Tin (II) Chloride Catalyzed Esterification of High FFA Jatropha Oil: Experimental and Kinetics Study

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ABSTRACT: Biodiesel is one of the promising energy source alternatives to fossil fuel. To produce biodiesel in a more economical way, the employment of the low-cost feed stocks, such as non-edible oils with high free fatty acid (FFA), is necessary. Accordingly, the esterification reaction of FFA in vegetable oils plays an important role in the biodiesel production. In this work, esterification of FFA contained in Crude Jatropha Oil in the presence of tin (II) chloride catalyst in a batch reactor has been carried out. The esterification reaction was conducted using methanol at the temperature of 40-60 °C for 4 hours. The effect of molar ratio of methanol to oil was studied in the range 15:1 to 120:1. The influence of catalyst loading was investigated in the range of 2.5 to 15% w/w oil. The optimum reaction conversion was obtained at 60 °C with the catalyst loading of 10% w/w oil and molar ratio of methanol to oil of 120:1. A pseudo-homogeneous irreversible second order kinetic model for describing the esterification of oleic acid with methanol over tin (II) chloride catalyst was developed based on the experimental data. The kinetic model can fit the data very well.

Keywords: Esterification, free fatty acid, tin (II) chloride, biodiesel, kinetics.

1. Introduction

Biodiesel is a promising alternative energy sources because of its great benefits. It is environmentally friendly since it is made from renewable resources and has lower emissions than petroleum diesel. This biofuel can be readily produced using local feedstock, hence it will be more cost efficient.

Biodiesel is commonly synthesized through transesterification of vegetable oils in the presence of alkaline catalyst (Budiman *et al.* 2009). Nevertheless, this process is only appropriate for feedstocks containing free fatty acids (FFAs) less than 1 mg KOH/g, and the alcohol and vegetable oil should be moisture free (Freedman *et al.* 1984). The high FFA content could lead to saponification reactions, which causes difficulty in glycerol separation and reduces biodiesel yield (Atadashi *et al.* 2011). It becomes a challenge since feed stocks containing a small amount of FFAs are usually expensive and edible vegetable oils. On the other hand,

the low-cost biodiesel raw materials, such as non-edible oils and waste cooking oils, are usually high in FFAs. Therefore, a different method of biodiesel production should be applied for high FFA feed stocks.

Acid-catalyzed esterification of FFA with short chain alcohols is another route to produce biodiesel. It also can be used as a pre-treatment for basic transesterification reaction to convert the FFA into methyl esters and avoid saponification, mainly when the high FFAs raw materials are utilized for biodiesel production (Aranda *et al.* 2008). Esterification of FFAs can be performed using either homogeneous or heterogeneous brønsted and lewis acid catalyst. The widely applied catalysts at industrial scale are the conventional homogeneous mineral acids, such as sulfuric acid. This catalyst has high catalytic activity, but it deals with several environmental problem as well as difficulties in product separation and catalyst recovery (Ali *et al.* 2007).

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Several techniques have been attempted to overwhelm the drawbacks of homogenous acid catalysis. The application of enzyme catalyst, solid acid catalyst, and catalyst-free reaction using supercritical or subcritical alcohols for FFAs esterification reaction have been reported (Dermibas et al. 2005). However, esterification in supercritical condition encounters a problem related to the high operation cost associated with the high temperature and pressure. Whereas, enzymatic esterification exhibits a disadvantage due to expensive and unstable activity of enzyme (Shibasaki-Kitakawa et al. 2007). As alternative, the use of heterogeneous (solid) acid catalysts might have a greater potential for a large-scale production (Kusumaningtyas et al. 2013).

Solid acid catalysis is attractive for commercial scale application as it is beneficial for green and benign chemical processes (Russbueldt & Hoelderich 2009). The employment of heterogeneous catalyst could diminish corrosion, toxicity and environmental problems. Lou *et al.* (2008) has reported that this type of catalyst provides an easier separation between products and catalyst. In addition, it is commonly excellent in terms of selectivity, recyclability and reusability.

Among the excellent heterogeneous acid catalyst for the FFAs esterification is tin (II) chloride dihydrate ($SnCl_2.2H_2O$), which is classified as Lewis acids catalyst. Lewis acids are species with deficiency of electrons that can act activating substrates rich in electrons (Ferreira *et al.* 2012). Tin (II) chloride is fascinating for biodiesel production because of its characteristic viz. a stable Lewis solid acid, highly water tolerant, easy to handle, and less corrosive. It is also shown that although used in homogeneous phase, this catalyst can be easily recovered and reused for esterification reactions (da Silva *et al.* 2011).

In this work, esterification of FFAs in crude jatropha oil (CJO) with methanol over tin (II) chloride dihydrate catalyst has been performed. Effects of the main parameters such as reaction temperature, catalyst concentration, and molar ratio of methanol to FFA have been examined experimentally. Kinetics of the FFA esterification was also investigated. Kinetics study is essential for reactor designs and optimization of catalytic chemical processes. A pseudo-homogeneous irreversible second order model was employed for the kinetic calculation. Pseudo homogeneous second order kinetic model were previously used for the esterification of oleic acid over ion exchange resin relite CFS and zinc acetate and fitted the experimental data very well (Tesser *et al.* 2005; Song *et al.* 2010).

2. Materials and Methods

2.1 Material

Tin (II) chloride dihydrate ($SnCl_2.2H_2O$) catalyst and 99.99% of methanol were from Merck. Crude jatropha oils with FFA content of 30.57% (w/w) was obtained from PT. Jatropha Green Energy, Kudus, Indonesia.

2.2 Esterification Reaction

The esterification reaction was carried out in a 500 ml three-neck flask batch reactors equipped with magnetic stirrer and reflux condenser as illustrated in Fig. 1. Initially, 46.25 gr of CJO was introduced into the flask along with methanol in a certain ratio. The solution was then heated and the sample was immediately taken to measure its acidity, which was considered as the initial acidity. When the desired temperature was reached, the catalyst was afterwards added into the mixture and the sample was taken right away to measure the acidity that was considered as time of zero. Esterification reactions were conducted in the temperature range of 40–60 °C. Tin (II) chloride catalyst concentration and molar ration of methanol to FFA were varied at 2.5-15% w/w oil and 15:1 to 120:1, respectively. Samples were withdrawn periodically during the reaction.

2.2 Analytical Procedure

Esterification reaction between a fatty acid and methanol can be represented as:

$$RCOOH\ (A) + CH_3OH\ (B) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} RCOOCH_3\ (C) + H_2O \quad \textbf{(1)}$$
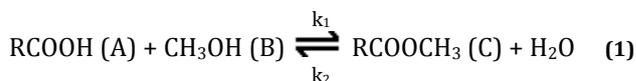
Reaction conversions were estimated from the FFA content of the medium by NaOH titration (Aranda, *et al.*, 2009). The acidity was estimated by the following equation:

$$a = \frac{V_{titr}.M_{OA}.C_{titr}}{m_{sampel}.1000} \quad \textbf{(2)}$$
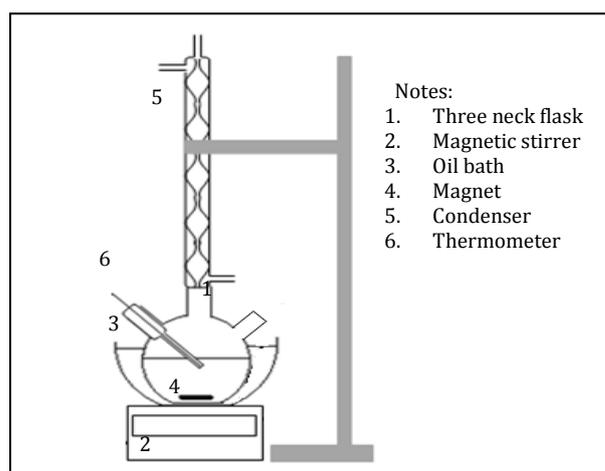
Fig. 1 Batch reactor apparatus set

Notes:
1. Three neck flask
2. Magnetic stirrer
3. Oil bath
4. Magnet
5. Condenser
6. Thermometer

The conversion was calculated by the equation as follows:

$$x_A = \frac{a_i - a_t}{a_i} \; x \; 100\% \qquad \textbf{(3)}$$

In which a is acidity index, v_{titr} is titrant volume (mL), M_{OA} is molecular weight of fatty acid, C_{titr} is titrant concentration (mole/L), m_{sampel} is mass of the sample (gram), X_A is FFA conversion, a_i is initial acidity index and a_t is acidity index at t time.

2.3 Kinetics Study

Kinetics study of the FFA esterification were established based on pseudo-homogeneous model. Three types of pseudo-homogeneous kinetics models were examined in this work, i.e.: pseudo-homogeneous irreversible first and second order, and reversible second order models. These models have been previously applied for interpreting the experimental data of heterogeneous catalyzed FFA esterification and provided good agreement (Song *et al*. 2010; Alenezi *et al*. 2010). In this study, oleic acid as the major fatty acid in CJO was used to represent the FFA in the calculation.

3. Result and Discussion

3.1 Effect of Catalyst Concentration

The influence of catalyst concentration on esterification conversion was observed at 2.5, 5, 10, and 15% w/w oil. During the operation, reaction temperature, molar ratio of methanol to FFA, and reaction time were kept constant at 60 °C, 60:1, and 240 minutes, respectively. The result as presented in Fig. 2, exhibits that the FFA conversion increases with the catalyst concentration up to 10% w/w oil and then level off with further increase of catalyst concentration to 15% w/w oil. It seems that the optimum catalyst concentration for this FFA esterification is 10%.

Catalyst plays an important role to enhance reaction rate, especially for the slow and reversible reaction. A catalyst provides an alternative route for the reaction with lower activation energy. Therefore, based on the Collision theory, it is stated that, when a catalyst involves in the collision between the reactant molecules, less energy is required for the chemical change to take place, and therefore more collisions have sufficient energy for reaction to occur. It leads to the increase in the reaction rate.

Basically, an increase in the amount of catalyst employed will increase the rate of reaction and improve the reaction conversion for the same reaction time. It is not surprising since the higher amount of catalyst means the higher amount of catalyst active sites are available to enhance the reaction (Srilatha *et al*. 2009; Yadav & Yadav 2012). However, the addition of the catalyst beyond the optimum concentration will not speed up
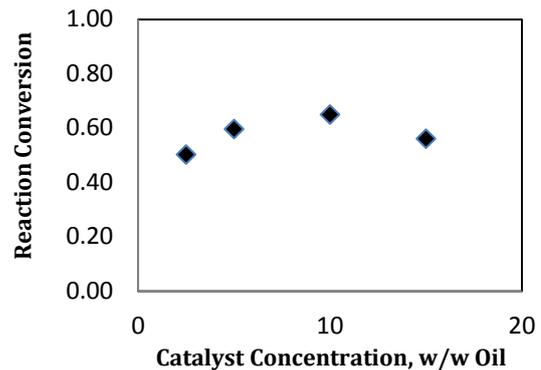
Fig. 2 Effect of catalyst concentration on esterification conversion

reaction rate or even it decreases the rate (Deshmane & Adewuyi 2013). This phenomenon occurs since an excessive addition of solid catalyst will form a slurry mixture of catalyst and reactant. This viscous mixture will deteriorate the mixing between catalyst and reactants, which accordingly reduces reaction rate and conversion (Gan *et al*. 2010).

3.2 Effect of Temperature and Reaction Time

In this work, effect of reaction temperature was examined in the range of 40-60 °C at different reaction time from 0 to 240 minutes. Catalyst concentration and molar ratio of methanol to FFA were fixed at 10% and 60:1, respectively. It was revealed in Fig. 3 that for a batch reactor, reaction temperature strongly correlates with the reaction time. The equal reaction conversion can be achieved at a lower reaction temperature by lengthening the reaction time (Freedman *et al*. 1984).

In this work, it can be observed in Fig. 3 that the reaction conversion increased dramatically just afterward the catalyst was introduced into the reaction system. It is called spontaneous reaction, which means that the reaction rate increases the most significantly at the beginning of the reaction. This phenomenon occurs due to the fact that at the initial period, there are only reactants (methanol and FFA) which exist in the reactor. This condition makes the reactants easier to diffuse into the catalyst active surface, thus, ester is formed rapidly (Rattanaphra *et al*. 2011).

However, the increase of the reaction rate was then reduced. It is due to the production of water during esterification reaction. At initial reaction time, there is still small amount of water produced. Hence the esterification reaction is fast. As the reaction proceeds, more water is yielded. The increased quantity of water in the reaction mixture will prevent the reaction progress to the right (esterification reaction). Based on the Le Chatelier's principle, the existence of high concentration of water will shift the reaction to the left (hydrolysis reaction). Consequently, the reaction slowly reaches its equilibrium, when the rate of esterification reaction and hydrolysis are equal (Gan *et al*. 2010).

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It is also demonstrated that reaction conversion enhanced significantly with the temperature. Gan, *et al.* (2010) associated this phenomenon with the low solubility of oil in methanol, which causes a significant mass transfer resistance between the reactants. Due to this low solubility, at lower reaction temperature, mass transfer rate controls the overall reaction rate. On the other hand, at the higher reaction temperature, solubility of oils in methanol increases which will also reduce the mass transfer resistance. Besides, viscosity of the oil decreases with the temperature, thus it enables a good mixing between catalyst and reactant. As a result, at the higher temperature, the overall reaction rate is controlled by the chemical reaction rate.

Meanwhile, Rattanaphra *et al.* (2011) correlate this tendency to the three-phase phenomenon. Oil and methanol are immiscible. Therefore, reaction with heterogeneous catalyst would create a-three phase system of oil-methanol-catalyst at which the mass transfer rate of reactant molecules between the three phases is very limited. As the reaction temperature is increased, all reactant molecules will gain more kinetic energy that will eventually accelerate the mass transfer rate among the oil–methanol–catalyst phases, resulting in a higher conversion of FFA to ester in a shorter time.

Based on the kinetics viewpoint, it is known that the higher reaction temperature will result in the higher reaction constant (k_1), which brings about the higher reaction rate and conversion. Westerterp, *et al.* (1984) states that reaction rate will multiply 2-5 times for every 10 ℃ rise in temperature. This fact is in accordance with the the collision theory. As stated by the theory, when reactants particles collide, only the effective collisions can cause a significant chemical change. Effective collision is defined as the collision holding an adequate energy called activation energy. This amount of energy is sufficient for breaking a bond and subsequently composing a new bond. This condition allows a chemical reaction to take place.
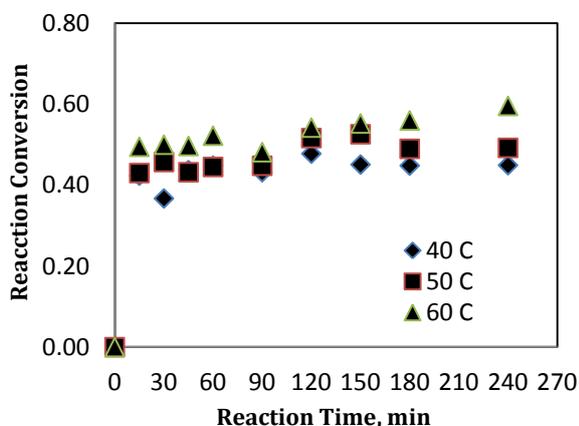
Temperature is also a measure of the kinetic energy of a system. It means that higher temperature implies higher average kinetic energy of molecules and more effective collisions per unit time. Therefore, the higher reaction temperature leads to the higher reaction rate and conversion (Fessenden & Fessenden 1986).

3.3 Effect of Molar Ratio of Methanol to FFA

The molar ratio of methanol to FFA is one of the most important variables affecting the conversion of esterification reaction. A Stoichiometric molar ratio of methanol to FFA is 1. However, the esterification reaction of fatty acid with alcohol is a reversible reaction. Therefore, it is necessary to increase the molar ratio of alcohol to acid leads to shift the chemical equilibrium to product formation (Srilatha *et al.* 2009). In this study, the dependence of acid conversion on molar ratio was assessed in the range of 15 to 120 at reaction temperature, catalyst concentration, and reaction time of 60 ℃, 10%, and 240 minutes, respectively. It is shown in Fig. 4 that the acid conversion increases with the molar ratio of methanol to FFA.

Considered from the mass transfer perspective, the increasing molar ratio of methanol to oil (FFA) will decrease viscosity of the reactant mixture. The lower viscosity will facilitate a good mixing between the reactants and catalyst, thus improves the mass transfer rate and subsequently enhances the reaction conversion (Gan *et al.*, 2010).

3.4 Kinetics Model

The esterification of FFA with methanol can be represented by the esterification of oleic acid and methanol as indicted by Equation (1). It is due to the fact that oleic acid is the major fatty acid contained in CJO. The apparent reaction rate can be written as:
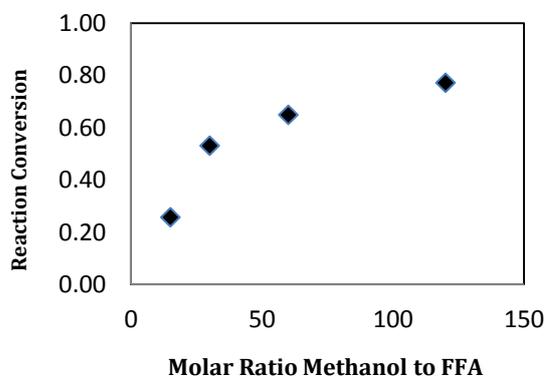

Fig. 3 Effect of temperature and reaction time on the conversion (Catalyst concentration and molar ratio of methanol to FFA were constant at 10% and 60:1)

Fig. 4 Effect of methanol to FFA molar ratio on reaction conversion

$$-\frac{dC_A}{dt} = k_1 C_A^\alpha C_B^\beta - k_2 C_C^\gamma C_D^\delta \tag{4}$$

where C_A, C_B, C_C and C_D denote the concentrations of oleic acid, methanol, methyl oleate and water, respectively; α, β, γ, and δ refer to their reaction orders; k_1 and k_2 are the kinetic constants for the forward and reverse reactions, respectively. For the kinetic modelling, this esterification reaction can be regarded as a reversible or irreversible reaction based on the assumption taken into account.

Irreversible kinetics model is developed based on the fact that the concentration of methanol is much higher than that of other components, then $k_1 C_B$ can be regarded as a constant. In the meantime, k_1 is extremely larger than k_2, hence Equation (4) can be abridged to (Song *et al.* 2010):

$$-\frac{dC_A}{dt} = k_1 C_A^n \tag{5}$$

with x and C_{A0} refer to the conversion and the initial concentration of FFA, Equation (5) can be written as:

$$C_A = C_{A0} (1 - x) \tag{6}$$

$$\frac{dx}{dt} = \frac{k_1}{C_{A0}} [C_{A0} (1 - x)]^n \tag{7}$$

$$\frac{dx}{dt} = \frac{k_1 C_{A0}^n}{C_{A0}} (1 - x)^n \tag{8}$$

$$\frac{dx}{dt} = k_1 C_{A0}^{(n-1)} (1 - x)^n \tag{9}$$

In this study, n=1 and n=2 were both tested to find the more appropriate reaction order.

If the reverse reaction and the contribution of all species' concentration to the reaction rate are taken into consideration, then the reversible reaction model can be applied. Reversible second order reaction kinetics of FFA esterification can be expressed as (Alenezi, *et al.*, 2010):

$$\frac{dx}{dt} = k_1 \left(\left(\frac{M}{1} \right) - x \right) (1 - x) - k_2 (x)(D_0 + x) \tag{10}$$

In the above equation, t is the reaction time (min), *M/1* is the ratio of methanol to FFA, and D_0 are the moles of water per mole of FFA in the feed.

In this investigation, three types of pseudo-homogeneous kinetics model were employed to interpret the experimental data. Kinetics Model 1 is irreversible first-order reaction, Model 2 is irreversible second-order reaction, and Model 3 is reversible second order mechanism. The best kinetics model was determined based on the visual observation on the graphs and by minimizing the Sum Squared Errors (SSE) between calculated values of rate (x_{Acalc}) obtained using MATLAB simulation and the experimental data (x_{Aexp}) of each model. The SSE is calculated using equation (11). A well-fitting model for describing the reaction kinetics provided reasonable values of the parameters with the least SSE value.

$$SSE = \sum_{i=1}^{N} (x_{Acalc,i} - x_{Aexp,i})^2 \tag{11}$$

By utilizing self-developed MATLAB simulation, the values of rate constants of the FFA esterification reaction estimated at different temperatures for each model can be obtained and are summarized in Table 1.

Correlation of the rate constants with the pre-exponential factor A and activation energy E_a is shown the Arrhenius equation:

$$\ln k_j = -\frac{E_{ai}}{RT} + \ln A_j \tag{12}$$

T denotes the reaction temperature (K), R is gas constant (8.3144 J/mole K), and j index means forward reaction for j=1, and reverse reaction for j=2. Subsequently, the values of the kinetic parameters are demonstrated in Table 2.

Table 1
Rate constants of the FFA esterification reaction estimated at different temperatures

Temperature (°C)	k_1	k_2
Model 1		
Irreversible First Order		
40	4.56×10^{-3}	-
50	5.79×10^{-3}	-
60	7.37×10^{-3}	-
Model 2		
Irreversible Second Order		
40	2.52×10^{-4}	-
50	3.33×10^{-4}	-
60	4.99×10^{-4}	-
Model 3		
Reversible Second Order		
40	0.408	68
50	0.835	1.16×10^2
60	1.81	1.74×10^2

Units of the rate constants for second order reaction are (L mole^{-1} min^{-1}) and for first order reaction is (min^{-1})

Plotting of the Kinetic Model 1, 2, and 3 against the experimental data are presented in Fig. 5, 6, and 7.

Table 2
Kinetics parameters for each kinetics model of the FFA esterification

No	Forward Reaction		Reverse Reaction		SSE
	E_{a1}	A_1	E_{a2}	A_2	
1	20.80	13.43	-	-	1.09
2	29.57	21.16	-	-	6.91×10^{-1}
3	64.50	2.33×10^{10}	40.70	4.29×10^8	2.02×10^{-2}

E_{a1} and E_{a2}, energies of activation (kJ/mole); A_1 and A_2, pre-exponential factor (min^{-1})
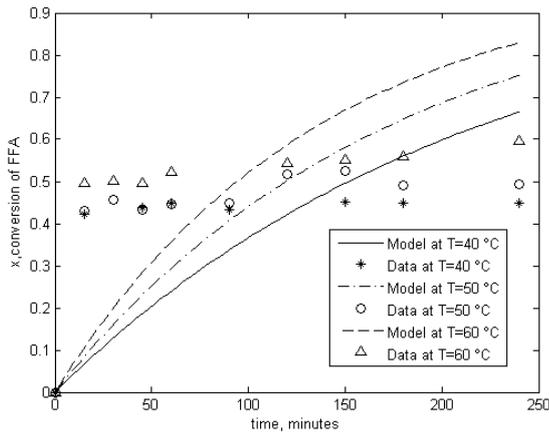
Fig. 5 Comparison of experimental points and fitted results of Model 1 (pseudo-homogeneous irreversible reaction with n=1) for the FFA esterification at 40, 50, 60 °C
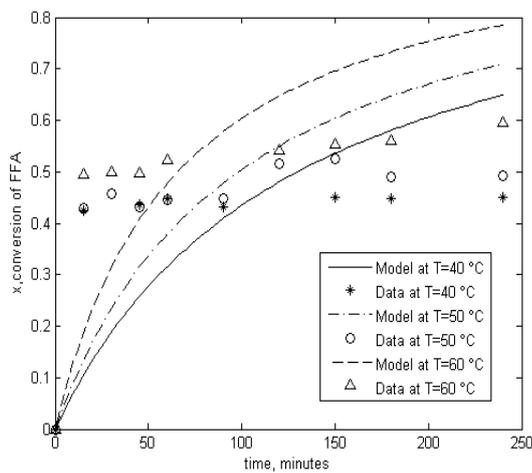

Fig. 6 Comparison of experimental points and fitted results of Model 3 (pseudo-homogeneous irreversible reaction with n=2) for the FFA esterification at 40, 50, 60 °C
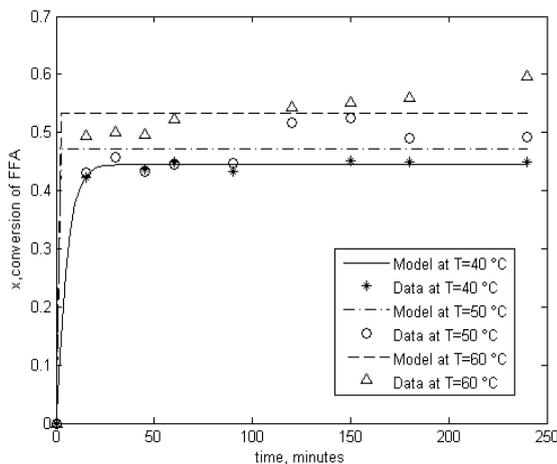

Fig. 7 Comparison of experimental points and fitted results of Model 3 (pseudo-homogeneous reversible second order reaction) for the FFA esterification at 40, 50, 60 °C

Based on the visual observation on the graphs in Fig. 5, 6, and 7 as well as the value of SSE given by the simulation of each model, it is revealed that Model 3 (reversible second order kinetic model) is the best model compared to the other two models. This model provides the calculated result which is closed to the experimental data. This result is in line with the previous work of Alenezi *et al.* (2010) and Tesser *et al.* (2005) reporting that the pseudo-homogeneous reversible second order kinetic model is acceptable to provide a good interpretation of the experimental data of heterogeneous-catalyzed FFA esterification.

In this study, the reversible second order kinetic model (Model 3) provides the activation energy value of 64.50 kJ/mole for the forward reaction. This value is higher than those reported by Song *et al.* (2010) that stated 32 kJ/mole. This difference comes about due to difference of the reaction operation condition. This FFA esterification reaction was conducted in the mild operation condition at the temperature ranging from 40 to 60 °C and atmospheric pressure. On the other hand, Song *et al.* (2010) carried out the experiments using sub and supercritical methanol under reaction condition of 220 – 320 °C at 6-10 MPa, which practically leads to the lower activation energy values than that of the reaction at a mild condition. Furthermore, the activation energy resulted in this work is slightly higher than that reported by Tesser *et al.* (2005), which provides Ea value of forward reaction of 58.576 kJ/mole for the esterification of oleic acid in the presence of ion exchange relite CFS catalyst. However, it can be stated that those two results of activation energy (Ea) have the same order of magnitude.

4. Conclusion

Esterification reaction of FFA with methanol over tin (II) chloride dihydrate in a batch reactor has been studied under different catalyst concentration, reaction temperature and reaction time, as well as molar ratio of alcohol to FFA. It was revealed that the higher catalyst concentration, temperature, reaction time, and molar ratio of alcohols to FFA will lead to the higher reaction conversion until it reaches the optimum one.

Furthermore, kinetic study was performed in this work. Three kinetics models *i.e.* pseudo-homogeneous irreversible first and second order and reversible second order models were examined to justify the experimental data. It was exhibited that Model 3 (reversible second order model) was the best kinetic model for this reaction. This model was acceptable to provide a good interpretation of the experiment results. The kinetic parameters were also determined. For this model, the activation energy value of 64.50 kJ/mole for the forward reaction was obtained.

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