

Comparison of static-mixer and blade agitator reactor in biodiesel production

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Abstract: One of the difficulties faced in the current technology for biodiesel production is the requirement for rigorous mixing of methanol with the feedstock oil in the reactor. Utilization of blade mixer is limited by the immiscible state of those substances. This research is devoted to the assessment of static-mixer utilization in a transesterification reactor for biodiesel production in terms of kinetics reaction (reaction rate coefficient k , activation energy E_a , and collision factor or coefficient factor A). The experiments were conducted by reacting palm oil (triglyceride or TG) with methanol (MeOH) at 50, 55, 60, 65, and 70°C, using potassium hydroxide (KOH) as catalyst. Molar ratio of TG and MeOH was 1 : 10.5 and KOH used was 1% of palm oil weight. Transesterification process using blade agitator with the same reaction condition was performed as base of comparison to those of static-mixer. The experiments showed that static-mixer has significant effect in reducing reaction time to reach required fatty acid methyl ester content (FAME) i.e. 96.5% than those of blade agitator. Transesterification reaction time with static-mixer is shorter than with blade agitator for all temperature levels. Reaction temperature of 65°C with five minutes of reaction time is demonstrated the best condition for running the static-mixer reactor. The static-mixer and blade agitator experiments exhibited two stages transesterification that give the initial and the final activation energy (E_{a1} and E_{a2}) and the initial and final collision factor (A_1 and A_2). The value of E_{a1} , E_{a2} , A_1 , A_2 for static-mixer experiments is 0.13 J/mol, 37.1 J/mol, 4.8, and 1,256, respectively. Meanwhile the value of E_{a1} , E_{a2} , A_1 , and A_2 for blade agitator experiments is 0.81 J/mol, 6.9 J/mol, 2.0 and 11.8, respectively.

Keywords: static mixer, blade agitator, activation energy, utilization, biodiesel, collision factor, transesterification.

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1 Introduction

Nowadays, most of the world energy needs are

supplied through petroleum fuels, coal and natural gases, which become very depleted due to intensive exploitation their deposit (Meher et al. 2006). Biodiesel is one of the important renewable energy as the substitute of the petroleum for transportation and household uses and it is regarded as a promising diesel replacement fuel. Biodiesel as an alternative fuel will have to take more important role as the world energy supply for future life since it can be produced from renewable resources such as vegetable oils or animal fats (Best, 2006). Biodiesel as a substitution for diesel fuel use has many benefits, such as for reduction dependency on foreign oil markets, substitution for diesel fuel or blends with diesel, and

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reduction vehicle emissions (Wirawan et al., 2008; Ajav et al., 2002). Moreover biodiesel is non-toxic and biodegradable. The existence of biodiesel also is very useful mainly in the remote area of Indonesia where diesel fuel is not available and its price become very expensive.

To produce biodiesel, catalytic and non-catalytic transesterification reactors have been developed by many researchers but the alkali-catalyzed process for biodiesel production is currently the method being implemented by biodiesel industry (Freedman et al., 1984; Nouredini and Zhu, 1997; Mittelbach and Remschmidt, 2004; Zhang, 2003; Kusdiana and Saka, 2001; Yamazaki et al., 2007). At present, the high cost of biodiesel is the major constrain to its commercialization. Numerous process and research for biodiesel production and reactor have been developed to reduce the high cost of biodiesel, especially for those methods concentrating on minimizing the raw materials cost and production cost as well. To be feasible, alternative fuel like biodiesel should be economically competitive when consumed, technically efficient when processed, and ready available when needed (Mootabadi et al., 2008; Petterson, 1993).

One of the difficulties faced in the current technology for biodiesel production is the requirement for rigorous mixing of methanol with the feedstock oil in the reactor. Utilization of blade mixer has limitation due to the immiscible state of those substances. Long reaction time as caused by the low reaction rate is directly related to low collision frequency among reactants. This collision frequency can be enhanced by better mixing mechanism during the process. Most of industrial biodiesel reactor using blade agitator for mixing, which creates a main flow in the reaction tank with circulation on axial and tangential direction, and with little turbulency (Paul et al., 2003). Reaction time for alkali-catalyzed transesterification is about 60-90 min to obtain approximately 90%–98% oil conversion to methyl esters (Zhang, 2003; Darnoko and Cheryan, 2000; Alamu et al., 2007).

Utilization of static-mixer to replace the blade agitator is potential to improve the mixing process in biodiesel reactor. Static mixer is a motionless mixers, comprises

of series of geometric mixing elements fixed within a pipe, which use the energy of the flow stream to create mixing between two or more fluids. Static-mixer performs a series of mechanism to mix reactants, namely dividing, rotating, channeling, or diverting the flow before recombining it. Static-mixer 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. Static-mixer mostly is applied in polymer processing. The power input to the mixing process is a result of pressure loss through the mixer (Oldshue, 1983; Paul et al., 2003). They are very effective in mixing liquids that are not readily miscible under normal conditions. Thompson (2007) has studied the possibilities of using static-mixer as a continuous-flow reactor for biodiesel production in laboratory scale. Biodiesel (canola methyl ester) was produced under varying conditions using a closed-loop static-mixer system. Sodium methoxide was used as the catalyst. Process parameters of flow rate or mixing intensity, catalyst concentration, reaction temperature, and reaction time were studied. The most favorable conditions for completeness of reaction were at 60°C and 1.5% catalyst for 30 min of transesterification reaction time. There is no previous studies related to the comparison between static-mixer and blade agitator process in biodiesel production. Jaszczu et al. (2009) reported the study flow mixing process in a static mixer for two immiscible viscous fluids. A comparison of numerical results and measured data for flow mixing process in circular duct has been made to check the results of numerical simulations. The mixing efficiency function has been proposed to performed process optimisation and obtains the most efficient conditions for industrial mixing process.

This paper was aimed at assessing the kinetics transesterification reaction (reaction rate coefficient k , activation energy E_a , and collision factor A) using static-mixer reactor at different temperature levels of 50, 55, 60, 65, and 70°C, respectively. To examine its utilization, transesterification process using blade agitator was also conducted at the same temperature reaction levels and finally their results were compared and

reviewed.

2 Materials and methods

2.1 Materials

Refined bleached deodorized Palm oil was obtained from PT. Royal Industries karawang, West Java, Indonesia with the following characteristics: acid value was 0.41 mg KOH/g oil, saponification value was 212.9 mg KOH/g oil, free fatty acid or FFA was 1 mg KOH/g oil, moisture content was 0.3%, and density was 0.84 g/mL. MeOH 99% and KOH as catalyst were purchased from Setia Guna Co. Bogor, Indonesia.

Analytical grade of ethanol, toluene, chloroform, chloric acid, periodic acid, potassium iodide, potassium dichromate, fenolftaline indicator, oxalic acid, natrium borax, and $\text{Na}_2\text{S}_2\text{O}_3$ were used to analyse the biodiesel quality. These materials were also obtained from Setia Guna Co. (Bogor, Indonesia) and were used to analyze some quality parameters on biodiesel such as free glycerol, total glycerol, methyl ester, saponification value, acid number, and FFA based on AOCS Official Method. The research was conducted at March 2008 until April 2009 in Center for Research of Agro-based Industry (CABI) Ministry of Industry, Republic of Indonesia.

2.2 Static-mixer reactor /vessel

The experiment was conducted by using a laboratory scale static-mixer reactor (25 L maximum capacity) equipped with a static-mixer elements for mixing reactant, a condenser for condensing methanol, a pump for reactant circulation (130 W), an inlet section for feeding of palm oil (feedstock), methanol and catalyst, two sample collection valve (top and bottom), and a heater for heating reactant (1,500 W). A settling/washing tank with capacity of 32 L was used to separate biodiesel from glycerol and to wash impurities from crude biodiesel. The Static-mixer consisted of 5 elements and each element had 6 cm length and 5 cm width. The static mixer was installed in mixing tube (pipe) with dimension of 30 cm length and 5 cm internal diameter. The reactor tank was also equipped with a blade agitator which was used to obtain data for comparison. Reactant mixture flow rate in the static mixer is 1.25 m/s (maximum speed). The schematic diagram of static-mixer is shown in

Figure 1.

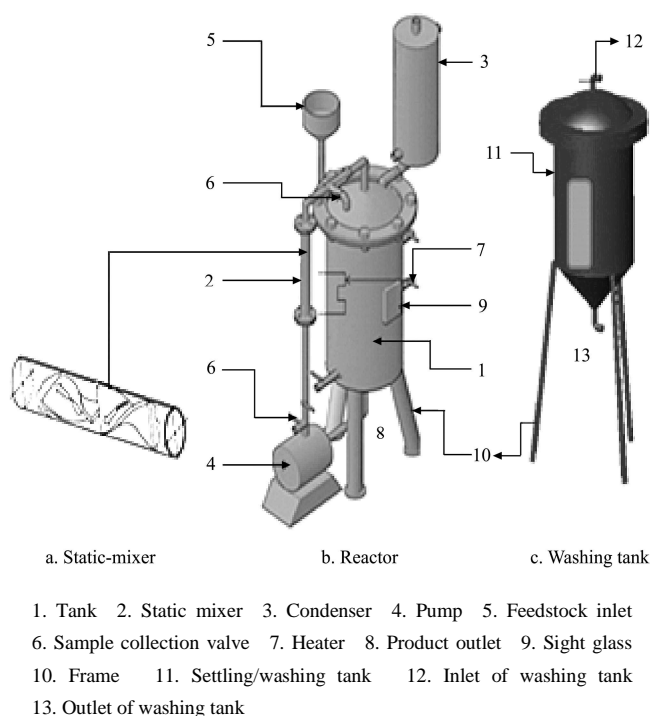


Figure 1 A static-mixer, b reactor, and c washing tank

2.3 Experimental procedures

Transesterification process was initially charged with palm oil (TG) in reactor tank and heated to the desired temperature (50, 65, 60, 65, or 70°C). These temperatures were selected due to boiling temperature of methanol (e.g. 64.5°C). Liquid Meoh was heated to desired temperature and pumped to the reactor tank. The reactions were conducted under atmospheric pressure with oil to methanol ratio 1:10.5. Koh used was 1% of the palm oil weight, and the excess of Meoh was given in order to make the reaction move to the products direction since methanolysis is a reversible reaction. Based on this molar ratio, the volume of palm oil was 11 L, MeOH was 5.5 L, and KOH was 101 g (the total volume of reactants was 16.5 L).

The circulation pump was operated at maximum speed (1.25 m/s). The measurement of flow rate was taken manually by measuring the amount of biodiesel volume per minute divided by the cross section of the pipe. The position of flow measurement is shown in Figure 2. The samples were collected at schedule time of 1, 5, 10, 15, 20, 30, 40, 50, 55, 60, 65, 70 and 90 min. The samples collected in glass jar were then settled until

two layers of crude biodiesel (upper layer) and glycerol (bottom layer) was appeared. The crude biodiesel was analysed by AOCS standard for free glycerol, total glycerol (AOCS: Ca 14-56), methyl esters, acid number (AOCS: Cd 3-63), saponification value (AOCS: Cd 3-25), and viscosity. AOCS standard for calculating methyl ester content is presented at Equation (1). Schematic flow diagram of reactor used in transesterification experiment is shown in Figure 2.

$$ME \left(\% \frac{W}{W} \right) = 100(A_s - A_a - 4.57G_t) / A_s \quad (1)$$

Where: A_s : Saponification value of biodiesel determined according to AOCS Official Method Cd 3-25 (mg KOH/g biodiesel); A_a : Acid value of biodiesel determined according to AOCS Official Method Cd 3-63, (mg KOH/g biodiesel); G_t : Total glycerol in biodiesel determined according to AOCS Official Method Ca 14-56 (% w/w).

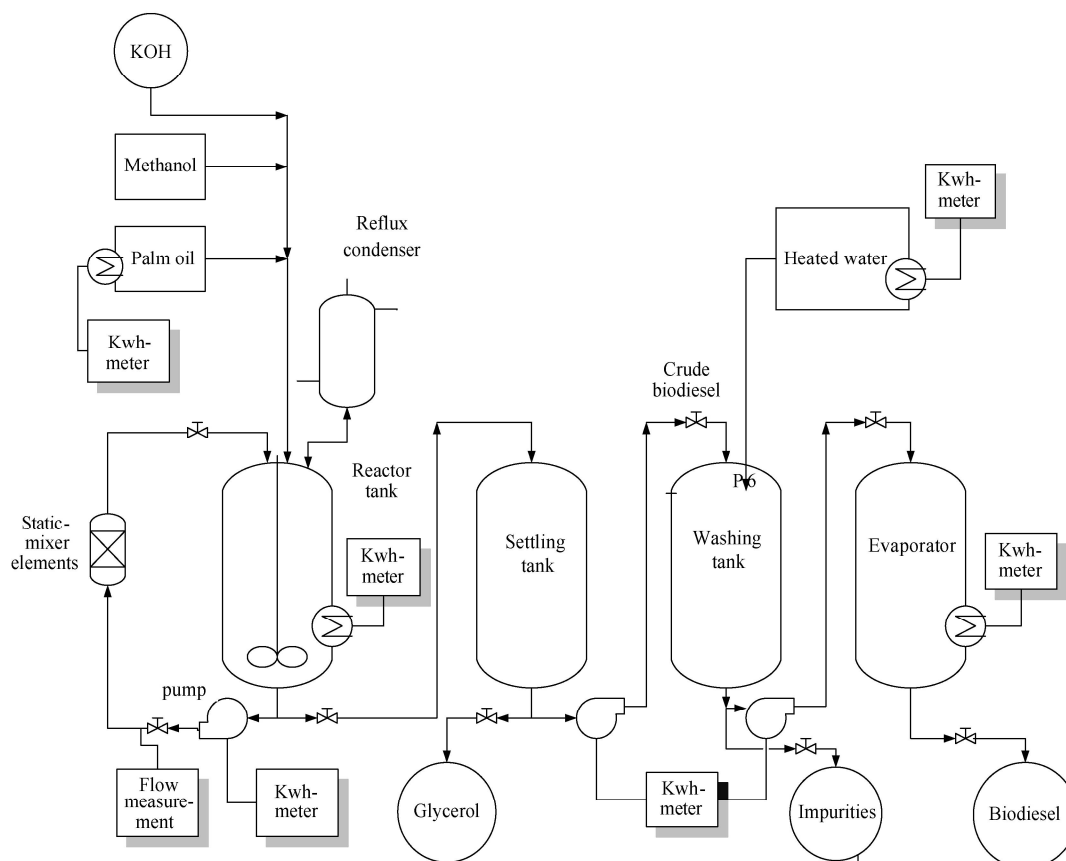


Figure 2 Schematic flow diagram of the reactor used for transesterification experiments

3 Results and discussion

3.1 Reaction rate

The typical concentration curves for the transesterification reaction using static-mixer and blade agitator are presented in Figure 3 and 4. The figures showed the progress of the transesterification reaction during 90 min reaction time. The figures revealed that the production rate of methyl ester using the static-mixer was faster than that of blade agitator during the initial period of the process. The experiments showed that static-mixer has significant effect on reducing reaction

time to reach required fatty acid methyl ester content (FAME) i.e. 96.5% than those of blade agitator. Transesterification reaction time with static-mixer was shorter than with blade agitator for all temperature levels. This is also confirmed by the measured viscosity and acid value of the biodiesel from both agitation system, as shown in Figure 5 and 6, respectively. This result is expected due to the distributive mixing from static-mixer will create stretching, dividing and reorienting the flow of the reactants or biodiesel in order to eliminate local variations in material distribution and produce a more homogeneous mixture. Distributive mixers must impose

high strain on the material together.

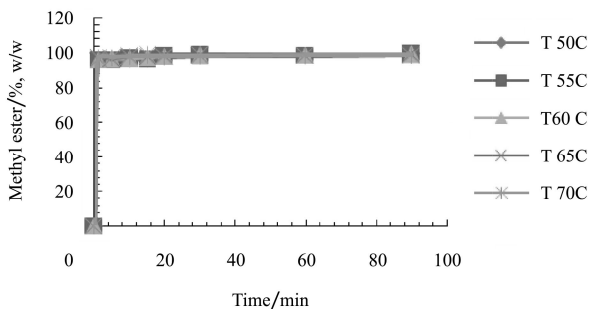


Figure 3 Effect of temperature on FAME formation using static-mixer

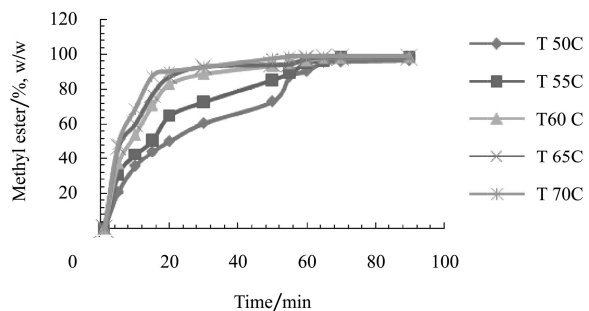


Figure 4 Effect of temperature on FAME formation using blade agitator

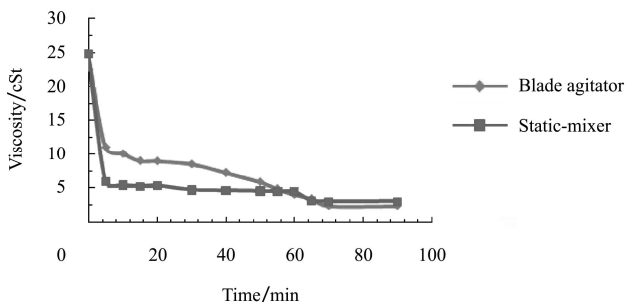


Figure 5 Viscosity of biodiesel produced by static-mixer and blade agitator at 70°C

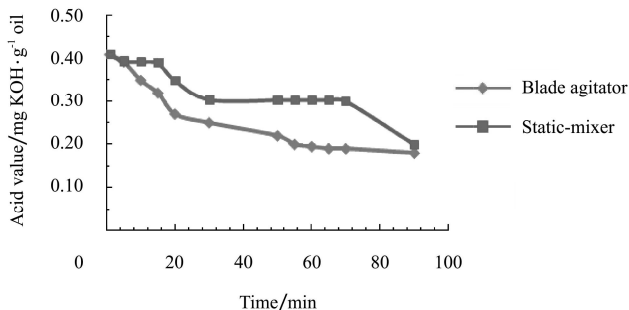


Figure 6 Acid value of biodiesel produced by static-mixer and blade agitator at 70°C

With splitting and reorienting the flow (Kenics 2007). Moreover, the effect of reaction temperature to the reaction time is not significant when using the

static-mixer. Conventional use of blade agitator is influenced highly by the reaction temperature as can be seen in Figure 7 and 8.

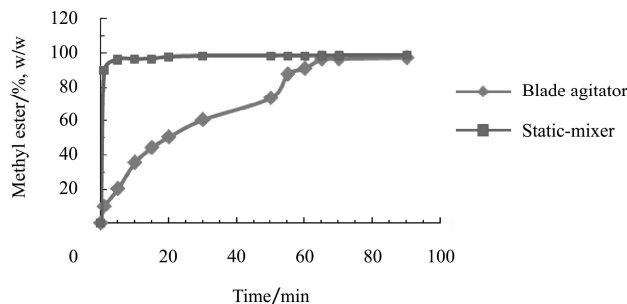


Figure 7 FAME production using static-mixer and blade agitator at 50°C

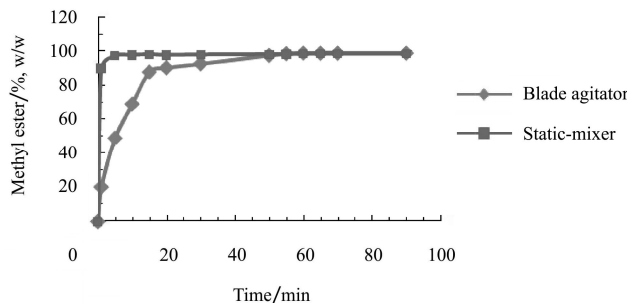


Figure 8 FAME production using static-mixer and blade agitator at 70°C

The differences in the reaction rate can be clarified through reaction kinetics study. Normally, Transesterification reaction proceeds in three steps i.e. TG reacts with methanol to produce diglycerides (DG), which in turn reacts with MeOH to produce monoglyceride (MG), finally, MG reacts with MeOH to give glyceride (GL). At each reaction step, one molecule of ME is produced for each molecule of MeOH consumed.

Kusdiana and Saka (2001) defined a simpler mathematical model for overall reaction in transesterification reaction by ignoring the intermediate reaction (DG) and (MG), so the 3 steps can be simplified to be one step as follows (Equation (2)):



where k is the rate constant of the overall reaction in the transesterification reaction. It was assumed that reactant of MeOH will remain unchanged because of the excess of MeOH. This reaction is assumed to proceed in the first order reaction as a function of the

concentration of triglycerides (TG) and reaction temperature. The rate constant can be determined based on the decreased amount of one reactant e.g. TG or alternatively based on the increased amount of the product that occurs in some reaction time interval (Barrow, 1973; Steinfeld et al., 1989). In this work, the reaction rate is predicted from the increase amount of one product, that is ME as can be described in Equation (3)

$$\frac{d[ME]}{dt} = -k[ME] \quad (3)$$

where $[ME]$ refers to the content of methyl esters that result after the treatment was carried out. Assuming that the initial concentration of $ME=0$ at time $t=0$ and it increase to ME at some later time t , the integration gives Equation (4) and (5), and finally k can be calculated based on Equation (6).

$$\int_{ME,0}^{ME,t} \frac{d[ME]}{[ME]} = -k \int_0^t dt \quad (4)$$

$$\ln \frac{[ME,t]}{[ME,0]} = -kt \quad (5)$$

$$k = -\frac{\ln[ME,t] - \ln[ME,0]}{t} \quad (6)$$

Since the FAME production is obviously much faster at the initial stage of the process if using static-mixer, the reaction rate is evaluated in two stages, i.e. the initial rate (k_1) and final rate (k_2) for both mixing mechanism. The change from initial to final rate is rather arbitrary, but still the result shows consistency. The result of k values for static-mixer and blade agitator is shown in Table 1, which clearly shows that the initial reaction rate (k_1) by static-mixer are one order higher than that by blade agitator. However, the final reaction rate of blade agitator are higher than that of static-mixer, which is

Table 1 Rate constant of palm oil transesterification using static-mixer and blade agitator

T /°C	Static-mixer				Blade agitator			
	k_1 /min ⁻¹	R^2 /%	k_2 /min ⁻¹	R^2 /%	k_1 /min ⁻¹	R^2 /%	k_2 /min ⁻¹	R^2 /%
50	4.554	100	0.0010	92.1	0.369	80.8	0.0060	70.4
55	4.556	100	0.0011	91.9	0.371	81.2	0.0063	70.8
60	4.556	100	0.0012	87.6	0.372	81.3	0.0065	71.0
65	4.565	100	0.0018	94.0	0.372	80.8	0.0068	80.9
70	4.566	100	0.0022	96.4	0.377	82.1	0.0070	66.0

reasonable since the amount of reactant is still higher in the reactor. Figurative presentation of the reaction rate as a comparison between the static-mixer and blade agitator for reaction temperature of 60°C is shown in Figure 9.

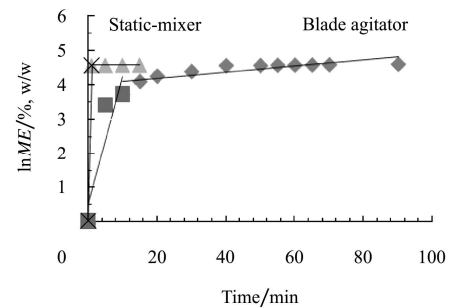


Figure 9 Concentration of ME in palm oil transesterification using static-mixer and blade agitator at 60°C

3.2 Activation energy (E_a) and collision factor (A)

According to the Arrhenius equation (Atkins, 1986), the correlation among constant rate, activation energy and collision factors can be represented by Equation(7):

$$\ln k = \ln A - E_a/RT \quad (7)$$

Where E_a is the activation energy, R is the molar gas constant (0.00813 kJ/(mol·k) and A is the collision factor. The data in Table 1 were used to determine E_a and A from plot of k versus the reciprocal of absolute temperature ($1/T$) as shown in Figure 10 and 11 for static-mixer and Figure 12 and 13 for blade agitator. The activation energy (E_a) and collision factor (A) as calculated from Equation (7) for both initial and final stage of the reaction is given in Table 2. The table also shows the results from with other studies. The value of E_a and A for the experiment, respectively was 0.13 J/mol and 4.78 min⁻¹ at the initial stage and 37.12 J/mol and 1,265 min⁻¹ at the final stage by using the static-mixer. It is difficult to compare the value with the other studies due to the adoption of two stages of rates in this study.

The investigation in activation energy and reaction rate coefficient also conducted by Darnoko and Cheryan (2000) for palm oil in a batch reactor using KOH as catalyst at 60°C. E_a of for hydrolysis of monoglyceride (MG) and k during transesterification was found to be 0.026 kJ/mol and 0.141 min⁻¹, respectively. In their experiments, the E_a was smaller and k value was higher

than those in our experiments. In addition, the time required to reach standard methyl ester content was 90 min.

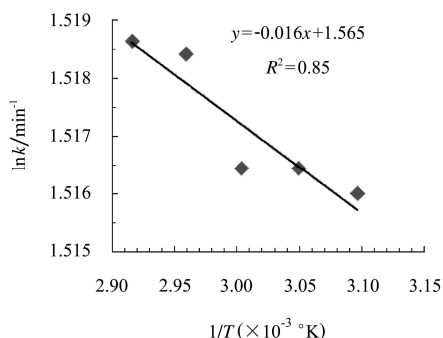


Figure 10 Initial stage reaction rate constant in Arhenius plot during the transesterification (static-mixer)

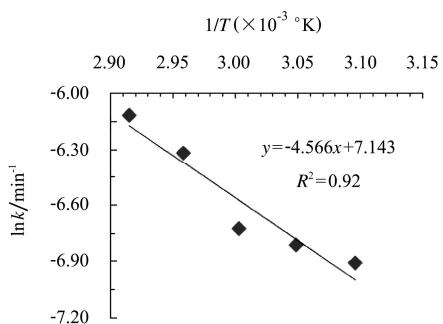


Figure 11 Final stage reaction rate constant in Arhenius plot during the transesterification (static-mixer)

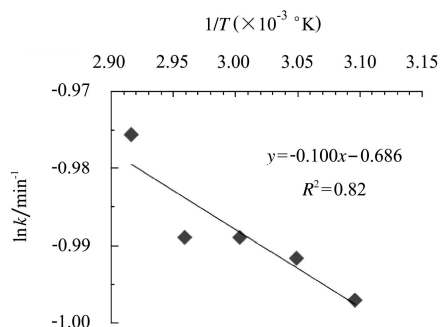


Figure 12 Initial stage reaction rate constant in Arhenius during the transesterification (blade agitator)

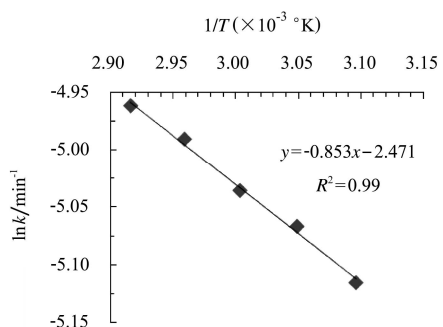


Figure 13 Final stage reaction rate constant in Arhenius during the transesterification (blade agitator)

Table 2 Comparison of Energy activation (E_a) and Collision factor (A)

Experimental Results			
E_a /J · mol ⁻¹	A /min ⁻¹	Experiment stages	
0.13	4.78	Initial stage static-mixer	
37.12	1,265	final stage static-mixer	
0.81	2	initial stage blade agitator	
6.93	11.83	final stage lade agitator	
Previous Studies			
E_a /J · mol ⁻¹	A /min ⁻¹	Methods	References
0.026	-	batch reactor (catalytic)	Darnoko and Cherryan(2008)
31.0 × 10 ³	4.2	bubble column reactor (superheated-non catalytic)	Joelianingsih et al. (2008)
69.0 × 10 ³	6,936	supercritical MeOH (non-catalytic)	Kusdiana and Saka(2001)

The constant rate of reaction rate for non-catalytic rapeseed oil transesterification in supercritical MeOH as reported by Kusdiana and Saka (2001) was 0.041 min⁻¹ at 543° K and 12 MPa, while E_a and A was 69 kJ/kmol and 6,936 min⁻¹, respectively. The rate constant was higher than the value obtained from static-mixer experiments. The E_a and A value was also higher than that in our experiments. Comparing to this experiment result, the differences are due to the reaction condition used. The Kusdiana and Saka's experiment was performed under supercritical condition (40 MPa), where the polarity of MeOH would decrease. As a result, non-polar TG can be solvated with supercritical MeOH to form a single phase of vegetable oil/MeOH mixture. Table 2 shows the results summary of energy activation and collision factor experiments from other sources.

The study about activation energy and collision factor also reported by Joelianingsih et al. (2008) for palm oil transesterification in a bubble column reactor by semi batch reactor in absence of catalyst. In Joelianingsih's experiments, transesterification reaction was done under atmospheric pressure, superheated MeOH vapor, and without stirring. Lower value of E_a and A were found to be 31 kJ/mol and 4.2 min⁻¹, respectively. While Joelianingsih's experiment was done under MeOH bubbles are dispersed in oil phase, and the system consists of two phases. The reaction rate might be controlled by the mass transfer at the gas-liquid interface.

These mixing mechanism consequently will influence the value of E_a , A , k and reaction time.

4 Conclusions

The following conclusions can be drawn from the transesterification experiments of biodiesel production from refined palm oil using static-mixer reactor and blade agitator:

Transesterification reaction time to reach standard methyl ester content by static-mixer is shorter than those by blade agitator, which indicates that mixing mechanism by static-mixer is more effective.

The Static-mixer gives one order higher reaction rate during the initial stage of the reaction compared to blade agitator.

The experiment results for static-mixer show the value for E_{a1} , E_{a2} , A_1 , and A_2 i.e. 0.13 J/mol, 37.1 J/mol,

4.8 min⁻¹ and 1,256 min⁻¹, respectively. Meanwhile the value of E_{a1} , E_{a2} , A_1 , and A_2 for blade agitator experiments is 0.81 J/mol, 6.9 J/mol, 2.0 min⁻¹ and 11.8 min⁻¹, respectively.

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