Kinetic Model Based on Eley-Rideal and Irreversible Mechanism for Multilevel Reaction of Biodiesel Synthesis

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Abstract. As a new technology, an ion exchange catalyst as a heterogeneous catalyst became a good potential in exchanging the homogeneous base. A kinetic model based on Eley-Rideal mechanism and irreversible multiple reaction of biodiesel synthesis by using heterogeneous catalyst has been simulated in this work. The aim of this study is to obtain the kinetic parameter value of biodiesel synthesis with ion exchange heterogeneous catalyst. In addition, a sensitivity analysis was also studied to evaluate the effect of kinetic parameter value against the change in concentration profile of biodiesel synthesis. A kinetic model data used in this study was obtained from different experiment literatures. Based on the kinetic model of Eley-Rideal mechanism, the results of reaction rate constant values (k₁-k₆) were 7.87x10⁻³, 8.75x10⁻⁷, 1.1x10⁻², 1.12x10⁻⁶, 9.14x10⁻³ and 5.09x10⁻⁴, respectively. In addition, for irreversible kinetic simulation, the most accurate value was showed that 1.5 mol/l of fatty acid at initial reaction has been changed after 180 minutes reaction into 1.5x10⁻⁴ mol/l of trygliceride, 2.25x10⁻⁴ mol/l of diglyceride, 2.4x10⁻² mol/l of monoglyceride and 1.453 mol/l of biodiesel yield. The obtained values of irreversible kinetic parameter (k₁-k₃) were 7.86x10⁻³, 1.11x10⁻² and 9.15x10⁻³, respectively.

Among renewable fuels, biodiesel has received a considerable attention to be more developed. Biodiesel is a renewable fuel that will be sustainable, economically, and environmentally friendly, due to it is synthesized from vegetable oil or animal fats [1-2]. Biodiesel is synthesized by transesterification reaction with the addition of catalyst. Homogeneous base catalyst is usually used, because it gives high conversion rates over 95% [3]. However, homogeneous catalyst has several weaknesses such as the catalyst cannot be recovered and the necessary to separate the glycerol from the end product [3]. Therefore, heterogeneous catalyst is a better option to overcome the problems, due to heterogeneous catalyst will be easier to be recovered and catalyst will be reusable, therefore it will reduce the production cost. Among several types of heterogeneous catalyst, ion exchange catalyst resin is more referable for transesterification reaction in biodiesel production due to it exhibit good physical strength, better conversion rates, and high biodiesel yield [4-5].

Previous researchers have conducted the development and optimization of biodiesel production using ion exchange catalyst resin. Unfortunately, the study of kinetic models to describe the transesterification reaction in more comprehensive is still limited. Kinetic modelling of transesterification by using homogeneous catalyst are more studied rather than heterogeneous catalyst [3]. Therefore, in this work, kinetic modelling based on irreversible multilevel reaction will be studied to determine the most accurate
reaction mechanism for transesterification reactions using ion exchange catalysts resin in order to produce biodiesel. Irreversible reaction is fitted with the one step reaction [6]. Besides it, kinetic parameters involved in the reaction will be estimated by using curve fitting method.

Biodiesel has received more attention all over the world among the other renewable fuel. Biodiesel has been synthesized from renewable and sustainable raw materials such as vegetable oil or animal fats [7], therefore biodiesel production will be economically and environmentally friendly [8]. Biodiesel is produced by transesterification reaction with the addition of catalyst. A catalyst has been known as a support to speed up the reaction. However, a homogeneous base catalyst is mostly used since it gives high conversion rates of over 95% [9]. Homogeneous catalyst has several weaknesses including the catalyst cannot be recovered and difficult to neutralize the glycerol at the end of the reaction [9]. Therefore, heterogeneous catalyst is more preferable due to it will ease the product in recovery process and also the catalyst will be reusable. This heterogeneous catalyst is useful for biodiesel production. Among several types of heterogeneous catalyst, ion exchange catalyst resin exhibits good results and suitable for transesterification reaction in biodiesel production due to their physical strength, better conversion rates, and high biodiesel yield [10,11].

The development and optimization of biodiesel production using ion exchange catalyst resin have been done by numerous researchers. However, the application of kinetic models to describe the reaction in more comprehensive is still limited. Most of previous researcher have modeled the kinetics of transesterification by using homogeneous catalyst rather than heterogeneous catalyst [9]. A kinetic model is a crucial thing to study the behavior of compound in a reaction. Therefore, in this work, we studied the kinetic modeling based on Eley-Rideal and irreversible mechanism to determine the most accurate reaction mechanism for transesterification reactions using ion exchange catalysts resin.

2.1. Kinetic Model of Eley Rideal Mechanism

The model used in this study is multilevel reaction-based kinetics. The irreversible reaction was modeled through six kinetic constant rates. The mechanism of the reaction was showed below:

\[
TG + A \underset{k_1}{\overset{k_2}{\rightarrow}} DG + B \\
DG + A \underset{k_3}{\overset{k_4}{\rightarrow}} MG + B \\
MG + A \underset{k_5}{\overset{k_6}{\rightarrow}} G + B
\]

where TG is triglycerides, A is alcohol, DG is diglycerides, MG is monoglycerides, B is biodiesel, and G as triacyl-glycerol.

This kinetic model was used as the basis model for kinetic parameter estimation. The reaction scheme for Eley-Rideal model in the transesterification reaction of triglycerides, by assuming the fraction of the vacant sites component is 1, is given as follows [12]:

\[
\frac{dTG}{dt} = -k_1[TG] + k_2[B] \\
\frac{dDG}{dt} = k_1[TG] - k_3[B] - k_4[DG] + k_5[B] \\
\frac{dMG}{dt} = -k_3[DG] - k_4[B] - k_5[MG] + k_6[B] \\
\frac{dB}{dt} = k_4[DG] - k_5[B] + k_6[MG] - k_6[B]
\]

2.2. Kinetic Model of Irreversible Mechanism
The mechanism reaction of this study is used multilevel reaction based kinetics. The overall process of biodiesel synthesis occurs through three sequential reaction stages containing reversible steps, forming the intermediate diglycerides and monoglycerides and then glycerol.

\[
TG + A \xrightarrow{k_1} DG + B
\]  \tag{8}

\[
DG + A \xrightarrow{k_2} MG + B
\]  \tag{9}

\[
MG + A \xrightarrow{k_3} G + B
\]  \tag{10}

where TG is triglycerides, A is alcohol, DG is diglycerides, MG is monoglycerides, B is biodiesel, and G as triacetyl-glycerol.

The reaction scheme for irreversible multilevel reaction model in the transesterification reaction of triglycerides is given as follows:

\[
\frac{d[TG]}{dt} = -k_1[TG]
\]  \tag{11}

\[
\frac{d[DG]}{dt} = k_1[TG] - k_2[DG]
\]  \tag{12}

\[
\frac{d[MG]}{dt} = -k_3[MG] + k_2[DG]
\]  \tag{13}

\[
\frac{d[B]}{dt} = k_1[TG] + k_2[DG] + k_3[MG]
\]  \tag{14}

2.3. Kinetic Data Collection

There are 4 data sets containing concentration of reactants and products of transesterification that will be used for kinetics parameter estimation. Data set 1 and 3 were obtained from experimental data on transesterification of Jatropha oil with methanol using MgZnAlO catalyst, at temperature of 150°C and 170°C, respectively [13]. Meanwhile, data set 2 was taken from experimental data on transesterification of triacetin using Amberlyst-15 catalyst (T = 60°C) [14]. Moreover, data set 4 was obtained from experimental data on transesterification of sunflower oil using ETS-10 (Na-K) catalyst (T = 35°C) [15]

2.4. Kinetic Parameter Estimation

Estimation of kinetics parameter was conducted by using curve fitting method. There are six kinetics constants to be estimated based on Eley-Rideal reaction scheme and three kinetic constants to be estimated based on irreversible multilevel reaction scheme. These kinetic rate constants will be estimated numerically by fitting the model equations with the experimental data.

2.5. Sensitivity Analysis

The sensitivity analysis of kinetic parameters was also conducted by changing the value of one constant by 50% lower and 50% higher than the estimated value without changing the value of the other constants. Changes in the value of these constants were carried out for each reaction rate constant. Then, comparison of the squared-sum of relative error (S) of the three values of change constant was also conducted.

3. Results and Discussions
3.1. Kinetic Model of Eley Rideal Mechanism

Heterogeneous catalyst has wide application in industry, so that numerous researchers found many modification in order to enhance the stability, yield and process of biodiesel synthesis. In this work, we examined the kinetic parameter of heterogeneous catalyst by using two different kinetic model. Biodiesel reaction is provided with two mechanism, irreversible and mechanism. As a comparison, the behavior of biodiesel production was observed with Eley-Rideal and irreversible mechanism for multilevel reaction in biodiesel synthesis. The fitting curve of data set 1-4 using Eley-Rideal mechanism are represented in Figure 1-4.

![Figure 1. Fitting curve data set 1](image1)

![Figure 2. Fitting curve data set 2](image2)

![Figure 3. Fitting curve data set 3](image3)

![Figure 4. Fitting curve data set 4](image4)

Based on curve fittings, kinetics parameter constant obtained for the transesterification reaction in each data are shown in Table 1. The value of kinetic parameter constant was obtained from the calculation in simulation by Eley-Rideal method and proven by error calculation. This error calculation showed the accuracy of kinetic parameter constant. The smaller error value showed more accurate kinetic parameter value. As shown in Table 1, data set number 3 showed smallest error value. This represents data showed high accuracy.

**Table 1. Kinetic parameter constants of Eley Rideal mechanism**
A sensitivity analysis is useful to observe the deviation and error value among the simulation process. Based on the simulation, it can be determined that the data set 3 has the smallest error as compared by other data. Based on the data set 3, sensitivity of the kinetics parameter was analyzed. The results are presented in the Table 2.

Based on sensitivity analysis, it can be seen that all kinetic parameters have shown high sensitivity. This is evident from the change in error value (deviation) when the kinetics parameter values are deviated from their initial values.

### Table 2. Sensitivity analysis result of data set 3 (Eley-Rideal mechanism)

| Constants | Value  | Error | Deviation |
|-----------|--------|-------|-----------|
| $k_1$     | 3.94E-03 | 2.08  | 2.27%     |
|           | 7.87E-03 | 1.04  | minimal   |
|           | 1.18E-02 | 4.8   | 8.5%      |
| $k_2$     | 4.38E-07 | 2.90  | 4.4%      |
|           | 8.75E-07 | 1.53  | minimal   |
|           | 1.31E-06 | 5.0   | 6.9%      |
| $k_3$     | 5.53E-03 | 7.5   | 10.1%     |
|           | 1.11E-02 | 2.51  | minimal   |
|           | 1.66E-02 | 4.1   | 8.5%      |
| $k_4$     | 5.63E-07 | 2.3   | 3.1%      |
|           | 1.13E-06 | 1.31  | minimal   |
|           | 1.69E-06 | 4.2   | 4.2%      |
| $k_5$     | 4.57E-03 | 3.5   | 4.67%     |
|           | 9.15E-03 | 1.69  | minimal   |
|           | 1.37E-02 | 4.4   | 5.12%     |
| $k_6$     | 2.55E-04 | 3.31  | 2.23%     |
|           | 5.09E-04 | 1.32  | minimal   |
|           | 7.64E-04 | 4.41  | 4.37%     |

3.2. Kinetic Model of Irreversible Mechanism
The fitting curve of data set 1-4 using irreversible mechanism are represented in Figure 5-8.

![Figure 5. Fitting curve data set 1](image1)

![Figure 6. Fitting curve data set 2](image2)

![Figure 7. Fitting curve data set 3](image3)

![Figure 8. Fitting curve data set 4](image4)

Based on these results, it can be determined that the data set 1 has the smallest error compared by others. Based on the data set 1, sensitivity of the kinetics parameter was analysed. The results are presented in the Table 4.

| Constants | Data set 1 | Data set 2 | Data set 3 | Data set 4 |
|-----------|------------|------------|------------|------------|
| $k_1$     | 7.86E-03   | 5.97E-04   | 9.86E-04   | 5.00E-03   |
| $k_2$     | 1.11E-02   | 4.71E-04   | 2.68E-03   | 1.39E-02   |
| $k_3$     | 9.15E-03   | 2.80E-04   | 1.56E-02   | 7.56E-03   |

Based on this table, it can be determined that the data set 1 has the smallest error compared by others.

Based on the data set 1, sensitivity of the kinetics parameter was analysed. The results are presented in the Table 4.
Table 4. Sensitivity analysis result of data set 1 (irreversible mechanism)

| Constants | Value    | Error | Deviation |
|-----------|----------|-------|-----------|
| $k_1$     | 3.93E-03 | 2.5   | 3.57%     |
|           | 7.86E-03 | 1.16  | minimal   |
|           | 1.18E-02 | 4.6   | 9.12%     |
| $k_2$     | 5.54E-03 | 8.77  | 12.10%    |
|           | 1.11E-02 | 4.21  | minimal   |
|           | 1.66E-02 | 9.52  | 8.32%     |
| $k_3$     | 4.57E-03 | 8.5   | 10.10%    |
|           | 9.15E-03 | 4.41  | minimal   |
|           | 1.37E-02 | 8.1   | 8.50%     |

The kinetic model for biodiesel synthesis by using heterogeneous catalyst has been simulated with high sensitivity percentage. As shown in Table 4, the deviation of each simulation kinetic rate constant was showed small percentage deviation. This indicated that the simulation was in good accuracy as compared with the experimental data. The smallest percentage error was established the fitted point of experimental data. In this case, it was showed that the kinetic rate constant will change if the simulation in less accuracy.

4. Conclusions

This reversible Eley-Rideal model reaction is matched with the experimental data set 3 which is proved by sensitivity analysis. In this study, the constant kinetic parameter value showed minimal percentage error with $k_1$ until $k_6$ value, $7.87\times10^{-3}$, $8.75\times10^{-3}$, $1.10\times10^{-2}$, $1.12\times10^{-6}$, $9.14\times10^{-3}$ and $5.09\times10^{-4}$, respectively. The irreversible multilevel reaction model is matched with the experimental data 1 which is synthesized biodiesel from Jatropha oil with methanol by using heterogeneous catalyst MgZnAlO. The validity was confirmed by sensitivity analysis method. In this study, the kinetic parameter value which is obtained in the study showed $k_1$, $k_2$ and $k_3$ value: $7.86\times10^{-3}$, $1.11\times10^{-2}$ and $9.15\times10^{-3}$, respectively.

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