

## Modified Kinetic Model of Biodiesel Production from Crude Palm Oil with Agitation to Increase Mixing Performance

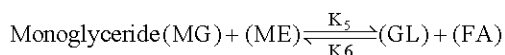
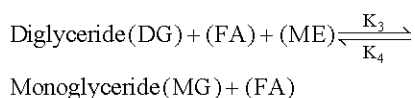
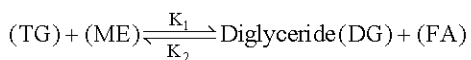
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**Abstract:** This study focuses on the effect of mixing on transesterification in biodiesel production. A stirred-tank reactor assisted by ultrasonic wave was used in experiment. Crude Palm Oil (CPO) was used as raw material in transesterification. The optimum condition for giving the highest yield is at temperature of 60°C, CPO to Methanol ratio 1:9 and Na<sub>2</sub>CO<sub>3</sub>/ceramic 3% by weight of CPO. The kinetic model fitted experimental data well and can be used to describe the mixing performance. Biodiesel production was strongly affected by the level of mixing, thus the stirring speed. At 300 rpm stirring speed, productivity of biodiesel is higher than 90% conversion of triglyceride. Ultrasonic wave did not increase biodiesel conversion but significantly enhanced the reaction rate.

**Key words:** Transesterification, biodiesel, kinetics, mixing, mass transfer, reaction

### INTRODUCTION

Due to increasing environmental concerns, global warming, air pollutions and decreasing fossil fuels the priority of using alternative environmental friendly fuels and renewable fuels sources have encouraged researchers to investigate alternative sources derived from plant oils or animal fats (Sharma *et al.*, 2008; Atadashi *et al.*, 2011). Biodiesel is a Fatty Acid Methyl Ester (FAME) that can be produced from transesterification of degummed crude palm oil. Triglyceride (TG) is an active reactant in crude palm oil for transesterification which reacts with Methanol (ME) in the presence of catalyst to produce FAME (FA) and Glycerol (GL) as a by-product as the following mechanisms (Lam *et al.*, 2010; Shahid and Jamal, 2008; Fukuda *et al.*, 2001; Freedman *et al.*, 1986; Nouredini and Zhu, 1997):



Several approaches have been used both in industrial practices and in the literature to improve process efficiency, minimize waste and improve product quality.

Recently, many researchers are focusing on heterogeneous catalysts, reactant's ratio, microwave-and ultrasound-assisted mass transfer and reactions, novel mixing or even reactive-separation to achieve the goals (Colucci *et al.*, 2005; Silva *et al.*, 2010; Simasatitkul *et al.*, 2011; Ganesan *et al.*, 2009; Shahla *et al.*, 2010; Lee *et al.*, 2009; Anastopoulos *et al.*, 2013; Margaretha *et al.*, 2012; Likozar *et al.*, 2016; Iyyaswami *et al.*, 2013; Kim *et al.*, 2015; Xiang *et al.*, 2016; Maran and Priya, 2015; Reyman *et al.*, 2014). On the other side of knowledge base the complex nature of mass transfer and the reactions in the process requires insightful understanding on how various factors affect the process efficiency in order to realize its full potential. The modeling approach will provide the essential information used in process design, scale-up, control and optimization. Therefore there has been considerable attention paid by many researchers (Hong *et al.*, 2011, 2012; Fabiano *et al.*, 2012; Aniya *et al.*, 2015; Roy *et al.*, 2014; De Oliveira *et al.*, 2005). Yet, there are many missing understandings to be filled up.

This study aims not only to show quantitatively how much indirect-ultrasound wave, a choice of applying heterogeneous catalyst and mechanical mixing promote the biodiesel conversion efficiency but we also attempt to give some insight on the mechanism of the batch process.

In our study the reaction batches were isothermally operated so we can assume that all rate constants are not

a function of temperature. Thus, the kinetic model of the reaction can be written as follows (Vincente *et al.*, 2005):

$$\frac{dC_{TG}}{dt} = -k_1 C_{TG} C_{ME} + k_2 C_{DG} C_{FA} \quad (1)$$

$$\frac{dC_{DG}}{dt} = k_1 C_{TG} C_{ME} - k_2 C_{DG} C_{FA} - k_3 C_{DG} C_{ME} + k_4 C_{MG} C_{FA} \quad (2)$$

$$\frac{dC_{MG}}{dt} = k_3 C_{DG} C_{ME} - k_4 C_{MG} C_{FA} - k_5 C_{MG} C_{ME} + k_6 C_{GL} C_{FA} \quad (3)$$

$$\frac{dC_{GL}}{dt} = k_5 C_{MG} C_{ME} - k_6 C_{GL} C_{FA} \quad (4)$$

$$\frac{dC_{FA}}{dt} = k_1 C_{TG} C_{ME} - k_2 C_{DG} C_{FA} + k_3 C_{DG} C_{ME} - k_4 C_{MG} C_{FA} + k_5 C_{MG} C_{ME} - k_6 C_{GL} C_{FA} \quad (5)$$

$$\frac{dC_{ME}}{dt} = -k_1 C_{TG} C_{ME} + k_2 C_{DG} C_{FA} - k_3 C_{DG} C_{ME} + k_4 C_{MG} C_{FA} - k_5 C_{MG} C_{ME} + k_6 C_{GL} C_{FA} \quad (6)$$

Where:

$C_i$  = Concentration of component

I = Unit of mole/L

t = Time in minute

k = Integer subscripts are rate constants in unit of L/mole•min

These well-established reaction steps and their corresponding ODE (Eq. 1-6) form a basis for the discussion in the following sections.

## MATERIALS AND METHODS

Firstly, crude palm oil was degummed by adding 1% by weight phosphoric acid into CPO at 80°C. Then Free Fatty Acid (FFA) was reduced to <0.5% by adding 3% by weight sulfuric acid into CPO and using various molar ratios of CPO-methanol at reaction temperature of 60°C. The degumming steps decreased FFA in CPO to be not larger than 0.2% by weight which was within standard for biodiesel production. Catalysts used in experiments are ceramic rings coated by NaCO<sub>3</sub>. Many factors were varied in this study to investigate their effects on rate of transesterification. The condition with molar ratio 1:9 of triglyceride-methanol mixture reacting at temperature of 60°C in the presence of catalysts 3% by weight of CPO with stirring speed at 250 rpm assisted by indirect ultrasonic wave at 35 kHz was used as default if no any other conditions were specified. Kinematic viscosity of

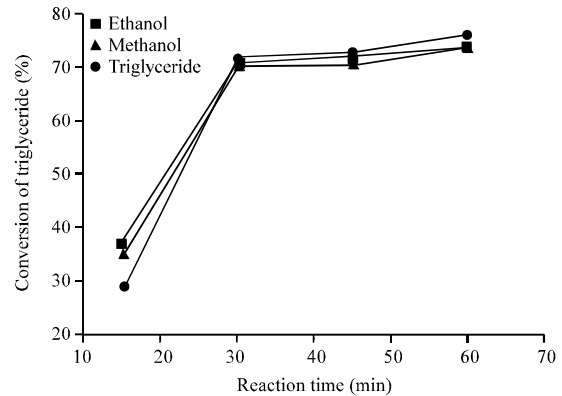


Fig. 1: Transesterification at the default condition (1:9 ratio)

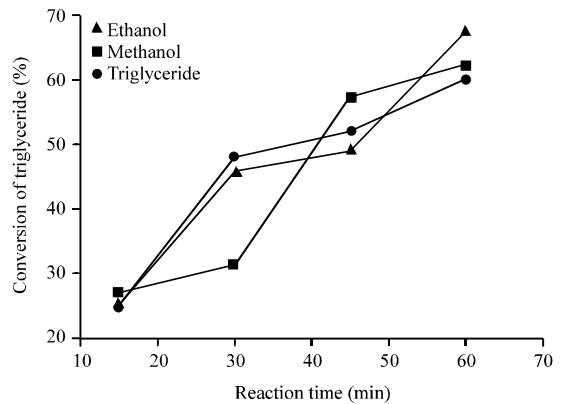


Fig. 2: Transesterification of molar ratio 1:12 of triglyceride-methanol mixture and others as default

the mixture at default condition was  $7.5 \times 10^{-7}$  m<sup>2</sup>/sec. Impeller diameter used for agitation was 0.073 m. Kinetic model from Eq. 1-6 was used to fit data in Fig. 4 and later figure for concentration of biodiesel (fitted triangles by solid line), concentration of triglyceride (fitted circles by dash line) and concentration of glycerol (fitted stars by dot line). There are three different lines in Fig. 1 and 2 which each line stands for each duplicate.

## RESULTS AND DISCUSSION

**Effect of ratio of reactants on distribution of oil bubbles in methanol:** Triglyceride-to-methanol ratio was varied from 1:18-1:6 which equivalent to molar fraction from 0.053 -0.143, respectively. It is found that the molar ratio of 1:9 produced higher conversion within a shorter time than other ratios as shown in Fig. 1. For using larger amount of ethanol such as 1:12 as shown in Fig. 2, reaction progressed at the beginning was very slow due

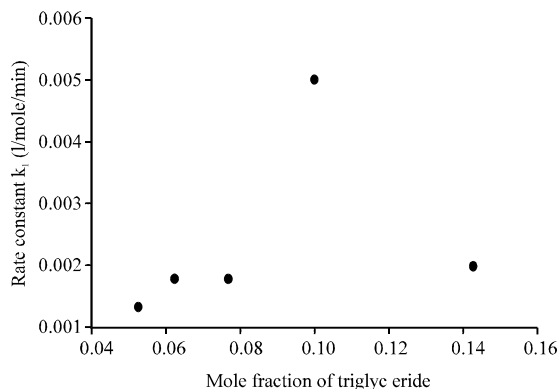


Fig. 3: Relationship between rate constant of triglyceride consuming and initial mole fraction of TG-ME mixture

to low mixing performance. Different reactant concentrations mixed by stirring distribute different sizes of oil bubbles in methanol and will affect interfacial mass transfer rate. In this study, reaction progress at the beginning is strong characterized by rate constant  $k_1$ . The rate constant is largest at molar fraction of 0.1 (the molar ratio 1:9) as shown in Fig. 3.

**Effect of catalysts loading on rate of transesterification:**

At a certain condition of the molar ratio 1:9, reaction temperature of 60°C and at fixed stirring speed of 250 rpm the reaction rate dramatically increased at the beginning of reaction time. This can be obviously seen with catalysts loading of 1.5% by weight which was in between the conditions in Fig. 4a, b. To make sure that catalysts' loading is sufficient, excess amount of catalysts loading of 3% by weight was used as default for other experiments.

**Effect of temperature on rate of transesterification:**

In this study the rate of triglyceride consumed was focused since its kinetics controls the rate of transesterification. Temperatures of 40, 50 and 60°C were performed and rate constant ( $k_1$ ) was determined to estimate activation energy required to change triglyceride to diglyceride and further produced biodiesel. At beginning of reaction time, temperature had strong effect on the reaction and the activation energy of transesterification at our default condition was 25.5 kJ/mole and pre-exponential term is 2,600 L/mole·min calculated respectively from the slope and from intercept point on y-axis of fitting line in Fig. 5 according to the Arrhenius's law (Choudhury *et al.*, 2014).

**Effect of mixing performance on rate of transesterification:**

From the kinetic model for

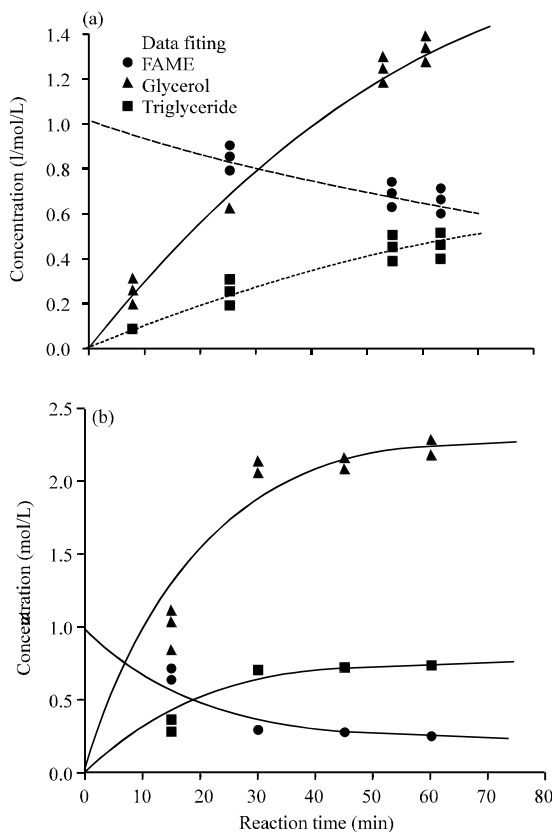


Fig. 4: Transesterification a) With 1.0% catalysts loading and b) With 3.0% catalysts loading and others as default

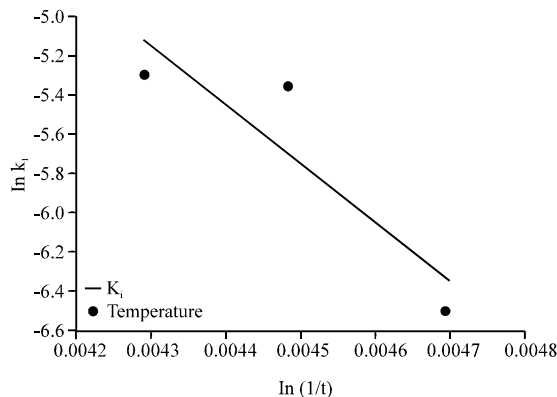


Fig. 5: Fitting of rate constant ( $k_1$ ) and temperature

transesterification the main reason why the reaction at the beginning occurs at vary small rate is that triglyceride (oil) and methanol were immiscible and mass transfer was significantly affected, causing slow biodiesel production rate if stirring speed of agitation is not sufficient. At the initial time of reaction, some sets of data may not well fit

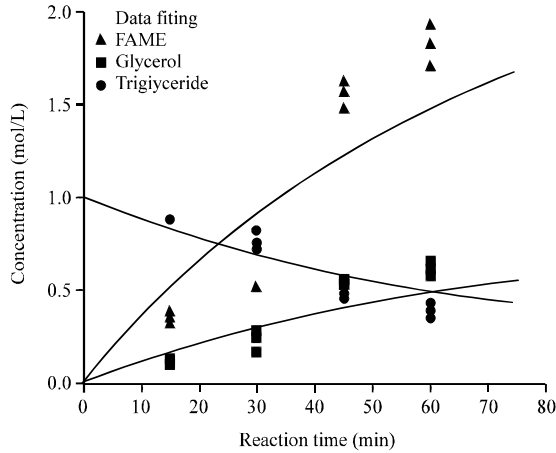


Fig. 6: Transesterification with stirring at 150 rpm and others as default

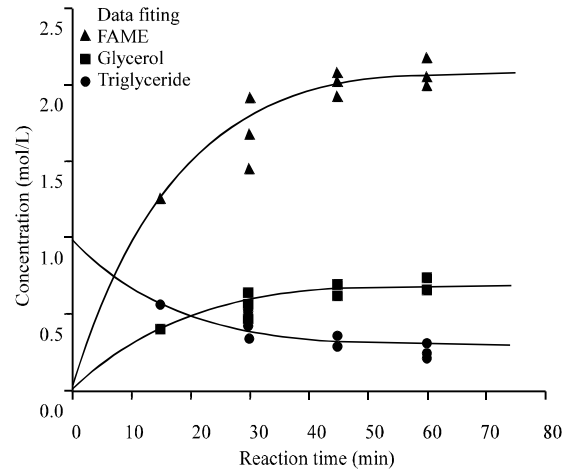


Fig. 7: Transesterification with stirring at 200 rpm and others as default

by unmodified kinetics model because normally biodiesel production by transesterification began with two separating phases of triglyceride and methanol. So with unsuitable ratio there was too low interfacial area for mass transfer due to insufficient mixing. However, triglyceride and methanol with suitable ratios will form a good emulsion of oil in methanol which enhances mass transfer between the two phases, playing important role on the whole process. Thus, stirring was used to make tiny oil bubbles suspending in excess amount of methanol to enhance interfacial mass transfer rate (Choedkiatsakul *et al.*, 2014).

We modified the regular rate equations of transesterification step by simply using mass transfer factor ( $\bullet$ ) for the rate of triglyceride disappearing in the kinetic model. The mass transfer factor is reasonable under two assumptions. Firstly, well mixing can be achieved when stirring speed at 300 rpm was used since >90% conversion can be achieved which after sufficient reaction time could be accepted to be the equilibrium conversion of this reversible reaction. Secondly by visual observation, molar ratio 1:9 triglyceride-to-methanol produced uniform size of oil bubbles suspended in methanol. The rate constants ( $k_1$ ) were determined by kinetic model fitting shown in Fig. 6-9 and values of rate constants of  $1.5 \times 10^{-3} \text{ L/mole}\cdot\text{min}$ ,  $4.5 \times 10^{-3} \text{ L/mole}\cdot\text{min}$ ,  $7.5 \times 10^{-3} \text{ L/mole}\cdot\text{min}$  and  $1.5 \times 10^{-2} \text{ L/mole}\cdot\text{min}$  were obtained respectively. These values of  $k_1$  did not satisfy Arrhenius's equation of which the rate constant should be not different at a given temperature so we propose a modified kinetic model for Eq. 1-6 at a certain temperature. For example, we fixed temperature at  $60^\circ\text{C}$  to demonstrate how the following model works:

$$\frac{dC_{TG}}{dt} = -k_1 \alpha C_{TG} C_{ME} + k_2 C_{DG} C_{FA} \quad (7)$$

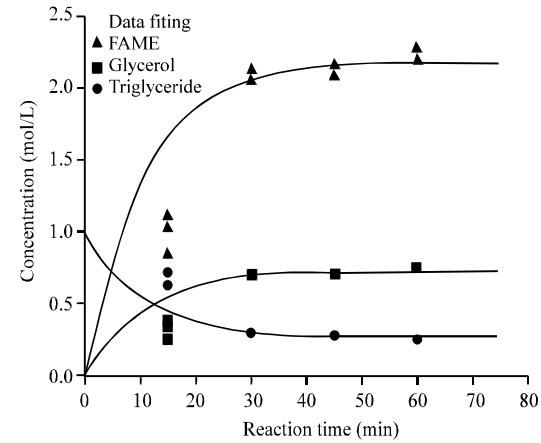


Fig. 8: Transesterification with stirring speed at 250 rpm and others as default

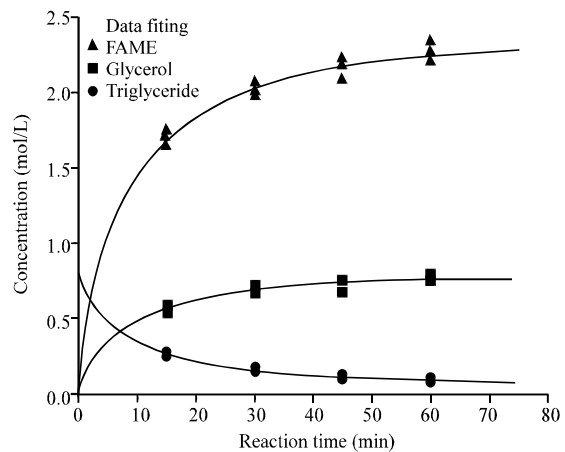


Fig. 9: Transesterification with stirring at 300 rpm and others as default

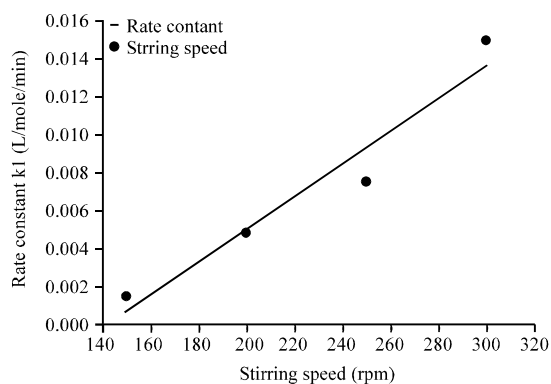


Fig. 10: Relationship between the rate constant  $k_1$  and stirring speed

Where  $k_1^*$  is the rate constant at temperature of  $60^\circ\text{C}$  with stirring speed at 300 rpm and  $\bullet$  stands for a factor due to different rates of mass transfer from methanol phase into oil phase which allowed the reaction to proceed at various stirring speeds.

Besides, Eq. 1 will be replaced Eq. 7 for modifying the traditional kinetic model, other equations with the presence of  $k_1$ , such as Eq. 2, 5 and 6 must be modified by replacing  $K_1$  by  $(K_1^* \bullet)$  into those equations to describe kinetic model of the consecutively reversible reactions.

Conversion of triglyceride is dominated by the rate constant  $k_1$  which was high if the oil-in-methanol emulsion was well-formed. Mixing time can be decreased by using sufficient stirring speeds. A Plot between  $k_1$  evaluated from Fig. 6-9 and stirring speed is shown in Fig. 10. Reynolds number ( $Re$ ) fell between 17,800 and 35,500 for different stirring speeds. It is well-known that the mixing time decreases directly-proportional to the stirring speed (Zlokarnik, 2001). A smaller mixing time promotes the reaction to occur faster. From the fitted line in Fig. 10, we can estimate  $\bullet$  by considering that at 300 rpm stirring, emulsion of oil in methanol was uniform distributed and macro mixing can be assumed as sufficient and was not the rate controlling step thus did not slow down the mass transfer rate. Mass transfer factor  $\bullet$  at 300 rpm is treated to be 1 for maximum value of the rate constant and at other stirring speeds  $\bullet$  can be determined by simply relating to the maximum value corresponding to the linear equation: in unit of (L/mole\*min):

$$k_1 = 8.64 \times 10^{-5}(\text{rpm}) - 0.0122$$

in unit of (L/mole\*min)

Rate constants were determined from data fitting by keeping other rate parameters ( $k_2$ - $k_4$ ) constant to simplify the calculation. The rate constants and mass transfer factors are summarized in Table 1.

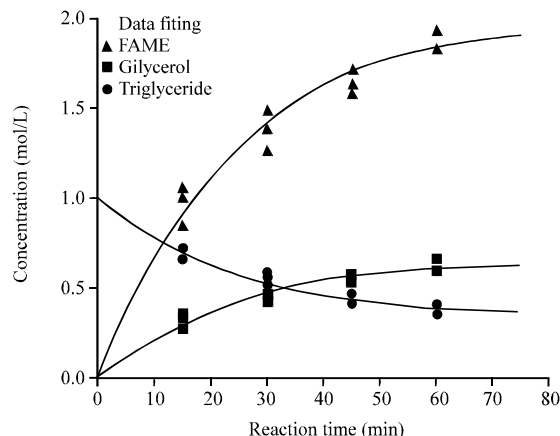


Fig. 11: Transesterification at 250 rpm without assisted by ultrasonic wave and others as default

Table 1: Rate constants  $k_i$  (L/mole\*min) at  $60^\circ\text{C}$  and mass transfer factor ( $\bullet$ ) at different stirring speeds (rpm)

Rpm	$\bullet$	$k_1$	$k_2$	$k_3$	$k_4$	$k_5$	$k_6$
150	0.053	0.0137	24	33	58	88	0.0009
200	0.370	0.0137	24	33	58	$1.88 \times 10^3$	3.3500
250	0.680	0.0137	24	33	58	$2.58 \times 10^3$	5.3500
300	1.000	0.0137	24	33	58	3.5	0.0009

<sup>a</sup>Values of  $k_2$ - $k_4$  are reported in a review of Giulio Santori *et al.* (2012)

**Effect of ultrasonic wave on rate of transesterification:**

From Fig. 8, it is clear that reaction assisted with ultrasonic wave shows a better mass transfer at the initial time of reaction (Choedkiatsakul *et al.*, 2014) since biodiesel production increases strongly during the first 30 min. It does also show that all components were almost well mixed and mass transfer was not the limiting step for further reaction to proceed. In contrast in the batch without ultrasonic wave as demonstrated in Fig. 11, biodiesel produced increased more gradually during the beginning as compared with that in Fig. 8. This is because the process needs a time for getting a good mixing to induce reaction to occur effectively.

**CONCLUSION**

The nature of transesterification involves mass transfer effect since triglyceride and alcohol are immiscible fluids. The reaction between the two fluids occurs in form of emulsion so the molar ratio of the two fluids play a crucial role on the rate of reaction. In this study the molar ratio of 1:9 was the optimum point for biodiesel production. Temperature and catalysts loading did not affect production yield strongly. This follows the kinetic theory. However the amount of catalysts and temperature should be large enough for the reaction to occur as fast as

possible (not constrained by the amount of catalyst and temperature). In our experiments, we chose 3% by weight of catalysts and temperature of 60°C as a reasonable condition as such. The activation energy of transesterification at our default condition was 25.5 kJ/mole and pre-exponential term was 2,600 L/mole·min. The main point of this research is how to enhance mass transfer rate in this emulsion system. We studied effect of stirring speed with ultrasonic wave aided on the rate of transesterification and we get high biodiesel production >90% conversion at 300 rpm stirring. Operations with and without ultrasonic wave was compared. It shows that ultrasonic wave did not give much different in term of yield but was helpful in term of reaction rate. The last point about enhancing mass transfer rate, we can conclude that if stirring speed is not large enough to get good oil-bubbles distribution it is difficult to get high productivity.

#### ACKNOWLEDGEMENT

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