Kinetic modelling of esterification of glycerol with acetic acid catalyzed by lewatite

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Abstract. One of the ester product of glycerol and acetic acid is triacetin which has wide industrial application. In this study the esterification of glycerol with acetic acid over Lewatite catalyst to produce triacetin, were carried out. Lewatite is one of ion exchange resin, the use of ion exchange resins as catalyst will not produce waste, not corrosive, high thermal stability and has good selectivity. The esterification reaction of glycerol with acetic acid were performed in a three-neck flask with stirrer (175 rpm) at temperature (90 °C, 100 °C and 110 °C) and atmosphere pressure. A 9.66 % selectivity of triacetin with conversion (77.4 %) was achieved at 100 °C within 90 minutes of reaction time. This research aimed to report experimental data and kinetic modeling of glycerol esterification with acetic acid to evaluate and compare model performance and capability. A kinetic model was developed using a first order pseudo-homogeneous model according to the experimental data. The surface reaction of acetic acid with glycerol was assumed to be rate-controlling. The effect of temperature to rate of reaction constants can be expressed as follows: 

\[ k_r = 8.138 \times 10^{11} \exp \left( -\frac{57.17642}{RT} \right) \text{ (1/s)} \]

1. Introduction
Crude glycerol produced in biodiesel industry need to be purified so can be utilized in cosmetic, food and pharmaceutical industry. However, glycerol purification is high cost, so it is necessary to look for high value derivative product of glycerol [1]. One of the ester product of glycerol and acetic acid is triacetin which has wide industrial application [2]. Triacetins are used as food aroma, solvent in perfume [3], plasticizer for resin [4], and as additive in fuel oil to increase octane number [5]. Some short chain oils such as triacetine, tripropionine, tributyrin have been proved to be good biodiesel additives to improve lubrication and viscosity [6]. In general, these reactions are carried out using homogeneous acid catalysts, which are corrosive, difficulty in separation and generate waste, leading to increased production costs and environmental problems [7]. Hence, the heterogeneous catalysts become alternative catalysts used in esterification reactions because has good physical and chemical properties [8]. The use of ion exchange resins will not produce waste, not corrosive, high thermal stability and has good selectivity [9]. In addition, heterogeneous catalysts were applied in various chemical synthesis reactions, indicating high and sustained catalytic activity [10]. Previous research was conducted experimentally to obtain optimum conditions in esterification reaction of glycerol and acetic acid over Lewatit catalyst, which obtained 3 % weight catalyst and
molar ratio of glycerol reactants to acetic acid was 1: 7. However the development of kinetic models can be relied upon to describe the design and optimization process. This research aimed to report experimental data and kinetic modeling of glycerol esterification with acetic acid to evaluate and compare model performance and capability. The reaction pathway is very important to use to build a kinetic model that can be applied to predict changes in the number of specific products obtained during the reaction process [11].

According to Smith [12], the liquid phase reaction with solid catalyst comprises the following steps:

- Mass transfer of the reagents from the liquid bulk to the catalyst surface
- Reaction at the surface of the catalyst
- Mass transfer of the product from surface of catalyst to the bulk of liquid

In irreversible reactions, the product concentration does not affect the rate of reaction. If the direct reaction and desorption stage are rapid, mass transfer of the product from surface of catalyst to the bulk of liquid can be ignored. Due to excess of acetic acid, the concentration of acetic acid in catalyst surface are assumed to be constant, then in steady state conditions obtained:

\[
\frac{dX_A}{dt} = K_0 \frac{3}{C_{A0}} \left( C_{G0} - \frac{1}{3} C_{A0} X_A \right)
\]

The value of mass transfer coefficient \((k_c)\) can be searched by using equation as follows:

\[
SSE = \sum (X_{calculation} - X_{data})^2
\]

Sherwood (Sh) value is calculated using the following Frossling equation:

\[
S_h = 2 + 0.6 \frac{Re^{1/2}}{Sc^{1/3}}
\]

According to Fogler [13], the overall rate of the reaction is determined by the slowest rate in the process mechanism. By applying the value of mass transfer coefficient \(k_c\) using (equation 3) and data \(K_0\), the modelling simulation will result the value of \(k_r\) (constant rate of reaction). If the value of \(k_c \gg k_r\) indicate that reaction on the surface catalyst control the rate reaction so \(K_0 \approx k_r\), otherwise if the value of \(k_r \gg k_c\) indicate that the mass transfer of reagents to catalyst is the rate controlling.

2. Methods

2.1. Materials

Lewatite catalyst and glycerol of high purity (96 %) was obtained by CV. Bratachem, Indonesia. Acetic acid (99 %), chloroform, ethanol, natrium thiosulfate and potassium dichromate were purchased from CV. Chemics, Indonesia. All reagent used without any further treatment. Lewatit catalyst was activated by HCl 1 N solution of 200 % volume. The catalyst mixture was stirred using a magnetic stirrer for 30 minutes and rinsed with distilled water to neutral pH.

2.2. Experimental procedure

The esterification reaction of glycerol with acetic acid were performed in a three-neck flask (250 ml) with stirrer (175 rpm) at temperature (90 °C, 100 °C and 110 °C) and atmosphere pressure. 73.31 ml glycerol was placed in the reactor together with catalyst and heated to reaction temperature. After the
mixture reaches temperature reaction, the 344 mL acetic acid that has been heated in a separate container is inserted into the reactor. To maintain the reaction temperature, the reactor was equipped with a water cooled condenser. Prior the reaction, solution sample was taken for analysis of total acid concentration, free acid concentration, and total glycerol concentration. The reaction product were taken every 15 minutes to analyze the free acid. The reaction was stopped after a reaction time of 90 minutes. The experiment was repeated with other temperature variations. The total acid (Ao) analysis was performed by volumetry using chloride acid, while the free acid (Ab) was analyzed using NaOH, and the total glycerol was analyzed by the FBI-A02-03 method. Calculation of the conversion of reagents based on acetic acid (free acid) were calculated using the following equations:

\[ \text{Acetic acid conversion (\%)} = \frac{A_0 - A_b}{A_0} \times 100\% \]  

3. Result and discussion

3.1. Qualitative analysis
The synthesized triacetin was characterized by Fourier Transform Infra Red Spectrophotometer (FTIR) and Gas Chromatografy Spectrometry (GC). FTIR analysis were intended to determine the presence of triacetin in sample. Figure 1 shows the IR spectra of reaction product. As displayed in Fig. 1 an intense and broad peak at 1724.26 cm\(^{-1}\) assignable to the bending vibration a functional group of ester. From (Figure 2) found that the GC spectra of samples have the highest similarity with the triacetin of 98\%. These results prove that product of reaction contain triacetin.

![Figure 1. FTIR spectra of esterification reaction product](image1.png)

![Figure 2. Gas chromatografy spectra of esterification reaction product](image2.png)

3.2. Acetic acid conversion
The effect of temperature on the esterification reaction is studied by reacting acetic acid and glycerol at different temperatures with a fixed initial molar ratio (1:7) and fixed catalyst loading (3% of weight reactant). The effect of reaction temperature is very important to observe for calculating the activation
energy of the reaction [14]. Figure 3 indicated that temperature reaction is the significant factor in acetic acid conversion which increasing temperature will increase acetic acid conversion, indicating that mass transfer can be ignored. The highest conversion at the temperature range of 80 °C – 110 °C was reached at 100 °C at value of 77.4 % after 90 minutes of reaction.

Table 1 shows the selectivity of the triacetin obtained by the esterification of glycerol with acetic acid over lewatit catalyst after 90 minutes of reaction. It can be seen that the increase of temperature increase the triacetin selectivity, so triacetin formation was predominant at higher reaction temperature. At temperature 100 °C, the selectivity of 82.86 % to monoacetin, 7.47 % to diacetin and 9.66 % to triacetin. Low selectivity to triacetin can be explained due to this product will be formed through the consecutive nature of glycerol esterification, which can be attributed to the occurrence of nucleophilic attacks by glycerol to form medium asylum ions on the surface of the catalyst and protonation of carbonyl oxygen atoms from acetic acid [15]. This intermediate material is preferably close to the glycerol molecule and subsequently produces successive nucleophilic attacks on the hydroxyl glycerol group. Other reason of low selectivity of triacetin because there is no sufficient time for monoacetin and diacetin convert to triacetin. The increasing reaction temperature up to 100 °C the conversion and selectivity increase, while at 110 °C both of conversion and selectivity decrease, this might relate with the maximum operation temperature of Lewatite catalyst (120 °C) resulting in a decrease of catalyst activity. Decrease in catalyst activity might due to the internal diffusion limitations inside the porous of catalyst. Several studies concluded that catalyst activity was predominantly influenced by acidity and textural characteristics of catalyst [16]. Fouling and sintering on surface catalyst were reported as the main causes of catalyst deactivation [17].

![Figure 3. Acetic acid conversion versus time for different reaction temperature](image)

**Figure 3.** Acetic acid conversion versus time for different reaction temperature

**Table 1.** Selectivity of monoacetin, diacetin and triacetin at various reaction temperature

| Temperature, °C | Monoacetin | Diacetin | Triacetin |
|-----------------|------------|----------|-----------|
| 90              | 41.47 %    | 53.31 %  | 5.32 %    |
| 100             | 82.86 %    | 7.47 %   | 9.66 %    |
| 110             | 49.07 %    | 38.51 %  | 4.81 %    |
An increase in the reaction temperature effect to the energy of reactant molecule in achieving its activation energy. This causes the collision between reactant molecules occur in high frequency leading to an increase in the reaction rate. The activation energy ($E_0$) and the parameter constant ($k_0$) are determined by using the linear regression technique of the Arrhenius equation (Equation 6) by entering the data of the reaction rate constant ($k$) at different temperature.

$$k = k_0 \exp \left(-\frac{E_0}{RT} \right)$$ (6)

3.3. Qualitative analysis

The kinetic study of the esterification of acetic acid and glycerol was performed to obtain wider information of the conversion of chemical species in the reaction mixture. A set of reaction at several temperatures have done to select suitable kinetic model represent behaviour of the reaction. Glycerol esterification could be assumed as irreversible reaction and the kinetic data were fitted to first order pseudo-homogeneous model that considers a constant ratio mole reactant and catalyst loading in the reaction liquid. The selection of the appropriate model was based on the value of activation energy within adequate range, standard error value and positive value of kinetics parameter. kinetics constants for chemical reactions, adsorption, and the phenomenon of mass transfer are usually influenced by temperature, changes in solubility with temperature depend on the nature of solutes and solvents. Therefore, solubility may not depend on temperature, at least under certain conditions [18]. Although the internal mass transfer in a heterogeneous catalyst might control the reaction rate, it is possible that the rate control step can be neglected for porous support or systems with partially dissolved catalysts. At the liquid-solid heterogeneous reaction, the mass transfer resistance affects the rate resistance of the reaction, which both of resistors can be combined in the overall resistance constant ($K_0$). The result of the calculation based on the proposed mathematical model is shown in (Figure 4). As shown in (Figure 4), the model used is good enough to describe the process that occurs during the reaction process. To determine a more decisive step between mass transfer and reaction rate, the mass transfer coefficient ($kc$) and the reaction rate coefficient ($kr$) value must be known. The $kc$ value is calculated by (Equation 3), thus the value of $kr$ at various temperatures can be determined. The calculation results of $kc$ and $kr$ values are presented in (Table 2).

| Temperature °C | Overall Constant $(K_0) \times 10^{-3}$ | Mass Transfer Constant $(kc)$ | Reaction Rate Constant $(kr) \times 10^{3}$ |
|---------------|----------------------------------------|-------------------------------|-------------------------------------------|
| 80            | 3.21                                   | 38.9                          | 4.53                                      |
| 90            | 9.77                                   | 40.08                         | 10.11                                     |
| 100           | 12.53                                  | 40.76                         | 13.57                                     |
| 110           | 20.16                                  | 40.90                         | 21.15                                     |

As seen in (Table 2), the value of $K_0$ is almost equal to $kr$. This shows that the rate of reaction is a decisive / controlling step in reaction. This is in accordance with previous studies with ion exchange resin catalysts such as Pereira [19] who evaluated kinetics and thermodynamic equilibrium in esterification of lactic acid with ethanol using Amberlyst-15. In esterification of citric acid with ethanol using an ion exchange resin catalyst, the reaction kinetics is determined by chemical reactions [20]. The reaction rate constant of $kr$ is a function of temperature, and is considered to follow the Arrhenius equation as shown in (Figure 4).
Regarding experimental kinetic data for esterification of acetic acid with glycerol presented in this study, higher glycerol conversion and selectivity of monoacetin in all reaction can be observed and acetic acid quickly reacts with glycerol to form monoacetin, diacetin and triacetin produced according to the reaction temperature. The Arrhenius plot of the rate constant (kr) (Figure 4), the effect of temperature to rate of reaction constants can be expressed as follows (equation 7) with an average error of 23.55%. Activation energy and frequency constant were obtained 57,176.47 kJ/mol and 8.138 x 10^{11} 1/s respectively. The adjusted correlation coefficient (R^2) of 0.9645 obtained for Arrhenius model, which indicates good performance of the models in predicting the kinetic behaviour for these esterification reaction investigated and it is in accordance with the assumption made that mass transfer step is negligible for type of Lewatit catalyzed reaction. Therefore the reaction rate in the Lewatit esterification of glycerol seems to be the controlling step.

\[
k_r = 8.138 \times 10^{11} \exp \left( \frac{-57,176.47}{RT} \right) \left( \frac{1}{s} \right)
\]  

(7)

4. Conclusion
The esterification reaction of glycerol with acetic acid was carried out over Lewatite catalyst at different temperatures (80°C, 90°C, 100°C and 110°C) with a fixed initial molar ratio (1:7) and fixed catalyst loading (3% of weight reactant). Among the various temperature reaction, 100°C presented highest conversion (77.4%) with 9.66 % selectivity of triacetin within 90 minutes of reaction time. The model used is good enough to describe the process that occurs during the reaction process. The rate constant of reaction was obtained by plotting temperature of Arrhenius equation. A model with a coefficient of determination of 0.9645 was obtained and the activation energy for triacetine formation using Lewatit catalyst was found to be -57kJ/mol. Mathematical model calculations show the surface reaction is a controlling step in reaction.

5. References
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