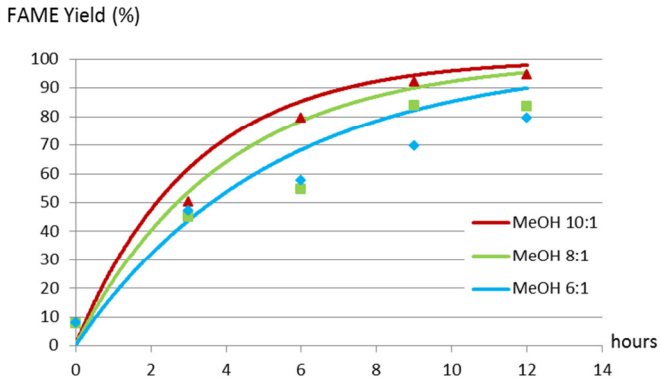

Fig. 5.20 Reaction model for the batch reactor with the bio-catalyst

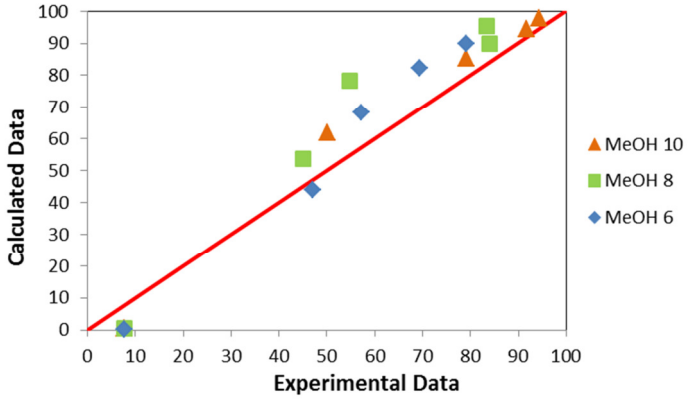

Fig. 5.21 Parity plot for the batch reactor with the bio-catalyst

Both the activated carbon catalyst and the bio-catalyst were analyzed by the scanning electron microscope (SEM) and the results are shown in Figs. 5.22 and 5.23 below.

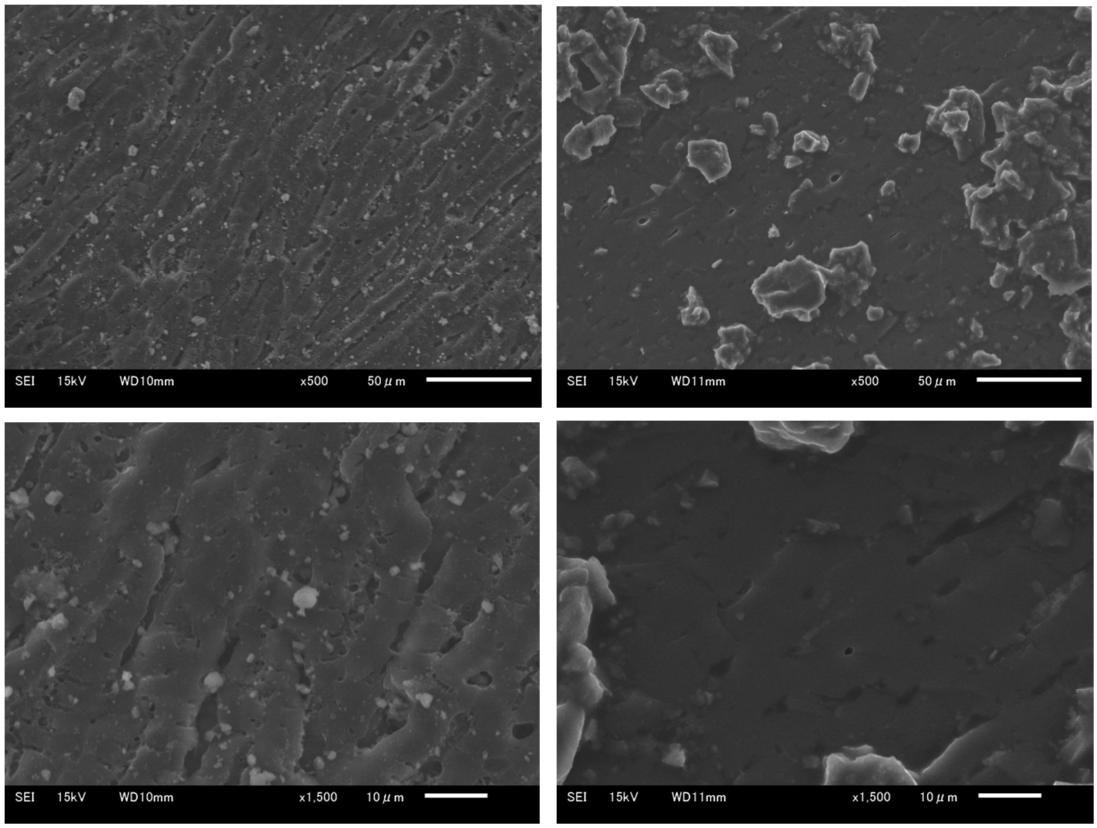

Fig. 5.22 SEM results of the activated carbon catalyst in the batch reactor magnified 500 times and 1500 times for (left) before the reaction and (right) after the reaction

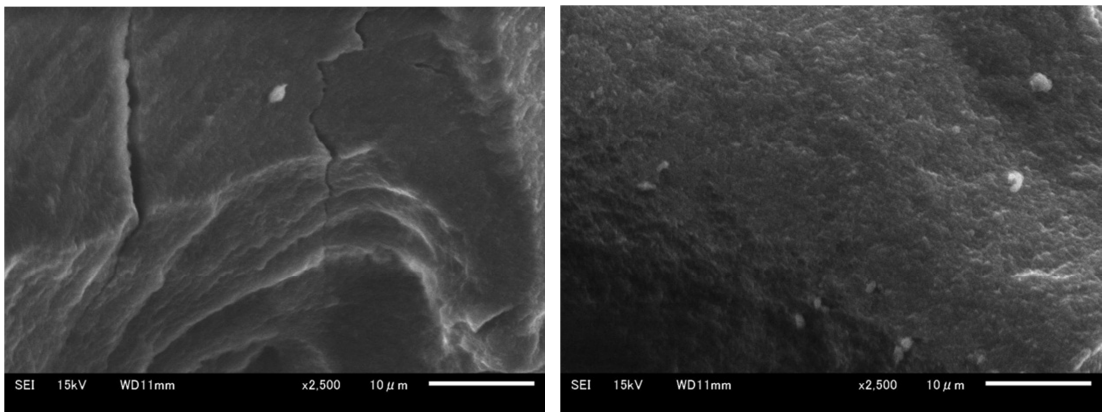

Fig. 5.23 SEM results of the bio-catalyst in the batch reactor magnified 2500 times for (left) before the reaction and (right) after the reaction

The analysis show the structures of both catalysts, where the activated carbon is porous, while bio-catalyst seemed to be non-porous. Even though theoretically, the porous catalyst should have better catalytic effect since it has more reactive site, but the results showed that the activated carbon catalyst might have the limited reactive site which restricted the effect of the mixing even though the droplet become smaller. Experiment results also showed that the bio-catalyst has a better catalytic activity which makes the enhancement of the diffusion limitation more effective.

5.3.2 Comparison of the batch reactor and the circulating column reactor under the conventional mixer testing for two catalysts

The results in this section will focus on the performance of both catalysts in the circulating column reactor compared with the batch reactor shown in section 5.3.1. Figure 5.24 shows the FAME yield results of the activated carbon and Figure 5.25 shows the FAME yield results of the bio-catalyst, respectively. Both results show the comparison with the batch experiment under the same reaction conditions.

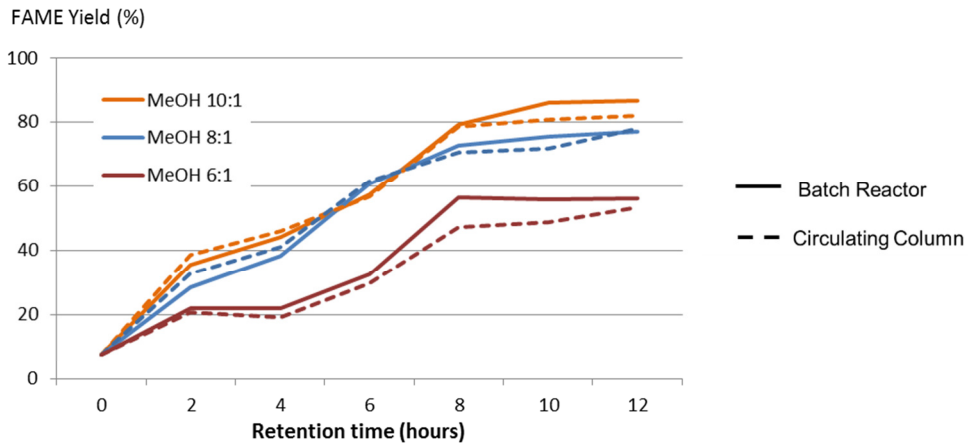

Fig. 5.24 Results of the activated carbon catalyst with the batch reactor and the circulating column reactor

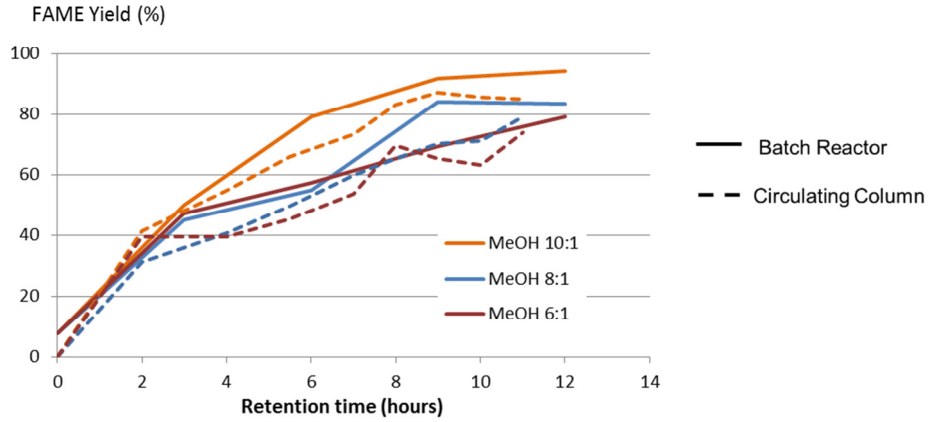

Fig. 5.25 Results of the bio-catalyst with the batch reactor and the circulating column reactor

The results in Figures 5.24 and 5.25 show that in both catalyst cases, the batch reactor has better product yield than the circulating column reactor. Then the kinetics was analyzed to confirm the trend of these results. The reaction model and the parity plot of the circulating column reactor are presented in Figures 5.26 and 5.27 for the activated carbon and in Figures 5.28 and 5.29 for the bio-catalyst, respectively.

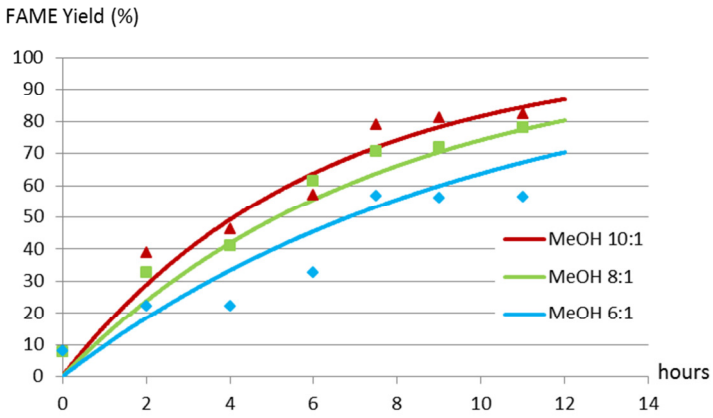

Fig. 5.26 Reaction model for the circulating column reactor by the conventional mixer with the activated carbon catalyst

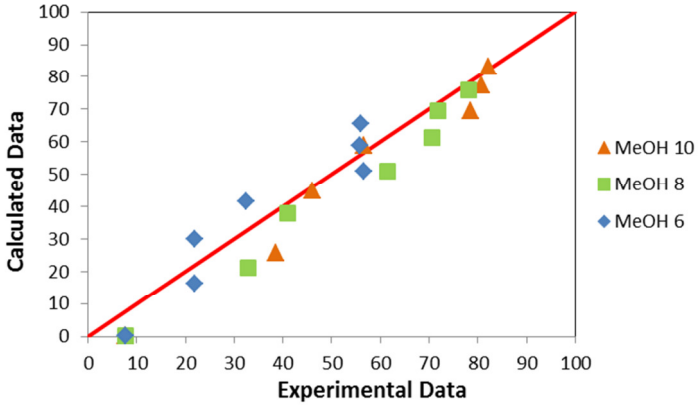

Fig. 5.27 Parity plot for the circulating column reactor by the conventional mixer with the activated carbon catalyst

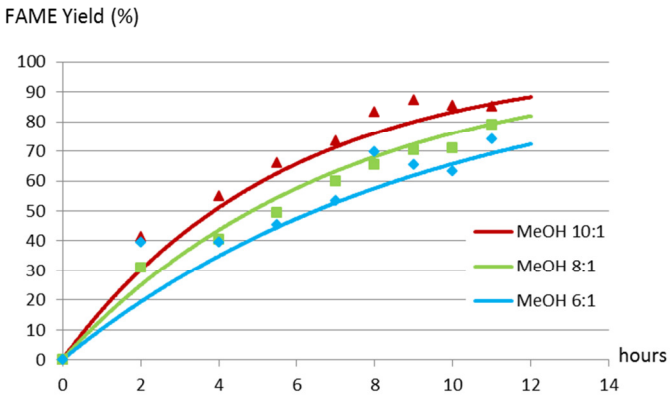

Fig. 5.28 Reaction model for the circulating column reactor by the conventional mixer with the bio-catalyst

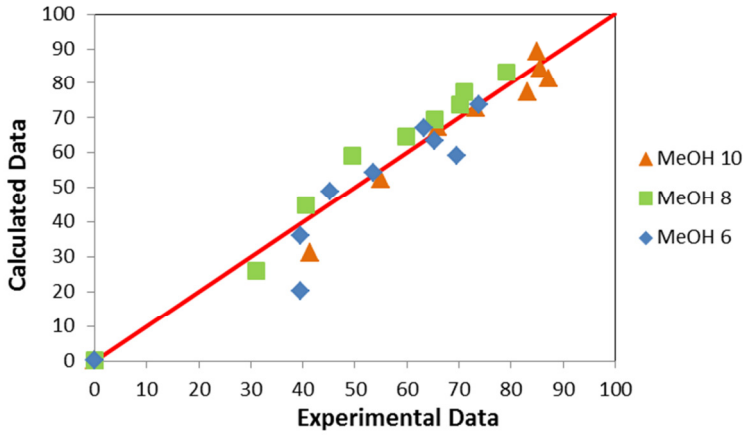

Fig. 5.29 Parity plot for the circulating column reactor by the conventional mixer with the bio-catalyst

These results are compared with the batch reactor model shown in section 5.3.1, by comparing Figures 5.26 and 5.27 with Figures 5.18 and 5.19, then comparing Figures 5.28 and 5.29 with Figures 5.20 and 5.21. Then the kinetic constant for both reactors are compared in Table 5.5 and the root-mean-square error for both reactors are also shown in Table 5.6.

Table 5.5 Kinetic constant for two catalysts in the batch reactor and the circulating column reactor

KINETIC CONSTANT (S^{-1})	BATCH REACTOR	CIRCULATING COLUMN
Activated carbon	0.08	0.079
Bio-catalyst	0.16	0.099

Table 5.6 Root-mean-square error for two catalysts in the batch reactor and the circulating column reactor

CATALYST	MOLAR RATIO OF METHANOL	BATCH REACTOR	CIRCULATING COLUMN
Activated carbon	10 : 1	7.399	7.614
	8 : 1	7.971	7.605
	6 : 1	8.698	7.186
Bio-catalyst	10 : 1	6.489	7.525
	8 : 1	6.850	3.496
	6 : 1	8.225	8.644

For both results of the FAME yield comparison and the kinetic comparison, in the case of the activated carbon catalyst, there is only a slight difference in the kinetic constant between two reactors, and there is a small FAME yield difference in the final stage of the reaction between two reactors. However, in the case of the bio-catalyst, the difference between both reactors is more significant. Based on these results, we

can conclude that the accessibility between the catalyst and the solution is the key factor to explain the reason why the batch reactor can perform better. In the batch reactor, the mixing is continuous so the droplet size of methanol in raw oil can remain small. But in the case of the circulating column reactor, the mixing only occurred before entering the column so there is no continuous mixing to allow the methanol droplets to maintain the small sizes, the bubbles are getting bigger following the reaction time and become the obstacle to the adsorption performance of the catalyst.

5.3.3 Comparison of the conventional mixer and the static mixer with circulating column testing for two catalysts

In the previous section 5.2.3, the reaction of the conventional mixer with the circulating column testing for two catalysts was presented, so this section will present the result of the static mixer comparing with the conventional mechanical mixer. Figures 5.30 and 5.31 show the comparison of the static mixer and the conventional mixer for the activated carbon catalyst and the bio-catalyst, respectively.

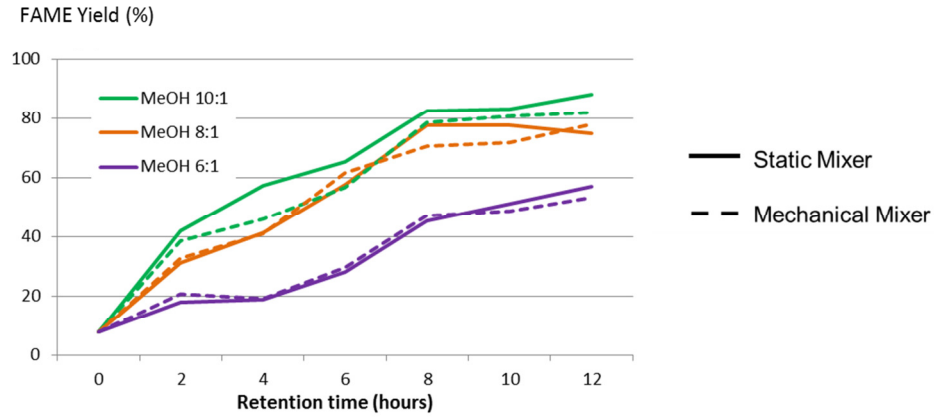

Fig. 5.30 Results of the circulating column reactor with the activated carbon as the catalyst

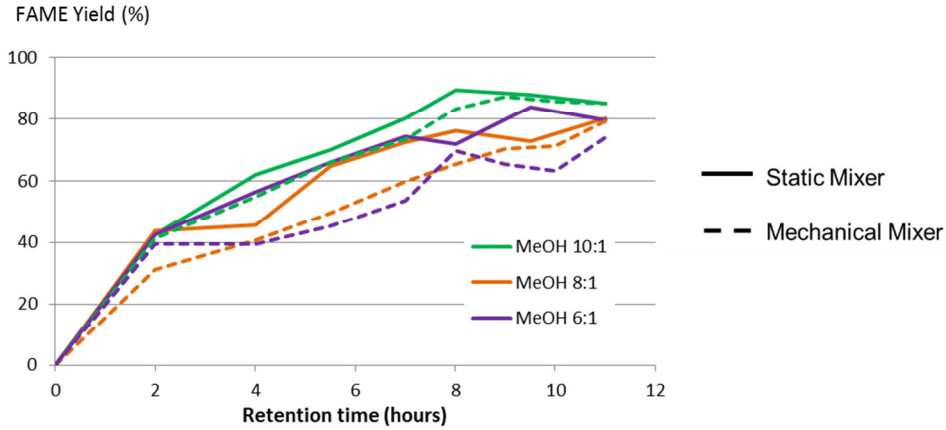

Fig. 5.31 Results of the circulating column reactor with the bio-catalyst as the catalyst

From Figure 5.30 for the activated carbon catalyst, it can be seen that at 10 molar ratio of methanol to raw oil, the result of the static mixer shows a higher FAME yield compared with the conventional mixing in the middle stage of the reaction. Nonetheless, the results of 6 and 8 molar ratios of methanol to raw oil show almost no difference between the two mixers.

However, in the case of the bio-catalyst shown in Figure 5.31, the results showed that while there is a small difference between the two mixers at 10 molar ratio of methanol to raw oil, at a lower molar ratio of methanol to raw oil, the difference is more clearly perceived. In the previous batch experiment results shown in Figure 5.17, it was shown that the FAME yield for the activated carbon at 10:1 molar ratio of methanol to raw oil is also similar to the FAME yield for the bio-catalyst at 6:1 and 8:1 molar ratio of methanol to raw oil. The connections between these batch and packed-bed column results might imply that the enhancement of the static mixer occurred only under the optimum reaction condition or at a certain amount of methanol.

The reaction kinetics was analyzed to check these results, and the reaction model and the parity plot of the static mixer in the circulating column reactor are presented in Figures 5.32 and 5.33 for the activated carbon and in Figures 5.34 and 5.35 for the bio-catalyst, respectively.

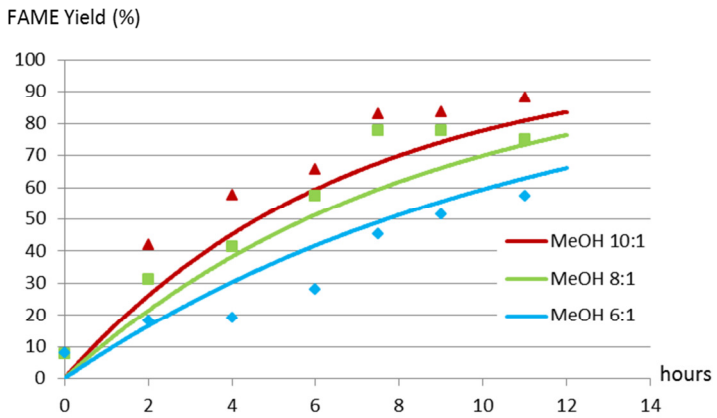

Fig. 5.32 Reaction model for the circulating column reactor by the static mixer with the activated carbon catalyst

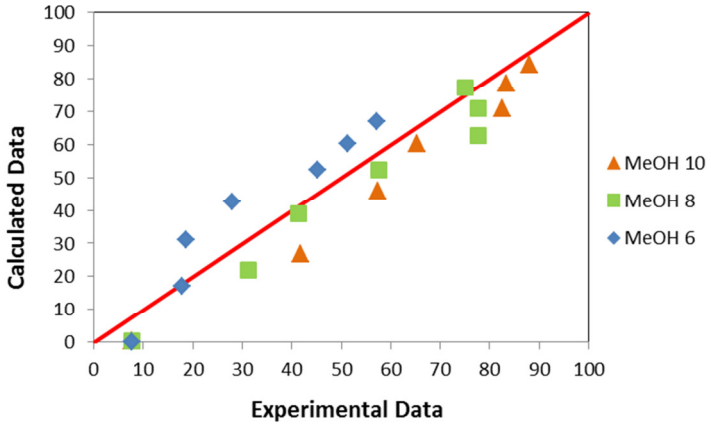

Fig. 5.33 Parity plot for the circulating column reactor by the static mixer with the activated carbon catalyst

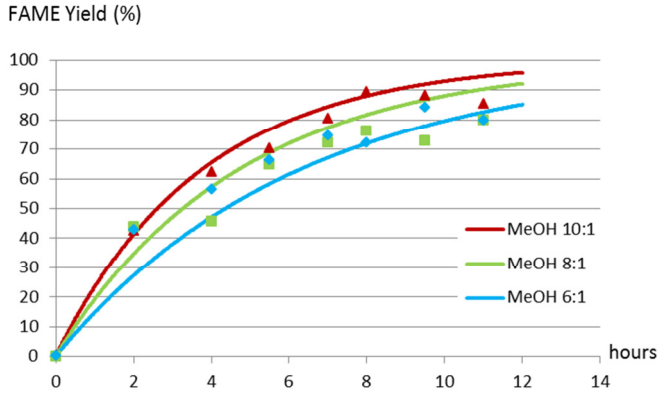

Fig. 5.34 Reaction model for the circulating column reactor by the static mixer with the bio-catalyst

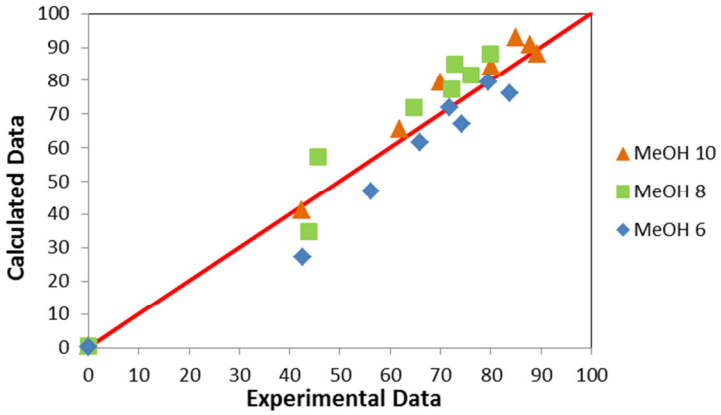

Fig. 5.35 Parity plot for the circulating column reactor by the static mixer with the bio-catalyst

Then these results are compared with the reaction model of the conventional mixer in section 5.3.2, by comparing Figures 5.32 and 5.33 with Figures 5.26 and 5.27 in the case of the activated carbon, and then comparing Figures 5.34 and 5.35 with Figures 5.28 and 5.29 in the case of the bio-catalyst. Then the kinetic constant of

both reactors are shown in Table 5.7, also compared with the different specific surface areas shown in Chapter 3. The root-mean-square error for each mixer is also shown in Table 5.8.

Table 5.7 Kinetic constant of two mixers in the circulating column reactor with two catalysts

KINETIC CONSTANT (S^{-1})	CONVENTIONAL MIXER	STATIC MIXER	MAGNIFICATION FACTOR
Activated carbon	0.079	0.082	1.038
Bio-catalyst	0.099	0.141	1.424
Magnification factor of the surface area from Chapter 3 (at 30 minutes of reaction)			1.560

Table 5.8 Root-mean-square error for the results of the two mixers in the circulating column reactor with two catalysts

CATALYST	MOLAR RATIO OF METHANOL	CONVENTIONAL MIXER	STATIC MIXER
Activated carbon	10 : 1	7.614	9.334
	8 : 1	7.605	8.024
	6 : 1	7.186	9.628
Bio-catalyst	10 : 1	7.525	4.745
	8 : 1	3.496	8.289
	6 : 1	8.644	7.845

The results of kinetic constants shown in Table 5.7 support the previous FAME yield results that the performance of the static mixer is better than the conventional mixer even when utilizing the heterogeneous catalysts. However, in the activated carbon catalyst, the difference is not as significant as the results from the bio-catalyst, so we can say that the catalyst activity also has the effect of supporting the performance of the static mixer.

Also, when comparing with the magnification of the surface area from Chapter 3, the static mixer can enhance the reaction 1.424 times higher than the conventional mixer with this heterogeneous catalyst, while the surface area could be increased 1.560 times larger. This suggests that there might be other factors which promote the enhancement of the reaction rate constant, but the surface area might play the biggest role in this enhancement since it has the direct influence to the adsorption ability of the catalyst because smaller molecules could be adsorbed better than the larger one.

5.3.4 Continuous column reactor experiment

As for the big-scale continuous experiment, the conventional mixer and the static

mixer is compared and the result is shown in Figure 5.36

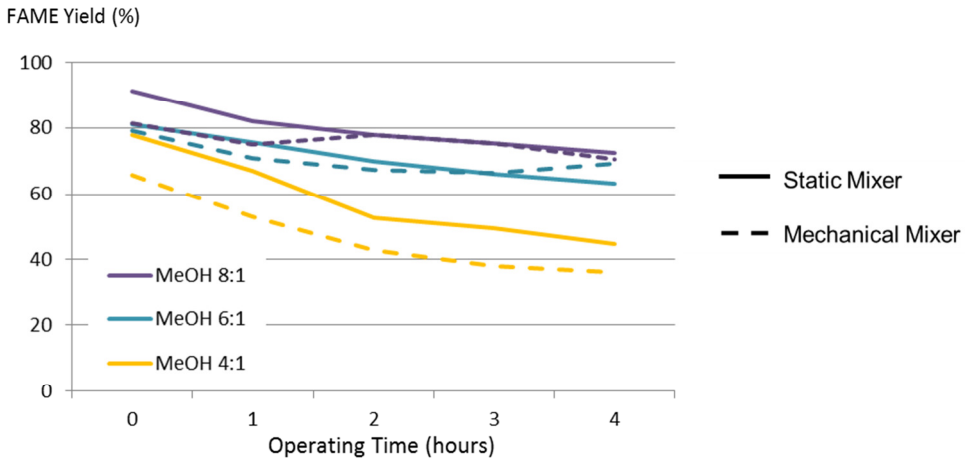

Fig. 5.36 Results of the big-scale continuous column reactor operating with the activated carbon catalyst and comparing two mixing methods

The result shows that the static mixer has the possibility to enhance the reaction rate, especially when 4 molar ratio of methanol to raw oil is utilized. At a low molar ratio, the difference between the static mixer and the conventional mechanical mixer is more significance, but the FAME yield is not high enough to reach the satisfactory results.

As stated in the section 5.2.5, the starting time of the reaction in this result is actually four hours after the start of the reactor. This presents quite interesting results that all FAME yield started to drop after the time zero. It suggested that at the time zero of this experiment, the activity of this catalyst is already decreased and caused the drop of the FAME yield. However, since this is only the preliminary study of applying the static mixer in the bigger scale reaction, more study should be done in order to confirm and analyze this phenomena.

In order to compare the performance of each reactor, the comparison of all the reactors investigated in this chapter which is the batch reactor, the circulating column reactor, and the big-scale continuous reactor, is shown in Figure 5.37 below. This comparison will only consider the reaction with the activated carbon with 8:1 molar ratio of methanol to raw oil. Therefore, only the yield at the end of the reaction for the batch reactor and the circulating column reactor was compared. While for the big-scale reactor, both the results of the starting operating time and the end of the operating time was shown.

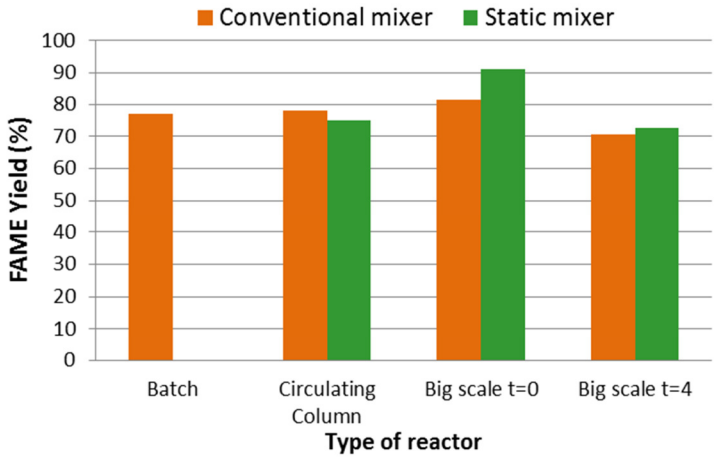

Fig. 5.37 Results of the FAME yield comparison for each reactor operated with the activated carbon catalyst

This result shows that while there is no significant difference between the batch reactor and the circulating column reactor in the FAME yield with the activated carbon as the catalyst, the result of the big-scale continuous reactor at the time zero is the highest compared with the other reactors, especially when the mixture was stirred by the static mixer.

According to this result, it suggests that more investigations should be done with the big-scale reactor but change the catalyst to the bio-catalyst. Since even in a smaller scale reactor, the bio-catalyst could support the enhancement of the static mixer so in the bigger scale there might be a possibility of further enhancement by combining this mixer technology and the new bio-catalyst together.

5.4 Conclusion

The main objective of this chapter is to investigate the performance of the static mixer by using heterogeneous catalysts in the transeseterification reaction. The results could be summarized as follows;

By comparing the catalytic activity between the activated carbon and the bio-catalyst, the results showed that the bio-catalyst has a better activity than the activated carbon by obtaining a higher FAME yield and a higher reaction rate constant.

Then we compared two reactors, the batch reactor and the circulating column reactor to investigate the reaction conditions, since the static mixer is unable to perform in a batch reactor when applying with heterogeneous catalysts. However, the results showed that the batch reactor could perform better since the accessibility of the

oil and methanol to the catalyst is much better than the circulating column reactor because the small size droplets of methanol could be maintained throughout the reaction.

However, the experiments were carried out to compare the conventional mechanical mixer and the static mixer in the circulating column reactor, and the results showed that the static mixer could enhance the reaction rate and this became more significant when the bio-catalyst was utilized. This suggests that using the high activity catalyst could help to promote the reaction enhancement with the use of the static mixer.

When the big-scale reactor is utilized, the results showed that it has a better performance than the smaller ones even with the low activity catalyst, also the reaction enhancement of the static mixer is more clearly shown. This also suggests that there is a potential of using the static mixer to enhance the biodiesel production process in the bigger scale reactor.

Chapter 6

Conclusions and future work

6.1 Conclusion

The focus of this study was to apply the static mixer in biodiesel production process because the static mixer is said to have potential for reaction enhancement. Both biodiesel productions by homogeneous and heterogeneous catalysts were taken into consideration of combining with the static mixer technology. First the static mixer was applied with the most conventional process for biodiesel production which is the transesterification reaction by the homogeneous alkali catalyst whereas the FAME yield was observed and the kinetic mechanism was studied and analyzed.

After the conventional reaction, another homogeneous acid catalyzed biodiesel pretreatment process was applied with static mixer to see whether the static mixer can enhance the other biodiesel-related reaction. The reductions of acid value of raw material were observed and the kinetics was also investigated.

In the last process, the static mixer was applied to the biodiesel production with the heterogeneous catalyst process. The heterogeneous catalysts are taken interests by many researchers recently since they are one of the efficient methods to lead towards a more sustainable biodiesel industry. The results obtained from these studies allow drawing the following major conclusions.

6.1.1 Reaction enhancement by the static mixer for homogeneous catalysts

Experiments with the static mixer on the alkali-catalyzed transesterification show that the static mixer can achieve higher FAME yields in the initial stage of the reaction and also the reaction could reach the equilibrium stage faster than the conventional mechanical stirrer. The kinetic studies show that more fine, uniform, and smaller droplets of methanol can be generated by the use of the static mixer which resulted in the increase of the surface area between the raw oil and methanol. However, the reaction enhancement of the static mixer effected the reaction only a limited of time in the initial stage of the reaction while the diffusion-controlled stage is still effective

The experiments on the acid-catalyzed esterification for free fatty acids reduction

in the raw material were done. The results showed that the static mixer also has a potential for esterification reaction enhancement by reducing the utilization of methanol and catalyst. The kinetic studies also showed that this enhancement might occur because the static mixer could enhance the forward reaction and decrease the activation energy.

6.1.2 Reaction enhancement by the static mixer for heterogeneous catalysts

At present, studies on heterogeneous catalysts for biodiesel production become more and more popular due to their sustainability. In this research two biomass-based catalysts are compared and combined with the static mixer technology. The two catalysts are the activated carbon and the bio-catalyst, and the results showed that the bio-catalyst could perform better than the activated carbon by obtaining higher FAME yields and higher reaction rate constants.

In order to apply the static mixer to heterogeneous catalysts, the circulating column reactor is utilized. However, the results showed that the conventional batch reactor could perform better than this reactor because the accessibility of the oil and methanol to the catalyst is much better since it could produce the small size bubbles continuously throughout the reaction.

The experimental results comparing the conventional mechanical mixer and the static mixer using the circulating column reactor suggest that the static mixer can enhance the reaction rate and the differences between two mixing methods become more significant when a high activity catalyst such as bio-catalyst is utilized since it can promote the enhancement by the static mixer to be more effective.

The big-scale reactor with the activated carbon catalyst was also tested, and the results showed that it has better performance than the small scale reactors. The results also implied that the reaction enhancement by the static mixer could be promoted further by utilizing the bigger scale reactor. The assumptions of why the big-scale can perform better are the contact between the oil solutions and catalyst and the temperature control. The feeding of the oil into the catalyst column for big-scale is feed continuously so there is almost no storage before the reactions occur. The time interval between after the mixing and the adsorption is smaller than the circulating column. And the temperature control of the big-scale reactor is better since the small scale is difficult to be controlled due to the environment of experiments in the laboratory.

6.2 Recommendations for the future work

As this research is focusing on the application of the static mixer to the biodiesel production process, the future work could be based on our present work as follows;

In the case of the alkali-homogeneous catalyzed reaction, the next possible step is to test the static mixer with the bigger scale process. Since the alkali-catalyzed reaction is the most conventional reaction in biodiesel reduction, testing the static mixer with the pilot scale might be able to confirm the effectiveness of the static mixer in the practical use.

For the acid-homogeneous catalyzed reaction, we only focused on the free fatty acid reduction in the raw material. Therefore, the future works can be focused on the biodiesel production part of the acid-catalyst reaction or the two-step alkali-catalyzed reaction combined with the acid-catalyzed esterification reaction which is also the conventional process when using the high acid value raw material.

As for the heterogeneous catalysts, it will require lots of future work in order to confirm that these technologies can be combined with each other. Also, in the commercial biodiesel plant, not many are utilizing the heterogeneous catalysts in the production because there is no conventional heterogeneous catalyst which is the most effective when considering both technological and economic factors.

However, based on our current work, many next future works could be recommended as follows; finding the catalyst which is the most suitable with applying with the static mixer since our results showed that these two technologies can support each other if we can find the optimum conditions. The bio-catalyst shows the potential to help promoting the reaction combining with the static mixer but there might be a possibility that if another catalyst is utilized together with this bio-catalyst, its reaction could be promoted further. For example, it was stated that this bio-catalyst adsorbed the oil itself not the methanol. Therefore, if we can find the other catalyst which can adsorb methanol faster than oil, combining these two catalysts together might show a promising result.

The bigger scale reactor should also be considered as the future work. Since applying the big-scale reactor means it is one step closer into developing into a pilot scale demonstration. In our work, the big-scale reactor was utilized with a low activity catalyst but still showed good results. If the higher catalytic activity catalyst is utilized there is a possibility that it will help to promote the reaction with the use of the static mixer.

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Appendix A

BS EN 14103:2003
Fat and oil derivatives – Fatty Acid Methyl Ester Determination of ester and liolenic aci4d methyl ester content

1. Scope

This method is suitable for FAME which contain methyl esters between C_{14} and C_{24}.

2. Normative references

EN ISO 5508; Animal and vegetable fats and oils- Analysis by gas chromatography of methyl esters of fatty acids (1990)

3. Principle

Determination of the percentage of methyl esters of fatty acids present in the sample by GC according to EN ISO 5508 with internal calibration

4. Glass ware

4.1 Screw-cap vial with PTFE-faced septa. 10 mL capacity.
4.2 Volumetric flask, 50 mL capacity
4.3 Pipette, of 5 mL capacity, accurate to 0.02 mL

5. Reactants

5.1 Heptane
5.2 Methyl heptadecanoate of known purity (99 % minimum)
5.3 Methyl heptadecanoate, 10 mg/mL solution: accurately weigh approximately 500 mg of methyl heptadecanoate (5.2) in a 50 mL volumetric flask (4.2) and make up to mark with heptanes

6. Aparatus

described in EN ISO 5508

7. Sampling

A recommended sampling method is given EN ISO 5555[1]

8. Preparation of the sample

Accurately weigh approximately 250 mg of sample in a 10 mL vial (4.1), then add 5 mL of methyl heptadecanoate solution (5.3) using pipette (4.3)

9. Chromatographic analysis

Refer to EN ISO 5508 and to annex A which described, by way of indication, analysis conditions which may be used.
The chromatographic conditions (injected quantity, oven temperature, carrier gas pressure and

split flow rate) shall be adjusted so as to correctly visualize the methyl ester peaks of the lignoceric (C_{24}) and nervonic ($C_{24:1}$) acids.
The integration shall be carried out as from the methyl myristate (C_{14}) peak up to that of the methyl ester in $C_{24:1}$ taking all the peaks into consideration, including the minor ones.

10. Expression of results

10.1 Determination of ester content

The ester content, expressed as a mass fraction in percent, is calculated using the following formula;

$$C = \frac{(\sum A) - A_{E1}}{A_{E1}} \times \frac{C_{E1} \times V_{E1}}{m} \times 100\%$$

Σ_A: is the total peak area from the methyl ester in C_{14} to C_{24}
A_{E1}: is the peak area corresponding to methyl heptadecanoate
C_{E1}: is the concentration, in milligrams per milliliter, of methyl heptadecanoate solution (5.3) being used
V_{E1}: is the volume, in milliliters of methyl heptadecanoate solution being used
m: is mass, in milligrams, of sample.

NOTE

1. In the case of vegetable oils, the result of calculation based on relative area as is considered to represent a percentage by mass.
2. If the average of two determinations is higher than 100.8% then discard the results and verify the experimental conditions as well as purify of internal standard by using this method to determine the ester content of a commercial or prepared mixture.

10.2 Determination of linoleic acid methyl ester

The linoleic acid methyl ester content L, expressed as a mass fraction in percent.

$$L = \frac{A_L}{(\sum A) - A_{E1}} \times 100\%$$

A_L: is the peak area corresponding to linolenic acid methyl ester

Appendix B

Langmuir-Hinshelwood mechanism results

Batch Reactor

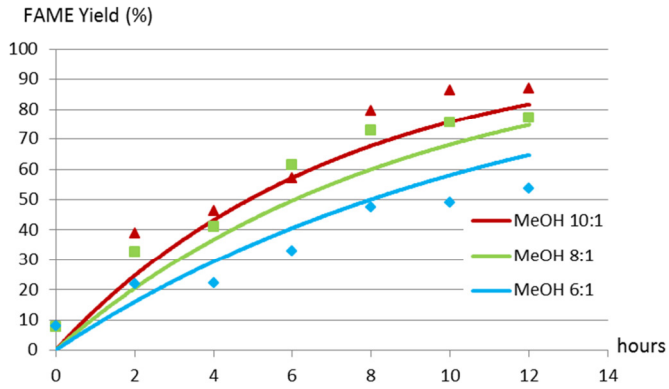

Fig. B-1 Reaction model for the batch reactor with the activated carbon catalyst

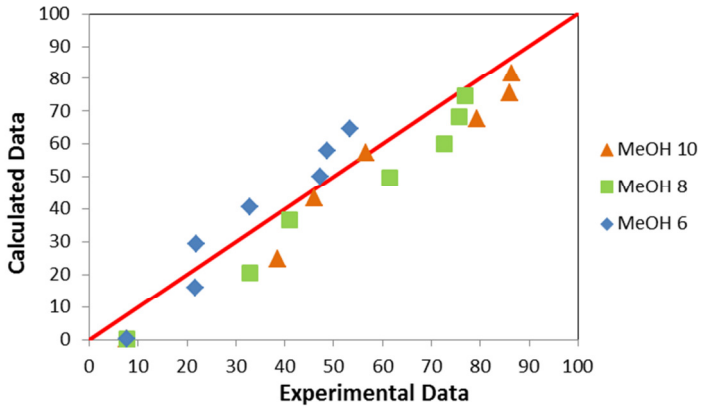

Fig. B-2 Parity plot for the batch reactor with the activated carbon catalyst

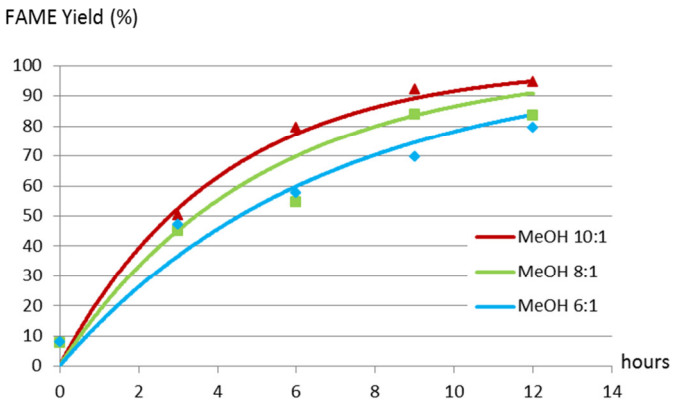

Fig. B-3 Reaction model for the batch reactor with the bio-catalyst

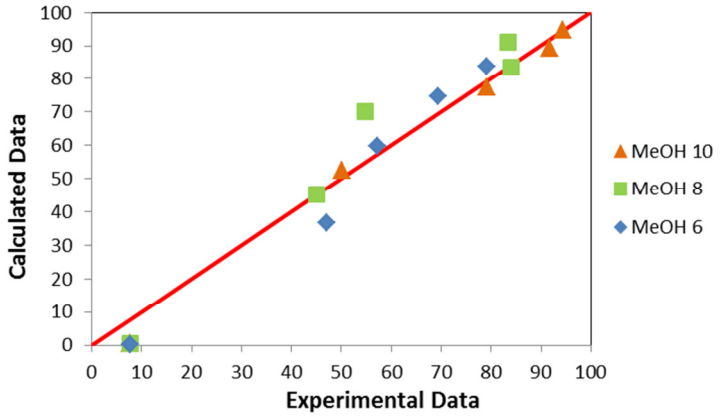

Fig. B-4 Parity plot for the batch reactor with the bio-catalyst

Circulating column with conventional mixer

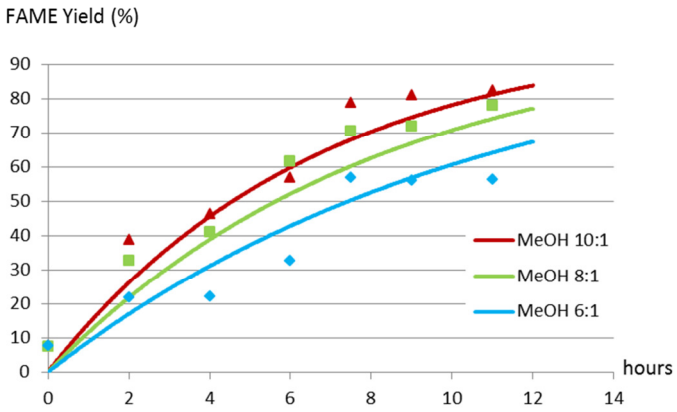

Fig. B-5 Reaction model for the circulating column reactor by the conventional mixer with the activated carbon catalyst

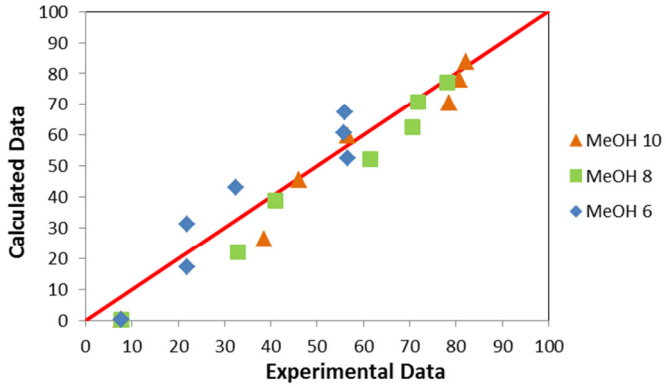

Fig. B-6 Parity plot for the circulating column reactor by the conventional mixer with the activated carbon catalyst

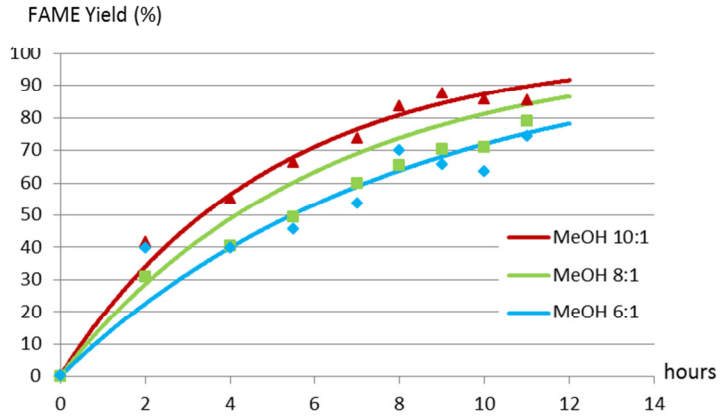

Fig. B-7 Reaction model for the circulating column reactor by the conventional mixer with the bio-catalyst

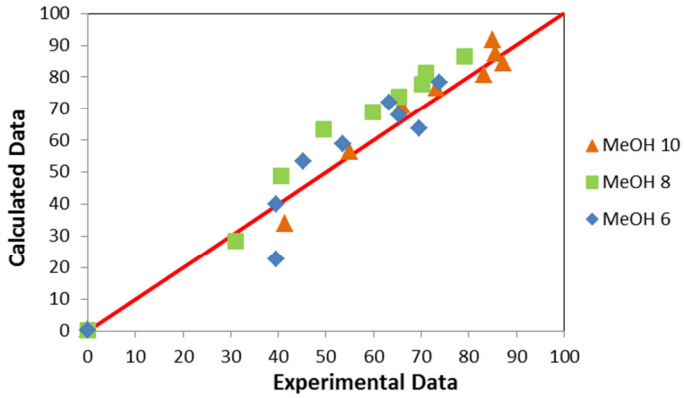

Fig. B-8 Parity plot for the circulating column reactor by the conventional mixer with the bio-catalyst

Circulating column with static mixer

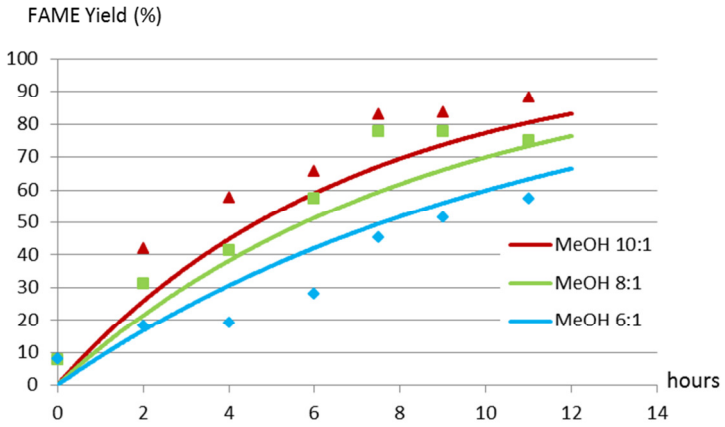

Fig. B-9 Reaction model for the circulating column reactor by the static mixer with the activated carbon catalyst

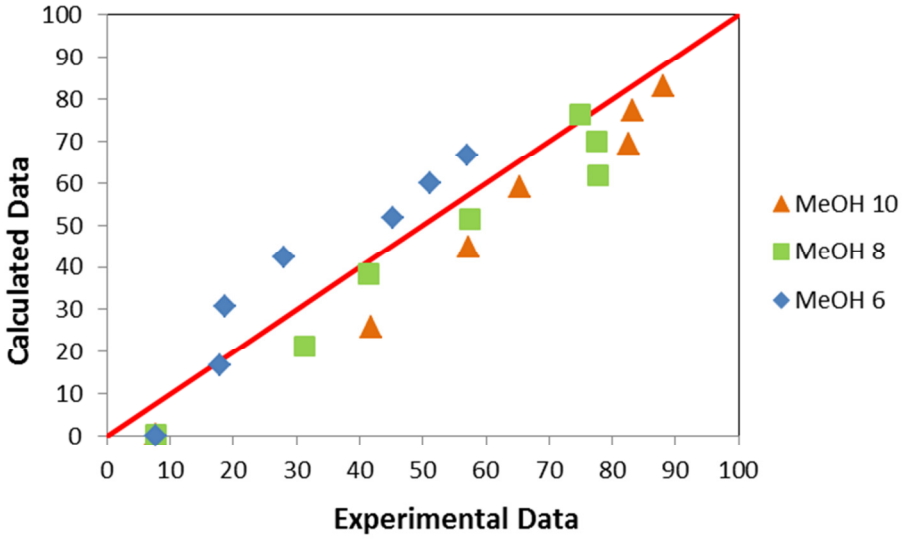

Fig. B-10 Parity plot for the circulating column reactor by the static mixer with the activated carbon catalyst

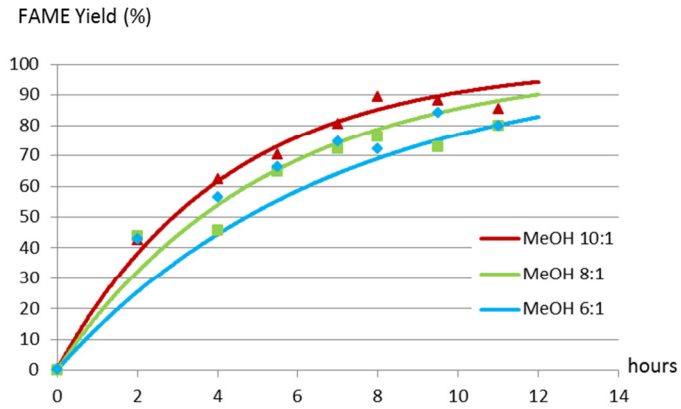

Fig. B-11 Reaction model for the circulating column reactor by the static mixer with the bio-catalyst

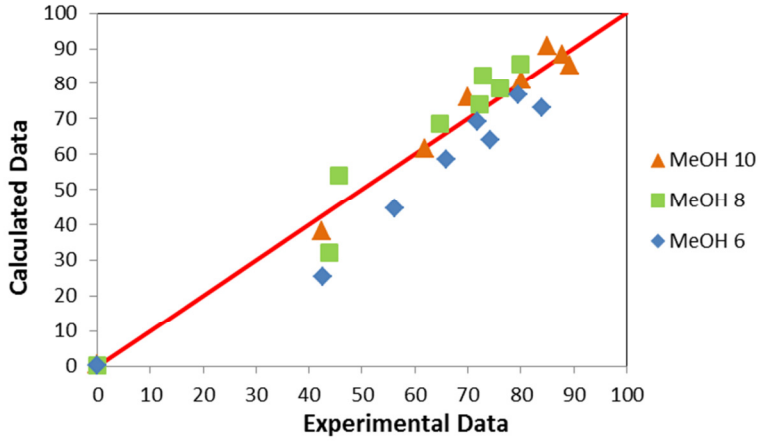

Fig. B-12 Parity plot for the circulating column reactor by the static mixer with the bio-catalyst