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Kinetic Study of Kapok Seed Oil Esterification using BMIM-PF6 Catalyst

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Abstract

Biodiesel offers better combustion efficiency, lower sulfur content and aromatic compounds, higher cetane numbers than diesel fuel, biodegradable and renewable properties that are not possessed by conventional fuels such as diesel fuel. This study aims to study the modeling of esterification process of Kapok seed oil using 3 % liquid ionic catalyst 1-Butyl-3-MethydidazoliumHexafluorophosphate (BMIM-PF6). The validation results of reaction kinetic models for experiments and simulations provide an adjacent correlation value, that is $R^2 = 0.99526$*, with the rate constant value (k) based on experimental data are 0.003815* L/mol.s *and 0.0038* L/mol.s *for the simulation data. Based on the simulation results, the proper reaction order for this esterification reaction is the first order reaction equation with a value of* $R^2 = 0.99526$*, while the second order reaction gives the value* $R^2 = 0.89453$*. The reaction kinetics parameters obtained from the experimental results are A = 0.012 L/mol.s and -Ea = -0.437 kJ/mol, while the reaction parameters of the simulation are A = 1.0384 L/mol.s and -Ea = -89.5 kJ/mol.*

Keywords: *Esterification, Ionic Liquid Catalyst, Kinetic*

INTRODUCTION

Indonesia is the country with the largest energy consumption in the Southeast Asian region and fifth in the Asia Pacific in primary energy consumption ranks, after China, India, Japan and South Korea. High GDP growth, reaching an average of 6.04% per year over the 2017-2050 period, is expected to increase Indonesia's energy needs in the future. This has led to Indonesia's role in the world energy market and in efforts to reduce global greenhouse gas emissions significantly. Indonesia's final energy consumption (without firewood) in 2016 is still dominated by fuel by 47%. When viewed by sector, the transportation sector has the largest share, which is 42%, higher than the industrial sector with a share of 36%. The transportation sector's energy consumption is almost entirely fulfilled by fuel. On the other hand, Indonesia has been a net importer of fuel since 2004. One third of Indonesia's fuel consumption in 2016 was filled by imports. If the energy demand which is dominated by fuel continues to increase without any change in energy usage patterns, especially in the transportation sector, then the sustainability of Indonesia's energy will be disrupted (BPPT, 2018). The increase in fuel consumption is proportionally inverse to the availability of energy reserves, especially petroleum, according to ESDM data cited by BPPT. In 2011 Indonesia's total oil reserves amounted to 7.73 billion barrels while in 2012 it decreased to 7.41 billion barrels. Based on the level of petroleum production of 329 million barrels per year in 2011 and 315 million barrels in 2012, the ratio of petroleum reserve (R/P) production is around 22 years (BPPT, 2018). For this reason, in order to support future energy needs, it is necessary to make an effort to find and discover new renewable energy that is continuous and environmentally friendly, one of the new energies that is environmentally friendly and renewable is biodiesel.

As an alternative fuel, biodiesel offers better combustion efficiency, lower sulfur content and aromatic compounds, higher cetane numbers compared to diesel fuel, biodegradable and renewable properties that are not possessed by conventional fuels such as diesel (Krishnamurthy *et al*., 2020). Raw materials for biodiesel production are very diverse and can be divided into several categories such as edible oil, non-edible oil, waste oil, animal fat, and algae lipids (Peres *et al*., 2013). For biodiesel production in developing countries including Indonesia, the availability of edible and non-edible oil raw materials is very abundant. Biodiesel from edible oil usually comes from plants, such as coconut oil, sunflower seed oil, palm oil and others. Although edible oil is very abundant in Indonesia, the needs of edible oil is not only as biodiesel raw material but is also used in the food industry. As a result, it is feared that large-scale biodiesel production made from edible oil will cause food prices to rise, increase hunger rates, decrease forest area due to conversion of forests to plantations and others. Therefore, non-edible oil raw materials such as cotton (Ong *et al*., 2014; Khan *et al*., 2015) are more potential to be used because they are not used as food and also low prices.

This alternative fuel is a mono-alkyl ester resulting from triglyceride transesterification or free fatty acid esterification (FFA) (Shell, 2012). The esterification process is a process that aims to reduce the viscosity and FFA content and transesterification is a process that aims to convert triglycerides into methyl esters (biodiesel) and glycerol as byproducts (Atadashi *et al*., 2012). Basically, the transesterification reaction requires a long reaction time and has a low yield, so to overcome this problem the reaction is added to the catalyst. Biodiesel production depends on the type of raw material, because the high content of free fatty acids in the alkaline catalyst transesterification reaction will produce a saponification reaction, therefore biodiesel production is usually carried out in 2 reaction stages, esterification using acid catalyst and transesterification using base catalyst. However, the process with 2 stages of this reaction has several problems, including which can cause saponification reactions and the formation of water. As the results of the soap and water formation are the increasing catalysts concentration need and decreasing biodiesel yield.

Ionic catalysts can be described as organic salts in the liquid phase at temperature below 100^0C. These catalysts have advantages such as low emission, good thermal and chemical stability, low vapor pressure, high solubility in organic or inorganic compounds and are easily separated and produce high purity products [8]. Even ionic liquid catalysts are also capable of being recycled and reused up to 5 times with conversions above 90% (Yan *et al*., 2020).

As a renewable fuel, industrial-scale biodiesel production will be the main target of countries around the world as a substitute for fossil fuels. For this reason, the kinetics model of transesterification and esterification reaction are needed to design chemical reactors (Aulia *et al*., 2012). In addition to modeling the reaction kinetics of a chemical reaction, it is also necessary to do a validation analysis of the model to determine the percent error and deviation from the experimental data obtained. The analysis technique commonly used is based on linear system theory which requires a state space model. Most of the process control system design techniques are based on linear models (Prasad and Beguette, 1998).

This study aims to study the simulation of Kapok seed oil esterification process with 1-Butyl-3-MethydidazoliumHexafluorophosphate (BMIM-PF6) using Matlab to test the validity of the kinetic models of the reaction produced biodiesel.

MATERIAL AND RESEARCH METHODOLOGY

The program used is matrix-based software (MATLAB). Research procedures include literature study, mathematical modeling and dynamics simulation. The kinetic models used are the esterification kinetic models approached by (Aulia *et al*., 2012), the kinetic models are reaction temperature, reactant molar ratio, and ionic liquid catalyst concentration.

Flow chart research methodology

The optimum data used was taken from the research results of Kapok seed oil esterification with liquid ionic catalyst (BMIM-PF6) by Widayat *et al* (2017). The kinetic models are as follows:

Irreversible order 1

For reactions A + B → C the reaction rate is

$$-r_A = -\frac{d\,C_A}{dt} = kC_A \tag{1}$$

With integration we get a new form of equation:

$$-\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = k\int_0^t dt \tag{2}$$

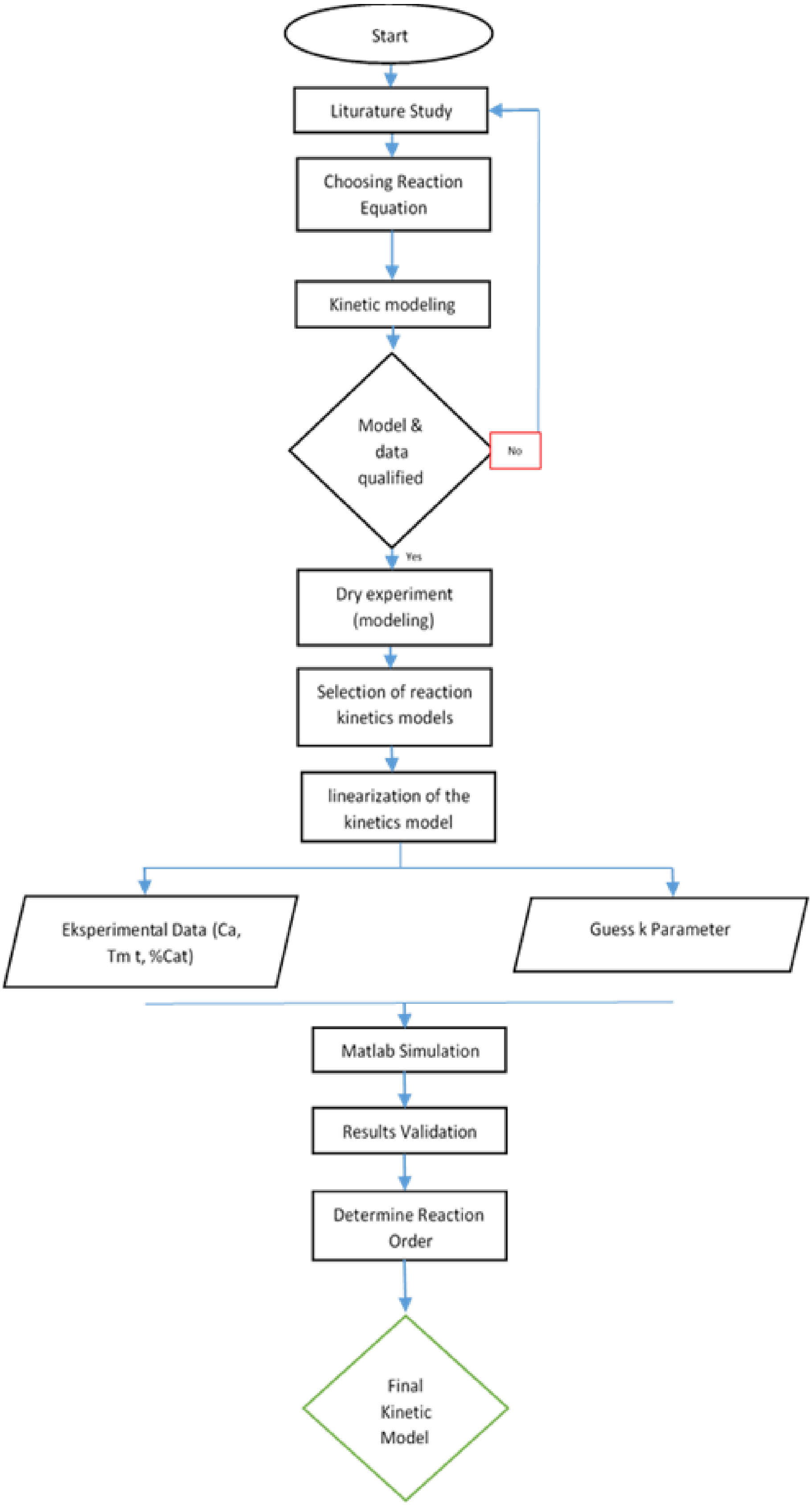


Figure 1. The flowchart of research methodology

$$-\ln\frac{C_A}{C_{A0}} = kt \tag{3}$$

In the form of conversion, the reaction rate equation becomes:

$$-\frac{dX_A}{dt} = k(1 - X_A) \tag{4}$$

With compiled and integrated obtained:

$$-\int_0^{X_A}\frac{dX_A}{1-X_A} = k\int_0^t dt \;\rightarrow\; -\ln(1 - X_a) = kt \tag{5}$$

By making a plot between ln $(1 - X_a)$ or $\ln(\frac{C_A}{C_{A0}})$ vs t, we will get a graph and produce a linear trend. If the experiment produces non-linear trend lines, then the modeling is not suitable (Levenspiel, 1999).

Irreversible order 2

For A + B → C + D reactions, the reaction rate is obtained

$$-r_A = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = kC_AC_B \tag{6}$$

From the decrease in the equation we get a new equation form:

$$-r_A = C_{A0}\frac{dX_A}{dt} = kC_{A0}^2(1 - X_A)(M - X_A) \tag{7}$$

With $M = C_{B0}/C_{A0}$

The integration form of equation 2.16 is:

$$\int_0^{X_A}\frac{dX_A}{(1-X_A)(M-X_A)} = C_{A0}k\int_0^t dt \tag{8}$$

After rearranging, we get equations with various forms, that is:

$$\ln\frac{1-X_B}{1-X_A} = \ln\frac{M-X_A}{M(1-X_{A)}} = \ln\frac{C_BC_{A0}}{C_{B0}C_A} = \text{In}\,\frac{C_B}{MC_A} \tag{9}$$

$$ln\frac{C_B}{C_A} = (C_{B0} - C_{A0})kt + \ln M \tag{10}$$

Kapok seed oil raw materials

Characterization of Kapok seed oil is an initial step to recognize the physical and chemical properties of the oil which will be synthesized into biodiesel. The characterization stage test of Kapok seed oil consists of density, viscosity, saponification number, acid number. The test was done in triplicates then the results are averaged. Acid number testing aims to analyze the content of free fatty acids in oil. Acid value indicate the need for milligrams of KOH to neutralize free fatty acids in 1 gram of oil or fat (Suroso, 2013).

The saponification test is used to determine the minimum methanol requirements according to the esterification reaction stoichiometry. Lathering is expressed by the number of milligrams of KOH needed to lather 1 gram of oil or fat. The saponification rate is determined by the molecular weight of the constituent fatty acids (Chanakaewsomboon *et al.*, 2020). The oil that is composed by short chain fatty acids means that it has a large saponification value and vice versa. The results of the Kapok seed oil characterization can be seen in Table 4.

The FFA content in cotton oil that is used as esterification raw material obtained a large FFA content of 23.7% while in the reference of 17.97% where the difference in the value of FFA is not significant (Widayat *et al.*, 2017). This difference occurs because research on references conducted in 2014 has different cotton oil raw material conditions. This is caused by various factors, one of which is climate difference, climate influences the growth of Kapok trees (Widayat *et al.*, 2017).

Factors affecting the rate of increasing FFA levels in raw material oils include temperature and humidity, therefore it is important to place oil in low humidity conditions and low temperatures to prevent FFA growth which results in a decrease in process efficiency and yield (Widayat *et al.*, 2017). In a study conducted by Widayat *et al* (2017), Kapok seed oil was esterified using a liquid ionic catalyst that was BMIM-PF6 and H_2SO_4 acid catalyst. The esterification reaction is carried out by varying the reaction temperature and the percent of BMIM-PF6 catalyst used. Then the Kapok seed oil esterification reaction was carried out using an H_2SO_4 catalyst with the best operating conditions obtained from the reaction using a liquid ionic catalyst. In a study conducted by Widayat *et al* (2017) also compared the results of reaction conversion using liquid ionic catalysts and H_2SO_4.

Table 1. Characteristics of Kapok seed oil

Parameters	Experiment result	Reference (Sofyan, 2014)
FFA	23,7%	17,97%
Acid Value (mg KOH/g	15,147	35,952
Saponification Value (mg KOH/g)	194,3	172,55
Density (kg/m^3)	0,93	0,9
Viscosity (mm^2/s)	13,6	-

The esterification reaction was carried out by varying the reaction temperature and the percent of BMIM-PF6 catalyst used. Then the Kapok seed oil esterification reaction was carried out using an H_2SO_4 catalyst with the best operating conditions obtained from the reaction using a BMIM-PF6. In a study conducted by Prasad and Beguette (1998) also compared the results of reaction conversion using BMIM-PF6 and H_2SO_4.

Furthermore, in this research an optimization of the Kapok seed oil esterification process with a liquid ionic catalyst is simulated using Matlab software. This simulation aims to find the optimum esterification operating conditions and determine how much is the suitability of the reaction kinetic models to the reaction order. So that it can be seen the extent of deviations between the results of experiments with simulations. In this study a simulation of variations in the amount of catalyst and reaction temperature is carried out, where the fixed variable is the reaction time, which is 180 minutes and oil methanol ratio 1: 8.

RESULT AND DISCUSSION

Reduction of FFA Concentration (CA mol / L) Based on Simulation Results and Experiments using 3% BMIM-PF6

Figure 2 show there is a slight difference between the reaction results obtained experimentally and simulation. The simulation is based on the best data and operating conditions obtained from the research of Widayat *et al* (2017). In this study, a more significant reduction in the FFA concentration (C_A) was obtained by using a first order esterification reaction simulation. This is due to the fact that the simulation was run statically under ideal conditions without regard to influences outside the system. The results of experiments conducted by Widayat *et al* (2017) show that the percentage of the best liquid ionic catalyst is 3%.

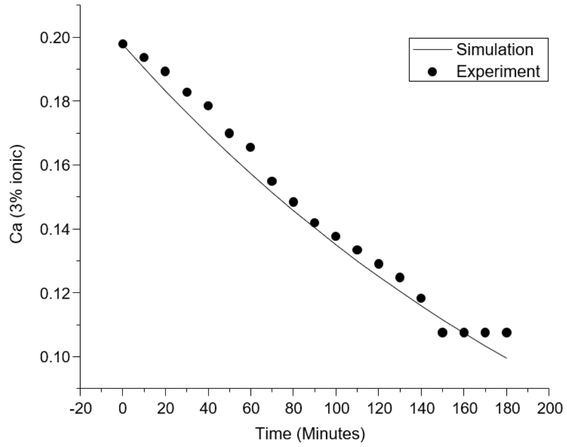


Figure 2. Correlation between oil concentration (C_A) and reaction time

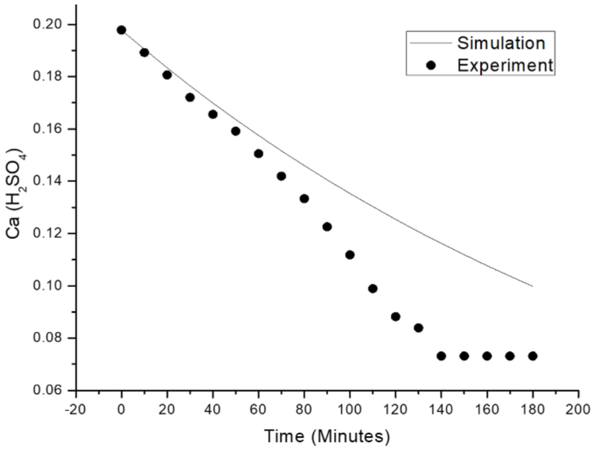


Figure 3. Correlation between FFA concentration and reaction time

Figure 3 show there is a significant difference between the results of reactions obtained experimentally and simulations. This simulation is based on 3% H_2SO_4 concentration data and 65°C operating temperature obtained from Maria's research (2017). The simulation results are strongly influenced by the initial guessing value of the reaction speed coefficient (k) in order 1 reaction. Guess the k value is done until the final concentration results close to the final concentration of the experiment (SSE minimization method) (Masduki *et al*., 2013).

Effect of catalyst variations on C_A concentration through simulation

Figure 4 show the simulation results show that the use of H_2SO_4 and liquid Ionic catalysts shows almost the same rate of reduction in Ca concentrations. The operating conditions used as simulation data are the operating temperature at 65 ^{0}C and the catalyst amount of 3%.

The reaction speed equation follows the first order reaction equation, which is:

$$-r_A = -\frac{d\,C\,A}{dt} = k.C_A \qquad (1)$$

The initial guess value of the reaction speed coefficient (k) uses the value of k from Widayat *et al* (2017), which is 0.003815 L/mol.s for liquid ionic catalyst and H_2SO_4 catalyst. Then the actual k price is validated to determine the actual C_A concentration rate through the MATLAB simulation with the Polyfit function of linearization equation (1).

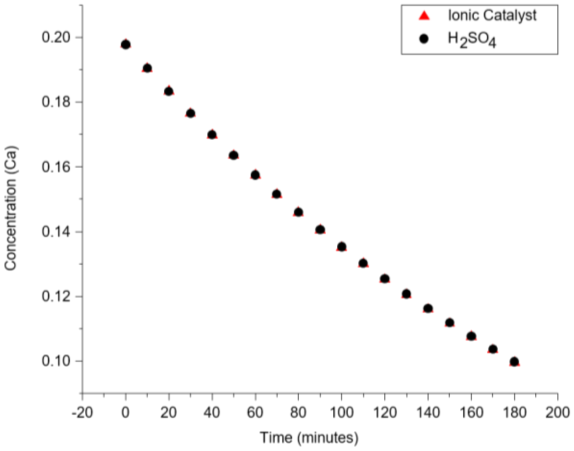


Figure 4. Correlation between FFA (Ca) concentration and reaction time

So that equation (1) can be described as follows:

$$-r_A = -\frac{d\,C_A}{dt} = kC_A \tag{1}$$

$$-\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = k\int_0^t dt \tag{2}$$

$$-\ln\frac{C_A}{C_{A0}} = kt \tag{3}$$

$$-ln\frac{C_{A0}(1-X_A)}{C_{A0}} \tag{11}$$

$$-\ln\,(1-X_A) = k \cdot t \tag{12}$$

$$y = m \cdot x \tag{13}$$

Next enter the reaction and conversion time values (1-X_A) obtained from the results of Maria's experiment (2017) into the Polyfit function in Matlab Software. The conversion value can be seen in table 2.

The data obtained in table 2 is then inputted into equation (6) to be linearized using the Polyfit function in MATLAB, so the new k value for the reaction uses 3% liquid ionic catalyst and H_2SO_4 catalyst with each value of 0.0038 L / mol. s and 0.0065 L / mol.s.

Based on Figure 5 and 6 we can see that the use of H_2SO_4 catalysts gives better results than the use of liquid ionic catalysts. This is evidenced by the value of the remaining concentration of FFA that reacts much less in reactions using H_2SO_4 catalyst. Basically, a strong acid catalyst works as a strong oxidizer, this catalyst is also exothermic if dissolved in water so that it can increase the affinity that can get rid of the emergence of water vapor in the reaction. H^+ ion concentration affects the reaction speed, because concentrated sulfuric acid is able to bind water (hygroscopic), so for equilibrium reactions that produce water can shift the direction of the reaction to the right (towards the product). This sulfuric acid catalyst is also very suitable for esterification reactions with oils containing FFA above 5% (Lieu *et al*., 2016).

Table 2. Effect of reaction time on conversion result with variations in catalyst types

t(minutes)	Xa Cat 3%	Xa H_2SO_4 3%
0	0	0
10	0.0217	0.0435
20	0.0435	0.0870
30	0.0761	0.1304
40	0.0978	0.1630
50	0.1413	0.1957
60	0.1630	0.2391
70	0.2174	0.2826
80	0.2500	0.3261
90	0.2826	0.3804
100	0.3043	0.4348
110	0.3261	0.5000
120	0.3478	0.5543
130	0.3696	0.5761
140	0.4022	0.6304
150	0.4565	0.6304
160	0.4565	0.6304
170	0.4565	0.6304
180	0.4565	0.6304

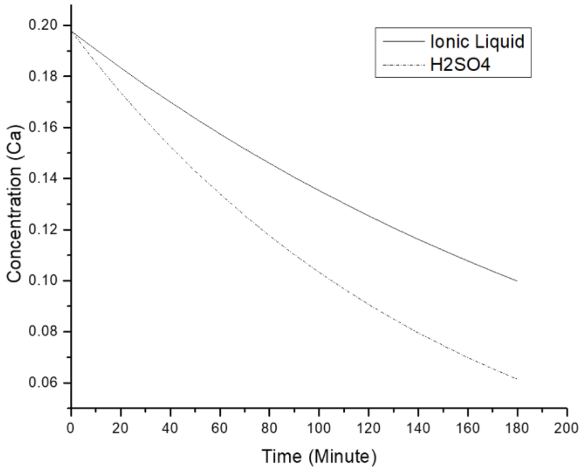


Figure 5. Correlation of reaction time with the rate of reduction of new Ca concentrations

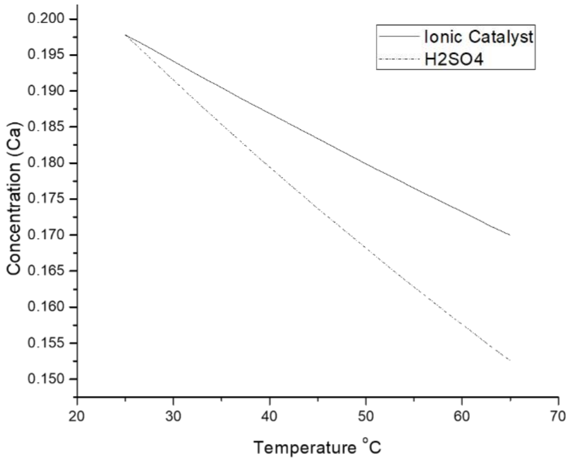


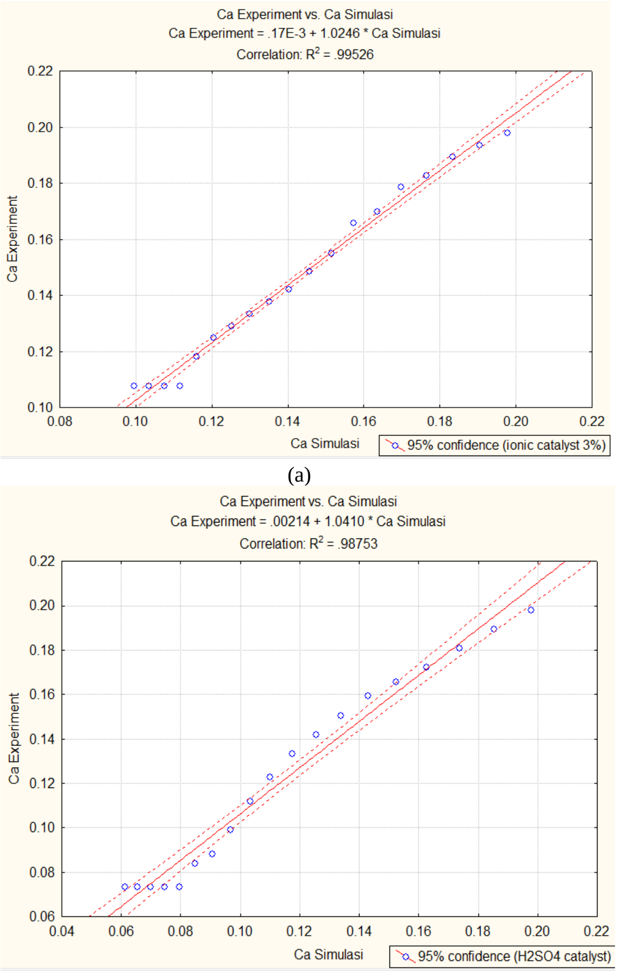
Figure 6. Correlation between reaction temperature with the rate of reduction in Ca concentration

The addition of sulfuric acid as a catalyst to accelerate the speed of the esterification reaction becomes a strong exothermic reaction. Water added with concentrated sulfuric acid will be able to boil, so the reaction temperature will be high. The higher the reaction temperature, the more molecules that have greater or equal energy activation, so the faster the reaction (Jaharani *et al*., 2016).

The catalyst will provide a route for the reaction to take place with lower activation energy so that the value of the reaction speed coefficient (k) will be greater, so that the reaction speed will also be greater (Purnami *et al*., 2015). In addition, because concentrated sulfuric acid is capable of binding water (hygroscopic), then for equilibrium esterification reactions that produce water, concentrated sulfuric acid can shift the direction of the reaction to the right (towards the product), so that the resulting product becomes more numerous (Ferdous *et al.*, 2013).

Validation of Ca concentration reduction rate between experiment results and simulation results

Figure 7 shows the correlation of C_A concentration from the simulation model and the experimental results model. Simulation data using C_A concentration data at operating conditions of $65^{o}C$, catalyst 3%, and the value of k for liquid ionic catalysts was 0.0038 L / mol.s, while the H_2SO_4 catalyst was 0.0065 L/mol.s. The data is then processed using Statistica 8.0 software to find the best correlation between the simulation model and the experimental model through Residual Regression Design. From Figure 7 shows that the simulation model and the experimental model give a very close correlation with the value of R^2 = 0.99526 for 3% liquid ionic catalysts, and R^2 = 0.98753 for H_2SO catalysts. The correlation value shows the suitability of the results from the first order kinetic models that is simulated with the results of experiments in the laboratory.



(a)

(b)

Figure 7. Correlation of Ca Simuation with Experiment Ca ((-) Ca Simulation versus Ca Experiment; (---) error limit (a) 3% liquid ionic catalyst, (b) H_2SO_4 catalyst)

The coefficient of determination (R^2) is the ratio of variance in the simulation model and variance in the experimental model. If the coefficient of determination (R^2) is close to 1, it means that the value predicted by the model is the same as the experimental value (Aulia *et al.*, 2012). Higher R^2 value for esterification reaction between Kapok seed oil and methanol using 3% liquid ionic catalyst gives a better description than the reaction kinetic models using H_2SO catalyst.

The dotted line is the error limit obtained from twice the standard deviation. Statistically in a normal distribution, about 93% of the value will be in this area. As can be seen in Figure 7, almost all values are within these limits. This shows that the first order reaction kinetic models for the esterification process is appropriate to describe the first order reaction kinetic models based on experimental data.

Comparison of order 1 and 2 esterification reaction kinetics

Figure 8 shows a comparison graph of the reduction in C_A concentration from the simulation results with reaction order models 1 and 2 against the reaction kinetic models experimentally. From Figure 8 it can be seen that the first order reaction gives a more significant decrease in C_A concentration per time compared to the second order reaction. If the remaining C_A reactant concentration becomes small, then the conversion value of the product produced will be greater by setting aside the side product.

This is also supported by the results of validation between the first and second order reaction models to the experimental results using Statistics 8.0 software. In Figure 9 we can see that the correlation value (R2) between order 1 and order 2 is better in order 1 with a correlation value approaching 1 which is 0.99526, while the order value has a correlation value of 0.89453. The reaction order is the sum of the reactant concentration exponents in the reaction rate law.

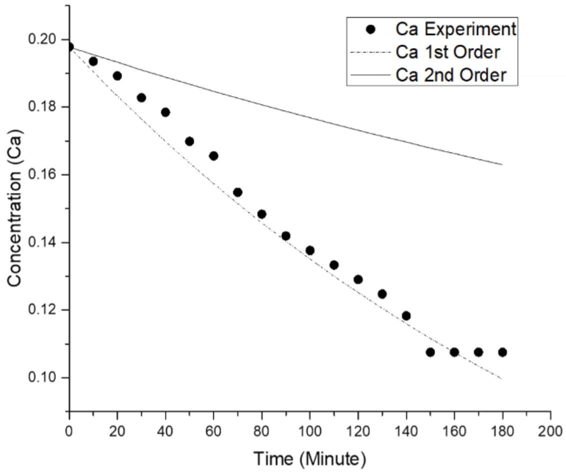


Figure 8. Comparison of the rate of reduction of C_A concentration in the first and second order esterification reaction kinetic models

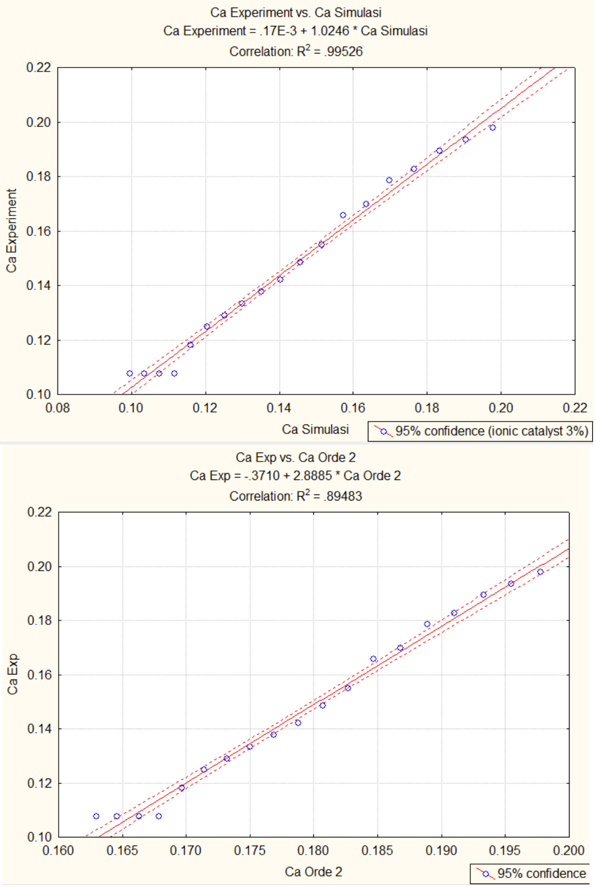


Figure 9. The correlation of C_A C_A concentration with Experiment Ca ((-) Ca Simulation versus C_A Experiment; (---) error limit (a) order 1, (b) order 2)

Determination of the reaction order is based on the greatest coefficient of determination R square and the smallest value of% error (Cardoso *et al.*, 2008). Based on these data the results are obtained that the appropriate order of reaction between the simulation and experimental data is order 1. In addition to the reaction order, the output of studying the reaction kinetics is the reaction rate coefficient. As one of the factors that influence the value of the reaction rate coefficient (k) is the temperature, therefore the operating temperature is varied.

The kinetics of first order esterification reactions

In the research of Prasad and Beguette (1998), the kinetic model of Kapok seed oil esterification reaction with liquid ionic catalyst is proposed in first order with the reaction taking place irreversibly. It is assumed that the esterification reaction is only influenced by one type of reagent that is excess FFA and methanol (1:18). FFA mole is small and limited due to high FFA molecular weight. Determination of reaction kinetics is based on the rate of reduction in the FFA (C_A) concentration of time.

$$-r_A = -\frac{d\,C_A}{dt} = kC_A \qquad (1)$$

The kinetics of the 2nd order esterification reaction

In this study, the simulation of the esterification reaction kinetic models also proposed is second order irreversibly. It is assumed that the esterification reaction is influenced by the concentration of FFA reagents and methanol is made proportional (1:1). Determination of reaction kinetics is based on the rate of reduction in the FFA (C_A) concentration of time. Determination of the reaction does not take into account the side reactions formed.

$$-r_A = -\frac{dC_A}{dt} = k.C_A.C_B \qquad (14)$$

C_A: FFA concentration
C_B: Methanol Concentration
$C_A = C_B$ concentration; then equation (2) becomes:

$$-r_A = -\frac{dC_A}{dt} = k.C_A^2 \qquad (15)$$

Every chemical reaction has a phenomenon of equation that is different from one another, which has a certain reaction kinetic model. Reaction kinetics is the study of the rate of reaction and the factors that influence it. The kinetic model of the FFA esterification reaction with Methanol can be determined by obtaining the conversion value of the product produced or the reduced concentration of reactants per unit time under temperature conditions, reactant ratios and variations in the amount of the best reaction catalyst. Reaction kinetics parameters include order, reaction rate coefficients and activation energy.

Widayat *et al* (2017) studied the kinetics of the reaction of Kapok seed oil esterification into biodiesel with a liquid ionic catalyst. From these studies the results obtained that the order of esterification reaction follows order 1, assuming the esterification reaction is only influenced by one type of reagent that is FFA Kapok seed oil. Assumptions based on high FFA molecular weights make FFA act as a limiting reaction with a smaller number of moles of FFA compared to Methanol. This is in line with research conducted by Chai *et al* (2014) in which FFA esterification follows a first-order reaction. However, in other studies conducted by Lieu *et al* (2016) the results show that the FFA esterification reaction order follows order 2 with an R^2 of 0.974. It is assumed that the reactant ratio between FFA and Methanol affects the product conversion (Levenspiel, 1999). Another thing is also found in the research conducted Mazubert *et al* (2014), where in the study of esterification of FFA and Methanol followed a two-level directional reaction order, which is assumed to be in the stoichiometry coefficient value involving two molecules (bimolecular).

Simulation of product formation rate

The rate of formation of Kapok seed oil esterification reaction products can be simulated by reviewing some initial parameters, such as the initial concentration of reactants, reaction time, reaction order, reaction speed coefficient, and reaction time. In the research of Widayat *et al* (2017) there was no reversible esterification reaction review, so only one of the kinetics coefficients of the reaction was determined (in this case the k_1 price). To construct the simulation the reversible reaction kinetics are used:

$$-\frac{dCa}{dt} = k_1.C_{FFA}.C_{MOH} - k_2.C_{ME}.C_{Water} \qquad (16)$$

Assumption where C_{Waters}= cME; k_2 value uses the initial guess value then equation (16) becomes:

$$-\frac{dCa}{dt} = k_1.C_{FFA}.C_{MOH} - k_2.C_{ME^2} \qquad (17)$$

From equation (17) a simulation will be performed to determine the composition of each component in the equation. The simulation is done using MATLAB software with ODE45 function. The results of the simulation can be seen in Figure 10.

In Figure 10 it can be seen that the esterification reaction is still not optimal because there is no equilibrium point between the reactants and the reaction results. This can happen because the reactant ratio is not right and is not proportional to the amount of catalyst used. The use of liquid ionic catalyst is also one of the important factors to get optimal conversion. Activation can be done before the liquid ionic catalyst is used. If seen in Figure 10, there is no contact between oil and methanol, this could be due to the reactant ratio that is too large (1: 8).

In addition to reviewing the reactant ratio, further research is needed to determine whether any by-products are produced (in this case water), so as to give a greater value of k2 (the reaction rate coefficient to the left). In addition to this, a reversible esterification reaction needs to be reviewed to conduct a trial to find the right k_2 price, as well as the right reaction temperature.

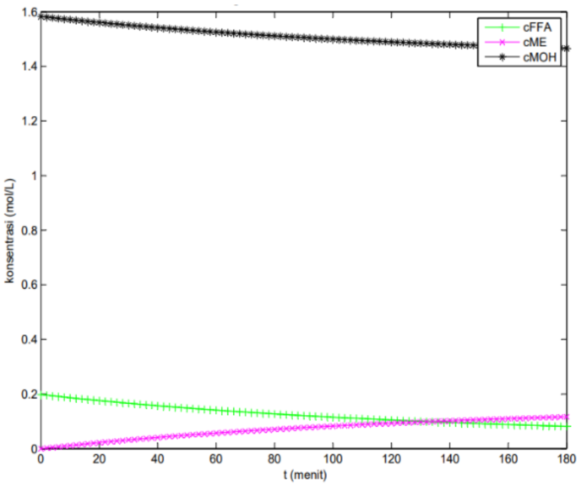


Figure 10. Graph The correlation between the rate of reduction of the concentration of FFA and Methanol with the rate of formation of the concentration of Methyl Esther.

Estimated reaction kinetics parameters

The kinetic model of Kapok seed oil and methanol esterification reaction can be viewed from the conversion of the product produced or the reduction in the concentration of the main reactants per unit time. Overview of the reaction kinetics parameters include the reaction order, the reaction rate coefficient (k), and the activation energy (-Ea). In the research of Prasad and Beguette (1998), a kinetic models of esterification reaction between Kapok seed oil and methanol was formed with the help of liquid ionic catalyst and sulfuric acid. The description of the esterification reaction is as follows:

$$\underset{\text{Fatty Acid}}{RCOOH} + \underset{\text{Metanol}}{CH_3OH} \longrightarrow \underset{\text{Metil Ester}}{RCOOCH_3} + \underset{\text{Water}}{H_2O}$$

The chemical reaction equation can be written in a simpler form to facilitate writing the speed of the chemical reaction as follows:

$$A + B \longrightarrow C + D$$

Information:

A = Fatty Acid
B = methanol
C = methyl ester
D = water

The equation of reaction speed:

$$r_a = -\frac{dCa}{dt} = k_1 [A] [B] - k_2 [C] [D] \qquad (18)$$

The above reaction is a pseudo homogenous reaction because one of the reactants is made excess (in this case the excess methanol is made), so the reaction tends to shift to the right and the k2 value becomes very small.

Judging from the reaction kinetics, the reaction rate of ester formation will be greater with an increase in temperature, stirring and adding a catalyst. This can be explained by the Arrhenius equation:

$$k = Ae^{-\frac{Ea}{RT}} \qquad (19)$$

with:

k = reaction rate coefficient
A = Collision frequency factor
T = temperature
Ea = Activation Energy
R = ideal gas coefficient

Based on the Arrhenius equation, it can be seen that the reaction rate coefficients are influenced by the values of A, E_a, and T, the greater the collision factor (A), the greater the reaction rate coefficients. The value of activation energy (E_a) is influenced by the use of catalysts, the presence of a catalyst will reduce the activation energy so that the greater k value. The higher the temperature (T), the greater the k value.

Table 3. Coefficient rate of esterification reaction VS temperature (with 3% ionic catalyst)

Temperature (K)	K	1/T
298	0.0017	0.0034
308	0.0026	0.0032
318	0.0040	0.0031
328	0.0047	0.0030
338	0.0060	0.0030

The reaction kinetic models that has been arranged in equation (5) is used as a model to determine the value of k at various temperatures (25, 35, 45, 55 and 65ºC) using 3% liquid ionic catalyst. The determination of k price is obtained from the simulation results using the Polyfit MATLAB function. From the results of simulation and data processing, it can be determined the reaction kinetics parameters (A, - E_a) in equation (19). Data of the reaction speed coefficient for each temperature can be seen in Table 3.

Based on the data presented in Table 3, the reaction parameters that can be determined in equation (19) can be determined. To determine these parameters, linearization is needed in the Arrhenius (19) equation, so that equation (19) becomes:

$$k = A . e^{-\frac{Ea}{R.T}} \tag{19}$$

$$\frac{k}{A} = e^{-\frac{Ea}{R.T}} \tag{20}$$

$$ln\left(\frac{k}{A}\right) = -\frac{Ea}{R.T} \tag{21}$$

$$ln\ k - In\ A = (-\frac{Ea}{R.T}) \tag{22}$$

$$ln\ k = \left(-\frac{Ea}{R.T}\right) + In\ A \tag{23}$$

$$y = m \cdot x \tag{24}$$

Where:
$Y = \ln k; X = \frac{1}{T}; C = \ln A; a = -\frac{Ea}{R};$ R = 8,314 J/mol.K

The Y and X functions in equation (24) are obtained from the data in table 3, then the data is simulated into MATLAB with the Polyfit function. The simulation results obtained the value of -Ea = -89.5 J / mol, and the value of A = 1.0384. While the experimental results the value of Ea = -0.437 kj / mol and the value of A = 0.012. The difference between simulation and experiment results is due to the different values of the reaction velocity coefficient, as shown in Figure 8.

Based on the data in Figure 11, it can be seen that as the esterification temperature increases, the reaction rate coefficient (k) increases because the reaction rate is proportional to the reaction temperature. Collisions between particles will be more perfect and faster the activation energy of the molecules is achieved due to an increase in reaction temperature (Aghel *et al.*, 2014). In this study, the temperature was limited to 65ºC. For the calculation of the activation energy value (-Ea) and the collision factor (A) mathematically solved. Activation energy is the minimum energy needed by reactants to react. Equations for settlement and calculation (-Ea) and A follow equation (24). The equation has a form that is identical to the line equation y = mx + C with the slope value is $-\frac{Ea}{R}$while the intercept value is ln A (Widayat *et al.*, 2017).

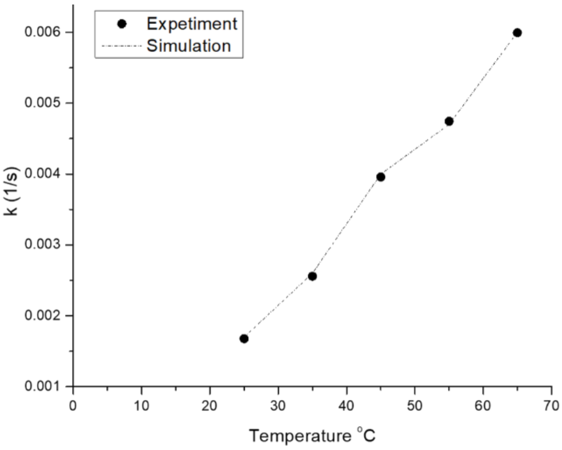


Figure 11. Comparison of the value of the reaction speed coefficient (k) from the results of simulations and experiments with 3% liquid ionic catalyst

Table 4. Reaction kinetics parameters based on simulation and experimental results

Parameters	Simulation	Experiment
A	1,0384	0,012
-Ea	-89,5	-0,437

The impact factor is related to the stirring speed, which the greater rotation speed, the greater impact factor will be obtained (Harianti and Sarto, 2009). In this study the stirring speed of 100rpm was used. For the kinetics parameters of the reaction both reaction simulation and experimental results can be seen in Table 3. Calculation of reaction kinetics parameters can be seen further on the attachment page. Then the kinetic model of the rate of etherification reaction of Kapok seed oil and methanol after being equipped with the value of the kinetic parameters becomes:

$$-r_a = -\frac{dCa}{dt} = 1{,}0384\ exp^{(\frac{-89{,}5}{R.T})}\ Ca \tag{25}$$

$$-r_a = -\frac{dCa}{dt} = 0{,}012\ exp^{(\frac{-0{,}437}{R.T})}\ Ca \tag{26}$$

Equation (25) is the kinetics equation of Kapok seed oil esterification reaction and methanol using a liquid ionic catalyst in a simulation, while equation (26) is the kinetic equation of the Kapok seed oil esterification reaction and methanol using a liquid ionic catalyst experimentally.

CONCLUSIONS

The best conversion process of Kapok seed oil and methanol esterification obtained from the MATLAB simulation results was 0.4565 for the amount of 3% liquid ionic catalyst, and 0.630435 for the 3% H_2SO_4 catalyst amount. The residual concentration of reactants (Ca) obtained based on the amount of liquid ionic catalyst 3% for the simulation results is 0.0996, and 0.1075 for the experimental results, with a% error of 7.37%. The reaction rate coefficient (k) obtained from the esterification process of Kapok seed oil and methanol with 3% liquid ionic catalyst was 0.0038 L/mol.s for the simulation results, and 0.003815 L/mol.s for the experimental results. Validation of the suitability of the reaction kinetic models between simulation and experiment using the Residual Regression Design method from Statistica 8.0 software, obtained a very close correlation with the value of $R^2 = 0.99526$ for 3% liquid ionic catalysts, and $R^2 = 0.98753$ for 3% H_2SO_4 catalysts. Validation of the suitability of first and second reaction kinetic modelss using Statistic 8.0 software gives a correlation value (R^2) = 0.99526 for order 1 and (R^2) = 0.89453 for order 2. Based on the correlation values it can be concluded that the reaction kinetics are ordered 1 Reaction kinetics of Kapok seed oil and methanol esterification process with 3% liquid ionic catalyst following order 1 reaction, where the reaction kinetics parameters are: Activation energy of the etherification reaction of -89.5 kJ/mol and A = 1.0384 L/mol.s for the simulation results, then the activation energy of the esterification reaction amounted to -0.437 kJ/mol and A = 0.012 L/mol.s for the experimental results.

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