Modeling of Glycerolysis Kinetic of Free Fatty Acid in Crude Palm Oil

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Abstract. Kinetics describing chemical glycerolysis reaction of free fatty acid (FFA) in crude palm oil (CPO) with crude glycerol has been investigated. In this study, the kinetics was explored under the conventional procedure using KOH as a homogenous catalyst. The FFA value was measured by the acid-base titration technique. The effect of FFA to glycerol molar ratio and reaction temperature are examined to determine the best condition for FFA reduction. The glycerolysis achieved a maximum FFA reduction from 6.15% to 0.28% under the following conditions: FFA to glycerol molar ratio of 1:4 and 75°C temperature. Under these conditions, the total reaction orders and the reaction rate constant of glycerolysis were determined by establishing six kinetic models. It was found that the highest $R^2$ was 0.89, which was presented from model 5 ($\alpha=2, \beta=0$): $\frac{X}{(1-X)} = kC_{A0}t$. The calculated rate constant, activation energy, and pre-exponential factor were 6.5608 L mol⁻¹ min⁻¹, 9,432 cal mol⁻¹, and 5.4×10⁶ L mol⁻¹ min⁻¹, respectively.

1. Introduction
Petroleum fuels have been used for many applications, most notably in the transportation and industrial sector. However, the rapidly increasing petroleum fuel consumption has caused an increase in the rate of depletion of fossil fuel reserves and pollution of the environment. Therefore, there is an urgent need to use alternative and renewable fuel, such as biodiesel. Currently, the main drawback of biodiesel production is the high raw material cost. Mohammadshirazi et al. [1] stated that the raw materials’ price is about 70-75% of the total biodiesel production cost because biodiesel is mainly produced from virgin vegetable oil. The use of low-quality raw materials could be one of the solutions to reduce total biodiesel production costs. These kinds of raw materials usually contain free fatty acids (FFA) with high contents.

Transesterification is considered more efficient and can produce biodiesel with high yield and purity. However, this process requires high purity oil as a raw material. Oil as raw material for transesterification reaction should contain FFA <0.5% or acid_number <1 mg KOH/g [2]. For raw
material with high content FFA, an appropriate production process should be used to obtain biodiesel with a good quantity and quality [3]. Aparamarta [4] reported that acid numbers more than 1 mg KOH/g would cause biodiesel yield decrease caused by increasing the soaps formed concentration due to catalyst deactivation and triglyceride hydrolysis. Generally, esterification is conducted before transesterification as the initial treatment of raw materials with high FFA content. However, esterification requires relatively high temperatures, large amounts of alcohol, and acid catalysts [5]. At the end of the reaction, the excess of alcohol and water formed will require more energy to remove from the mixture. Furthermore, the use of catalysts commonly H₂SO₄ also makes the application of the process limited due to the use of corrosive material.

Glycerolysis can be used as pre-treatment for reducing acidity. This technique's benefit is that no alcohol is required during the process, and the water formed can be vented and immediately vaporized [6]. Glycerolysis converts the FFA in oil into neutral glycerides by added glycerol and with or without a catalyst. Glycerolysis has the potential to apply due to it can utilize crude glycerol from biodiesel transesterification [7]. Kumoro [8] reported that the presence of sodium hydroxide as a catalyst and 80 °C of temperature reaction provided 91.03% of reaction conversion for glycerolysis of FFA in waste cooking oil. Meanwhile, Kombe et al. [9] also reported the application of glycerolysis for pre-treatment of non-edible crude jatropha oil. They found that the highest glycerolysis efficiency of 98.67% under the following condition: oil to glycerol mass ratio of 1.2:24, temperature of 65°C, and reaction time of 73 minutes.

Knowledge of the kinetic model of a process is essential for technological and economic analysis. Such knowledge will be a valuable tool for process design and scale-up [10]. In the present study, crude palm oil (CPO) with high FFA content was reacted with crude glycerol as low-cost reactant obtained from the by-product of transesterification. The objective of this work was to determine the effect of FFA to crude glycerol molar ratio and reaction temperature on the performance of the glycerolysis process. Then, kinetic models for glycerolysis of CPO at the maximum of FFA conversion were evaluated. The reaction rate constant, pre-exponential factor, and activation energy were finally calculated.

2. Materials and method

2.1. Materials

CPO was obtained from Nagan Raya District, Aceh, Indonesia. It was stored and maintained with normal laboratory conditions. The initial FFA of CPO was 6.15%, equivalent to the acidity of 13.47 mg KOH/g. Meanwhile, crude glycerol used was obtained from the biodiesel side-product of the transesterification reaction. The chemicals used were phosphoric acid, potassium hydroxide (KOH), phenolphthalein, and ethanol 96%. All the chemicals were procured from Sigma–Aldrich.

2.2. Glycerolysis of CPO

In the first step, CPO was degummed with phosphoric acid 1.5% (v/v of oil) at temperatures 65–70 °C for 15 minutes. Afterward, the mixture was transferred into separating funnel for separation of oil and gum. The oil from the upper layer was transferred to a centrifuge for the complete separation process. The glycerolysis reaction was carried out in a 500 mL round bottom three-neck flask. A specified amount of catalyst KOH and crude glycerol was added to the flask and stirred to form a potassium glycerolic solution. In a separate flask, CPO was heated on a hotplate, then, the solution was added and maintained at a specified reaction condition. The stirring speed and catalyst loading were 250 rpm, and 0.75 %-w of oil was kept constant during the process. The schematic apparatus used for glycerolysis of CPO is presented in Fig. 1. Samples were taken from the flask every 5 minutes for the first 15 minutes, and a 15-minute interval until terminated after 90 minutes. The influence of the molar ratio of FFA to crude glycerol and reaction temperature were investigated.
Figure 1. Schematic apparatus: (1) three-neck round bottom flask; (2) condenser; (3) thermometer; water bath; (4) hole of sampling; (5) hot plate with magnetic stirrer; (6) statif; and (7) water bath.

2.3. Product analysis
The progress of glycerolysis reaction at different experimental conditions has been monitored in terms of FFA content using the acid-base titration technique. Firstly, 5 grams of sample is mixed with 50 mL of ethanol 96% and heated for 5-10 minutes. Afterward, the sample is added 2-3 drops of phenolphthalein and titrated with a 0.1 N KOH. The endpoints were determined by changes in the color of the solution to a reddish-brown. The FFA can be calculated using Eq. (1).

$$\text{FFA} (\%) = \frac{\text{ml of KOH} \times N \text{ KOH} \times 256}{\text{mass of sample} \times 1000} \times 100$$

3. Results and discussion
3.1. Effect of process parameters
The effect of FFA to crude glycerol molar ratio and reaction temperature was evaluated, aiming to determine the optimum glycerolysis condition. In the first set of experiments, the effect of FFA to crude glycerol molar ratio (1:2, 1:3, 1:4, and 1:5) on the FFA value was investigated with a constant reaction temperature of 65 °C. In the second set of experiments, the effect of reaction temperature (55, 65, 75, and 85 °C) on the FFA value was investigated with a constant FFA to crude glycerol molar ratio of 1:4 (based on the lowest FFA value of the first experiments). Figure 2 shows the reaction progress in terms of the change in FFA value at various FFA to glycerol molar ratio and reaction temperature. It can be observed that the FFA significantly decreased during the initial 15 minutes of reaction time. However, after 30 minutes of reaction time, FFA has tended to be constant. A similar result trend was reported by Rizal et al. [11] for esterification of waste cooking oil and Satriana et al. [12] for glycerolysis of avocado oil.

The experimental results showed that FFA value generally decreases as FFA to crude glycerol molar ratio increases from 1:2 to 1:4 (Fig. 2(a)). According to the stoichiometry of glycerolysis reaction, molar ratio FFA to glycerol needed to run the glycerolysis reaction is 1:1 (Eq. 2). Since glycerolysis is a reversible reaction, usually glycerol is taken in excess with an objective of driving the reaction in the right direction [6,13].

$$\text{FFA} + \text{Glycerol} \leftrightarrow \text{Monoglyceride} + \text{H}_2\text{O}$$

However, further increase in the molar ratio of FFA to crude glycerol 1:5 seems not effective in enhancing the FFA reduction. The temperature of the reaction also affects the reaction rate (Fig. 2(b)). Generally, the increasing temperature increased mass transfer and improved glycerol solubility in oil.
Thus, the glycerolysis temperature must be high enough. However, undesirable taste and color change can occur as a consequence of using high temperatures. Based on the experimental data, the maximum FFA conversion of 95.45% was obtained at a FFA to crude glycerol molar ratio 1:4 with reaction temperature 75 °C in which initial FFA of CPO 6.15% reduced to 0.28%. This best process condition was used in the subsequent experimental studies of modeling of glycerolysis kinetic.

Figure 2. The reaction progress: (a) effect of FFA to crude glycerol molar ratio; and (b) effect of temperature.

3.2 Glycerolysis Kinetics
The kinetic model of glycerolysis was based on the following assumptions: (a) the effect of mass transfer was negligible, and (b) the effect of the reverse reaction and other reactions were ignored. The kinetic model can be written as Eq (3).

\[
A + B \rightarrow C + D \quad - \frac{dC_A}{dt} = k C_A^\alpha C_B^\beta
\]

Where \( C_A/t \) represents consumption of FFA per minute, \( C_A \) is concentration of FFA after time \( t \), \( C_B \) is concentration of glycerol after time \( t \), \( k \) is a rate constant, \( \alpha \) and \( \beta \) are the order of reactants FFA and glycerol, respectively. Also:

\[
X = \frac{(FFA)_{t-1} - (FFA)_t}{(FFA)_{t-1}}
\]

\[
C_A = C_{A0} (1 - X)
\]

\[
C_B = C_{A0} (\theta_B - X)
\]

\[
\theta_B = \frac{C_{B0}}{C_{A0}}
\]

where \( C_{A0} \) and \( C_{B0} \) are the initial concentration of FFA and glycerol, \( X \) is the conversion of FFA and \( \theta_B \) is ratio \( C_{B0} \) to \( C_{A0} \). Therefore, Eq. (3) can be rewritten as:

\[
\frac{dx}{dt} = k C_{A0}^{\alpha + \beta - 1} (1 - X)^\alpha (\theta_B - X)^\beta
\]

In this study, six models were taken into consideration to figure out the reaction order, namely, \( (\alpha=0, \beta=0), (\alpha=1, \beta=0), (\alpha=0, \beta=1), (\alpha=1, \beta=1), (\alpha=2, \beta=0), (\alpha=0, \beta=2) \). For each model, we substitute the value of \( \alpha \) and \( \beta \), then definite integrals of Eq. (8) were determined from the zero to \( X \) conversion, while the reaction time ranged from zero to \( t \) minutes. The calculation for each model was then implemented into a linear equation. Following are the equations for each of the six models:

Model 1
\[
\alpha = 0, \beta = 0
\]

\[
C_{A0} X = kt
\]
For Eqs. (9) to (14), we consider the left-side component as an ordinate variable (y variable), and t (for Eqs. (9) to (11)), $C_{A0}t$ (for Eqs. (12) to (14)) are abscissas (x variables), respectively. For all six models, the y variable was plotted against the corresponding x variable. The slope of the straight line can reflect the rate constant $k$ of reaction. According to the model on Eqs. (9) to (14), the plots have been transformed in the form of $y = mx$. The plotting with the highest $R^2$ value was selected to determine reaction order and reaction rate constant, which is the slope of the straight line passing through the origin.

Figure 3 presents the coefficient of correlation $R^2$ for all six models. According to the kinetics plots obtained for all models, model 5 was the best fit plot with the highest coefficient of correlation $R^2$. Figure 4 presents the kinetics plots obtained for model 5 ($\alpha=2, \beta=0$). It was found that the highest $R^2$ was 0.89, so this value was used to determine the overall reaction order as well as reaction order with respect...
to CPO and crude glycerol. It was also found that the reaction orders of FFA and crude glycerol were 2 and 0, respectively. Therefore, the overall reaction order was 2 which is consistent with Supardan et al [6] and Gole and Gogate [13]. Table 1 shows the value of reaction orders and rate constants for six models. Model 5 found the reaction rate constant was 6.5608 L mol\(^{-1}\) min\(^{-1}\).

![Figure 4. Kinetic plots for model 5 (α=2, β=0)](image)

**Table 1. Value of reaction order of the experimental data for all models**

| Model | Order of FFA | Order of crude glycerol | Overall order | Rate constant | Unit |
|-------|--------------|-------------------------|---------------|---------------|------|
| 1     | 0            | 0                       | 0             | 0.0003        | mol L\(^{-1}\) s\(^{-1}\) |
| 2     | 1            | 0                       | 1             | 0.0281        | min\(^{-1}\) |
| 3     | 0            | 1                       | 1             | 0.0018        | min\(^{-1}\) |
| 4     | 1            | 1                       | 2             | 0.2017        | L mol\(^{-1}\) min\(^{-1}\) |
| 5     | 2            | 0                       | 2             | 6.5608        | L mol\(^{-1}\) min\(^{-1}\) |
| 6     | 0            | 2                       | 2             | 0.0121        | L mol\(^{-1}\) min\(^{-1}\) |

**Table 2. Estimated Arrhenius parameters**

| Parameters | Unit     | Value      |
|------------|----------|------------|
| Intercept  | -        | -4,747.80  |
| Slope      | -        | 15.50      |
| \(R^2\)    | -        | 0.99       |
| \(E_a\)    | (cal mol\(^{-1}\)) | 9,431.89   |
| \(A\)      | L mol\(^{-1}\) min\(^{-1}\) | 5.4×10\(^6\) |

The influence of reaction temperature on the reaction rate was obtained by fitting \(k\) value to the Arrhenius equation of Eq. (15).

\[
k = A \cdot e^{\left[\frac{-E_a}{RT}\right]}
\]  

The pre-exponential factor \(A\) and activation energy \(E_a\) determined by plotting inverse temperature and the natural logarithm of the kinetic constants. Table 2 presents a summary of the estimated Arrhenius
The pre-exponential factor was found as $5.4 \times 10^6$ L mol$^{-1}$ min$^{-1}$ and the activation energy as 9,432 cal mol$^{-1}$. Freedman et al. [16] reported that the activation energies for glycerolysis reaction of soybean oil range from 8,000 to 13,000 cal mol$^{-1}$.

4. Conclusion

The alkali catalyzed glycerolysis of CPO using crude glycerol under low temperature has been implemented for FFA reduction. The highest FFA reduction from 6.15% to 0.28% was achieved by FFA to glycerol molar ratio of 1:4 and reaction temperature 75°C. Fitting lines and function equations were accomplished, and the rate constant $k$ was represented from the slope of the line with the highest coefficient of determination $R^2$. The rate constant was 6.5608 L mol$^{-1}$ min$^{-1}$, with a coefficient correlation was 0.89. The overall reaction order was 2 with reaction order of FFA and glycerol were 2 and 0, respectively. The estimated pre-exponential factor ($A$) was found to be $5.4 \times 10^6$ L mol$^{-1}$ min$^{-1}$ and the activation energy ($E_a$) as 9,432 cal mol$^{-1}$.

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6. References

[1] Mohammadshirazi A, Akram A, Rafiee S and Kalhor E B 2014 Renew. Sustain. Energy Rev. 33 44
[2] Kara K, Ouanji F, Lottfi E M, Mahi M E, Kacimi M and Ziyad M 2018 Egypt. J. Petrol. 27 249
[3] Hong I K, Jeon H, Kim H and Lee S B 2016 J. Ind. Eng. Chem. 42 107
[4] Aparamarta H W, Gunawan S, Azhar B, Aditya H T, Widjaja A and Ju Y H 2019 Int. J. Technol. 10 551
[5] Berrios M, Martin M A, Chica A F and Martin A 2010 Chem. Eng. J. 160 473
[6] Supardan M D, Adisalamun, Lubis Y M, Annisa Y. Satriana and Mustapha W A W 2017 Pertanika J. Sci. Technol. 25 1203
[7] He Q S, McNutt J and Yang J 2017 Renew. Sustain. Energy Rev. 71 63
[8] Kumoro A C 2012 Res. J. Appl. Sci. Eng. Technol. 4 869
[9] Kombe G G, Temu A K, Rajabu H M, Mrema G D and Lee K T 2013 Adv. Chem. Eng. Sci. 3 248
[10] Noureddini H and Zhu D 1997 J. Am. Oil Chem. Soc. 74 1457
[11] Rizal M, Suraiini N, Syamsuddin Y and Supardan M D 2020 IOP Conf. Ser. Mater. Sci. Eng. 845 012036
[12] Satriana, Arpi N, Supardan M D, Gustina R T and Mustapha W A W 2018 AIP Conf. Proceed. 1940 020100
[13] Gole V L and Gogate P R 2014 Fuel Process. Technol. 118 110
[14] Saha R and Goud V 2015 Biomass Convers. Bior. 5 195
[15] Satriana, Arpi N, Lubis Y M, Supardan M D and Mustapha W A W 2016 Eur. J. Lipid Sci. Technol. 118 1880
[16] Freedman B, Butterfield R O and Pryde E H 1986 J. Am. Oil. Chem. Soc. 63 1375