First Order Kinetics of Biodiesel Synthesis Using Used Frying Oil through Transesterification Reaction

Agus Haryanto¹*, Amieria Citra Gita¹, Tri Wahyu Saputra², and Mareli Telaumbanua¹

¹Department of Agricultural Engineering, Faculty of Agriculture, the University of Lampung, Indonesia; ²Department of Agricultural Engineering, Faculty of Agricultural Technology, University of Jember, Indonesia

*Corresponding author email: agus.haryanto@fp.unila.ac.id

Received: March 9, 2019
Accepted: April 11, 2020
Online: April 30, 2020

Abstract – This research aims to study the first-order kinetics of biodiesel production from used frying oil (UFO) through transesterification with methanol. Used frying oil was collected from fried peddlers around the campus of the University of Lampung. Technical grade methanol and NaOH catalyst were purchased from a local chemical supplier. The experiment was carried out with 100 ml of UFO at various combinations of oil to methanol molar ratio (1:4, 1:5, and 1:6), reaction temperatures (30 to 55°C, the ramping temperature of 5°C), and reaction time of 0.25 to 10 minutes. First-order kinetic was employed using 126 data pairs (87.5%). The acquired kinetic model was validated using 18 data sets (12.5%) observed at a reaction time of eight min. Results show that biodiesel yield was increased with reaction time, its molar ratio, and temperature. The maximum return of 78.44% was achieved at 55°C and molar ratio of 1:6. The kinetic analysis obtains the reaction rate constant (k) in the range of 0.045 to 0.130. The value of k increases with the reaction temperature and molar ratio. The analysis also reveals the average activation energy (Ea) of the UFO transesterification reaction with methanol and NaOH catalyst to be 21.59 kJ/mol. First-order kinetic is suitable to predict biodiesel yield from UFO because of low %RMSE (3.39%) and high R² (0.8454).

Keywords: biodiesel, used frying oil, kinetics, first order, transesterification.

Introduction

Biodiesel can be defined as a fuel comprised of mono-alkyl (methyl, propyl, or ethyl) esters of long-chain fatty acids derived from vegetable oils or animal fats (Ahmad et al., 2013). Biodiesel has properties so similar to diesel fuel that it can be used to substitute diesel fuel (Demirbas, 2007; Srivastava and Prasad, 2000; Javed Ali and Anurag Semwal, 2014). The advantage of biodiesel is renewable compared to non-renewable diesel oil. Therefore, the development of biodiesel is one way to reduce dependence on petroleum. Also, biodiesel utilization may reduce greenhouse gas (GHG) emissions. A study in the United States revealed that GHG emission associated with biodiesel production from soybean and its utilization is the lowest compared to that of gasoline, diesel fuel, or corn grain ethanol (Hill et al., 2006). Biodiesel contains low sulfur and has better lubricity that is good for engines (Hazarat et al., 2015). Biodiesel is made from organic feedstock so that it is an ecologically friendly fuel due to its possibility to be decomposed biologically (Bajpai and Tyagi, 2006).

In Indonesia, biodiesel is used as a blend to diesel fuel and commercially marketed as BXX, with XX represents the volume percentage of the biodiesel in the mix. Based on the regulation of Minister of Energy and Mineral Resources No. 12/2015 on the Supply, Utilization, and Trade of Biofuels as Other Fuel, by 2016, diesel fuel has to be marketed with a 20% biodiesel mixture or B20 for all sectors including PSO (public service...
obligation) and non-PSO transportations. The blend will increase to 30% by 2020 (Berita Negara Republik Indonesia No. 406, 2015).

Biodiesel production using vegetable oils or animal fats has resulted in high biodiesel prices due to high feedstock cost. A model of medium-sized biodiesel industry based on continuous-transesterification of crude degummed soybean oil with an annual capacity of 10 million gallons requires feedstock cost at US$17.507 million or 87.35% of the total production cost of US$20.041 million (Haas et al., 2006). Other works reported feedstock cost in a range of 61.2 to 77.4% depending on feedstock types and system capacity (Santana et al., 2010; Zhang et al., 2003; Tasić et al., 2014). Therefore, the cheap feedstock is good for biodiesel production. It has been recommended that UFO should be the primary feedstock for biodiesel, whereas fresh edible and non-edible oils are used as a supplement for the feedstock deficit (Gui et al., 2008).

The used frying oil is an oil that has been used for food preparation and no longer suitable for human consumption (Gui et al., 2008). During the deep-frying process, the oil undergoes some chemical and physical changes (color, odor, and viscosity) that may cause health problems, such as gastrointestinal disorders (Raqeeb and Bhargavi, 2015) and even cancer (Venkata and Subramanyam, 2016; Yuniwati and Karim, 2009). Therefore, utilization of UFO for food and food-related stuff such as frying food and making chili sauce is not recommended. Dumping the UFO directly into the soil can cause environmental problems due to its high value of chemical oxygen demand. Producing biodiesel from UFO is an appropriate solution (Adhiatma et al., 2012) because of its low cost. The development of biodiesel from UFO will provide a more acceptable option in using used oil.

The potential of UFO in Indonesia increases with the increasing vegetable oil consumption. Fujita et al. (2013) reported that a family in Bogor consumes cooking oil of 3 liters per month (36 L/y). UFO can be converted into biodiesel through transesterification reaction with methanol and inexpensive sodium hydroxide (NaOH) catalyst as simply presented in Equation (1).

\[
\text{Oil} + \text{Alcohol} \rightarrow \text{Biodiesel} + \text{Glycerol} \quad (1)
\]

The transesterification is an equilibrium reaction so that the maximum biodiesel product is obtained with the excess of methanol. The disadvantage of this reaction is that there may be a side reaction in the form of soap, which will deactivate the catalyst so that it can reduce biodiesel yield, especially if the free fatty acid content in the oil is reasonably high. Kinetics of transesterification reaction is essential to predict the biodiesel yield at certain times and conditions. The kinetic parameters to be determined include the reaction rate constant, a factor of collision frequency, and activation energy. Typically, transesterification reaction is performed at much higher of alcohol mole than oil mole that the concentration of alcohol can be assumed constant, and the rate of reaction is, therefore, dependent only on the concentration of oil (Turner, 2005). Hence, the first-order model is widely applied to analyze the kinetics of transesterification reaction for biodiesel synthesis (Aisyah et al., 2012; Farag et al., 2013; Emeji et al., 2015; Moradi et al., 2015; Mohadesi et al., 2018; Aniokete et al., 2019).

The factors used to determine the reaction kinetic are temperature and reaction time. The molar ratio of oil to alcohol influence biodiesel yield. Therefore, the effect of the molar ratio on the reaction kinetic is also important (Trejo-Zárraga et al., 2018) to determine the efficient operation of biodiesel production. The purpose of this study is to determine the kinetic parameters of the UFO transesterification reaction to a molar ratio of oil to methanol.

**Materials and Methods**

**Materials**

Used frying oil was obtained from fried food sellers around the campus of the University of Lampung. The oil used for cooking food was originated from palm oil. The collected UFO was filtered using a tea filter to separate solid particles. Technical grade methanol and NaOH were purchased from a local supplier (CV Panca Mandiri, Bandar Lampung). Free fatty acid (FFA) content, acid number, and viscosity of UFO were determined according to our previous work (Haryanto et al., 2015). Fatty acids of oil were analyzed by gas chromatography-mass spectroscopy (GCMS-QP2010 Ultra, Agilent Technologies Inc., Palo Alto, CA, U.S.A.) equipped with a capillary column (30m, 0.25 mm, 0.25 mm film thickness). The GC-MS analyses were carried out in split mode injection with split ratio 1:200),

\[\text{Oil} + \text{Alcohol} \rightarrow \text{Biodiesel} + \text{Glycerol} \quad (1)\]
using nitrogen as the carrier gas (1.31 mL/min flow rate) and the inlet pressure of 80.2 kPa. The sample volume injected was 1μL. The injector temperature was fixed at 280 °C. The oven temperature was held at 60 °C for 0 min and then programmed at 8 °C/min to a final temperature of 280 °C, where it was maintained for 2 min.

**Research procedure**

The treatment in this study was a combination of variations in the molar ratio of oil to methanol (MR), temperature, and reaction time. Lin and Hsiao (2012) reported that the optimal reaction for biodiesel synthesis occurred at MR of 1:6 with an average yield of 97.49 %, and a further increase of MR to 1:9 did not influence the yield. Kumar et al. (2011) also reported little difference in triglyceride conversion between the MR 1:6 and 1:10. Therefore, the variation of MR in our work consisted of three levels, namely 1:4, 1:5, and 1:6. The reaction temperature consisted of six levels, namely 30 to 55 °C, with ramping of 5°. Kumar et al. (2011) reported that almost complete conversion of jatropha oil transesterified with methanol is achieved in 10 minutes at 60°C. Hence, in this work, we used a maximum reaction time 10 minutes consisted of eight levels (0.25, 0.5, 1, 2, 3, 6, 8, and 10 minutes).

Each experimental unit was carried out with 100 mL of UFO and NaOH of 0.5% of the oil weight. Hossain & Mazen (2010) studied biodiesel production using waste soybean oil with methanol and NaOH catalyst (0.5, 1.0, and 1.5% of oil weight). The results show that the highest biodiesel yield is produced using 0.5% and 1% catalyst with no significant difference. Initially, we prepared a methoxy solution by mixing 0.5 gram NaOH into methanol and stirring until all NaOH particles dissolve. The amount of methanol is calculated based on the predetermined MR, namely 14.9 mL for MR 1:4, 18.2 mL for MR 1:5, and 21.8 mL for MR 1:6. The UFO was heated in an Erlenmeyer glass equipped with a reflux condenser to a specified temperature, and the methoxy solution was then poured into it and stirred at 300 rpm using a magnetic sterrer for a specified duration. The solution was then left to still for 24 hours. Biodiesel was separated from glycerol and washed using warm aqua dest several times until clean (marked by clean wastewater). Biodiesel yield was calculated by Equation (2):

\[
\text{Yield} = \left[ \frac{B}{O} \right] \times 100\% \tag{2}
\]

**Transesterification kinetic**

The following kinetics model was structured based on the assumption that transesterification is a first-order reaction and is a function of reaction temperature and the concentration of oil. The assumption is based on the fact that the reaction was performed using an excess of methanol. The kinetics equation is constructed in the following (Kusdiana and Saka, 2001):

\[
\text{Reaction rate} = -\frac{d[O]}{dt} = k \cdot [O] \tag{3}
\]

Integrating Equation (3) results in:

\[
\frac{[O]_t}{[O]_0} = \exp(-kt) \tag{4}
\]

The oil concentration at \( t = 0 \) is \([O]_0\) and at different \( t \) is \([O]_t\), where \([O]_0 > [O]_t\). Noting that at any time the conversion of oil into biodiesel is \( X \), we will have \( X = 1 - \frac{[O]_t}{[O]_0} \), and by substituting into Equation (4) and dividing all terms by \([O]_0\) we have:

\[
1 - X = \exp(-kt) \tag{5}
\]

In this case, oil conversion to biodiesel \((X)\) is equal to biodiesel yield calculated by Equation (2). Therefore, Equation (5) can be presented as:

\[
1 - \text{Yield} = \exp(-kt) \tag{6}
\]

Plotting of Equation (6) with \( t \) as abscissa and the negative value of natural logarithm \((1 - X)\) as ordinate can be used to determine the values of the reaction rate constant \((k, \text{mole/minute})\) at various temperatures. Values of \(k\) are then used to determine the activation energy value \((E_a)\) of the reaction using the Arrhenius equation:

\[
k = A \exp(-E_a/RT) \tag{7}
\]

where \(A\) is constant for molecular collision, \(T\) is the absolute temperature (K), and \(R\) is the universal gas constant (8.314472 J/mol.K).

**Model validation**
The acquired kinetic equation model was validated using the biodiesel yield data set measured at reaction time 8 minutes at all molar ratios and temperatures. The goodness of predicted yield was assessed from its determination coefficient ($R^2$) of prediction-observation plot and $\%RMSE$ (percentage root mean squared error):

$$%RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (\bar{y}_{obs} - y_{pre})^2} \times 100$$

where $\epsilon$ is residuals defined as the difference of observed yield ($y_{obs}$) and predicted yield ($y_{pre}$), and bar sign over the $y_{obs}$ mean average value. The lower $\%RMSE$, the better the prediction will be.

**Results**

**Characteristics of UFO**

Used frying oil used in this study had characteristics as given in Table 1. Fatty acid composition of the UFO was dominated by palmitate (42.84%), oleate (35.71%), and linoleate (12.43%), which all together contribute 91% of the total.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific mass</td>
<td>g/mL</td>
<td>0.912</td>
</tr>
<tr>
<td>Viscosity at 30°C</td>
<td>cSt</td>
<td>61.75</td>
</tr>
<tr>
<td>Free fatty acid (FFA)</td>
<td>%</td>
<td>1.43</td>
</tr>
<tr>
<td>Acid number</td>
<td>g KOH/L</td>
<td>0.720</td>
</tr>
<tr>
<td>Methyl Laurate</td>
<td>%</td>
<td>0.75</td>
</tr>
<tr>
<td>Methyl Myristate</td>
<td>%</td>
<td>1.58</td>
</tr>
<tr>
<td>Methyl Palmitate</td>
<td>%</td>
<td>42.84</td>
</tr>
<tr>
<td>Methyl Linoleate</td>
<td>%</td>
<td>12.43</td>
</tr>
<tr>
<td>Methyl Oleate</td>
<td>%</td>
<td>35.71</td>
</tr>
<tr>
<td>Methyl Stearate</td>
<td>%</td>
<td>5.15</td>
</tr>
<tr>
<td>Not known</td>
<td>%</td>
<td>1.54</td>
</tr>
</tbody>
</table>

**Biodiesel yield**

Figure 1 shows the relationship between reaction time and reaction temperature to the biodiesel yield at three different oil-to-methanol molar ratios. It reveals that biodiesel yield increases with reaction time.
Figure 1. Effect of reaction duration (0 to 10 min), temperature (30 to 55 °C), and molar ratio (1:4 to 1:6) on the biodiesel yield.

Kinetic Parameters

Figure 2 shows the relationship of reaction time \( t \) to \( [O]/[O_0] = 1 - \text{Yield} \) at various temperatures and molar ratios. The relationship between \( t \) and \( [O]/[O_0] \) can be satisfactorily presented exponentially for all treatments.
Discussion
Characteristics of UFO

Based on fatty acid composition that is dominating the UFO (Table 1), it is a strong indication that the cooking oil commonly used in Indonesia is originated from palm oil. Kheang et al. (2006) reported UFO derived from palm oil is composed mainly of these three fatty acids with a weight percentage of 38.5 (palmitate), 45.7 (oleate), and 8.8 (linoleate). As a leader for a palm oil producer, it is not surprised that cooking oil consumed by most peoples in Indonesia is produced from palm oil.
Biodiesel yield

Figure 1 shows that initially, the yield of biodiesel obtained from the experiments increases sharply as the reaction time increases. But, after practically one minute, the increase in biodiesel yield began to slope. Susilowati (2006) reported that biodiesel yield from kapok seed oil increases with the increasing reaction time. The longer the reaction time, the higher chance of collisions between oil and methanol, and the higher conversion will be (Parhusip et al., 2012).

Biodiesel yield generally increases more methanol mole. Transesterification is an equilibrium reaction, which means the reaction rates of forward and reverse will be the same rate at equilibrium condition. One way to shift the attitude towards the product (right) is by increasing methanol. The results indicate that the more methanol we add, the more biodiesel yield we get. In the molar ratio of oil to methanol 1:6, the highest biodiesel yield (78.44%) was gained at 55°C and reaction time of 10 minutes. Other works reported that optimum biodiesel conversion has resulted in the molar ratio of triglycerides to methanol 1:6 (Majid et al., 2012; Venkateswarulu et al., 2014).

In general, biodiesel yield also increases with temperature. At a molar ratio 1:6 and reaction time of 10 min, for example, biodiesel rises from 66.19% at 30°C to 78.44% at 55°C. Increasing the temperature of reactants results in faster movement of the particles, and therefore they collide more frequently (Connors, 1990). This process, in turn, will speed up the reaction.

Kinetic Parameters

Equation (6) shows that \([O_1]/[O_0]\), which is equal to \(1 – Yield\), relates to an exponential function of \(-kt\). The graph shows that the plot of reaction time vs. \([O_1]/[O_0]\) can be represented satisfactorily by the exponential Equation with a high regression coefficient (close to 0.9). It means that the first-order assumption for the transesterification reaction of UFO using methanol can be adequately accepted. Figure 2 also shows that reaction rates are greatly affected by temperature, which also demonstrated by other studies (Walas, 1989; Cornish-Bowden, 2012). The significant effect of temperature on reaction rate is obvious from Arrhenius relation as presented by Equation (7). Equation (6), however, has no intercept (the coefficient is 1), and some studies have confirmed it (Moradi et al., 2015; Farag et al., 2013; Mohadesi et al., 2018). Our results (Figure 2), provided intercept between 0.575 (at MR 1:6 and temperature 35°C) to 0.752 (at MR 1:6 and temperature 55°C). It could have resulted from the temperature effect. The presence of intercept was also reported by other works (Aisyah et al., 2012; Talebian-Kiakalaieh et al., 2013; Emekji et al., 2015; Aniokete et al., 2019).

Based on the reaction rate constants as collected from Figure 2, an Arrhenius plot was made to represent the relation between the values of \(k\) with the inverse of absolute temperature (1/T) at three levels of the molar ratios as presented in Figure 3. The figure shows that the relationship between 1/T to the natural logarithm values of \(k\) can be well represented linearly, indicated by a high regression coefficient (> 0.90). Upadhyay (2006) explains that raising the temperature will increase the collisions and hence increases the reaction rate. A further implication of this is that increasing temperature also increases the value of \(k\). The dependence of constant rate \(k\) on temperature has already described by the Arrhenius expression. Based on the slope values obtained from Figure 3 and referring to the Arrhenius equation, we calculated the global activation energy value (\(E_a\)) and the constant of molecular collision frequency, and the results were presented in Table 2. We observe that the molar ratio of oil to methanol slightly affected \(E_a\) values, which are 23.61, 17.33, and 23.83 kJ/mol, respectively, at a molar ratio of 1:4, 1:5, and 1:6. The average value of \(E_a\) is 21.59 kJ/mol, which is in the range of values reported by other works, i.e., 26.97 (Kwartiningsih et al., 2007), 30.2 (Issariyakul and Dalai, 2012), 41.94 (Buchori and Sasonko, 2012), 38.46 (Said et al., 2010), 52.51 (Azizet al., 2016), 30.69 (Haryanto et al., 2017), and 23.69 (Jaya and Selvan, 2014).
Figure 3. Linear plot of the Arrhenius equation at three different molar ratios.

Table 2. Activation energy \((E_a)\) and molecular collision frequency constant \((A)\) of UFO transesterification.

<table>
<thead>
<tr>
<th>Molar ratio</th>
<th>(E_a) (kJ/mol)</th>
<th>(A) (min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:4</td>
<td>23.61</td>
<td>545.65</td>
</tr>
<tr>
<td>1:5</td>
<td>17.33</td>
<td>54.36</td>
</tr>
<tr>
<td>1:6</td>
<td>23.83</td>
<td>708.12</td>
</tr>
</tbody>
</table>

A part of the Arrhenius equation is the collision frequency factor \((A)\), which is also known as the pre-exponential factor. This factor represents the frequency of collisions between reactant molecules. From Table 2, the value of the pre-exponential element is 545.65 min\(^{-1}\) at MR 1:4 and increases to 708.12 min\(^{-1}\) at MR 1:6. This implies that the more methanol is given, the higher a chance that molecular collisions may occur. However, at MR 1:5, the value of the pre-exponential factor drops considerably to 54.36 min\(^{-1}\). It is still unexplained yet as to why this could have happened.

Model validation

Figure 4 shows a comparison between biodiesel yields measured at a reaction time of 8 minutes, and the prediction yields calculated using the acquired kinetic parameters. We can confirm that the predicted yields are close to the measured values with %RMSE of 3.39%. The expected return is classified as excellent because the amount of %RMSE is less than 10% (Li et al., 2013; Despotovic et al., 2016). Furthermore, Figure 4 shows the model can be satisfactorily used to predict the biodiesel yield with the determination coefficient \((R^2)\) of 0.8454. According to Sugiyono (2008), the predicted values have a strong correlation with observed values at \(R^2\) values of 0.81-0.99. The figure also shows that 16 data points (out of 18) fall in the area of the observed yield ± 5%. Again, this is a strong indication that the equation model is appropriate to predict biodiesel yield.
Conclusion

The highest biodiesel yield of 78.44% was achieved at the optimum condition of the oil-to-methanol molar ratio of 1:6, temperature of 55°C, and reaction time of 10 min. The kinetics of transesterification reactions can be suitably explained using a first-order reaction model with an intercept between 0.575 and 0.752. The values of the reaction rate constant in the transesterification reaction of UFO tend to increase with increasing temperature. The reaction rate constants also increase concerning the molar ratio of oil to methanol with the lowest value of $k = 0.045$ (temperature of 30°C, the molar ratio of 1:4) and the highest $k = 0.130$ (temperature of 55°C, molar ratio of 1:6). The activation energy in the transesterification reaction of UFO is, on average of 21.59 kJ/mol. The first-order kinetic model is suitable and can be satisfactorily used to predict biodiesel yield, which is reflected in the low %RMSE (3.39%) and high $R^2$ (0.8454).

Acknowledgment

The research was financially supported by the DGHE (Directorate General of Higher Education), Ministry of Research, Technology, and Higher Education, through the FUNDAMENTAL Research program with contract number 071/SP2H/LT/DRPM/IV/2017585 (June 2, 2017).

References

Daya Mineral Nomor 32 Tahun 2008 Tentang Penyediaan, Pemanfaatan, dan Tata Niaga Bahan Bakar Nabati (Biofuel) Sebagai Bahan Bakar Lain.


