Ultrasound-assisted Esterification of Glycerol for Triacetin Production

A F A Raemas1,2, J Cahyonugroho1,3, A D Wicaksono1, R L Dewi1, Hadiyanto1,2,*

1Department of Chemical Engineering, Faculty of Engineering, Diponegoro University
2Central of Biomass and Renewable Energy Laboratory, Advance Laboratory, Diponegoro University
3Advance Materials Laboratory, Advance Laboratory, Diponegoro University

No. 13 Prof. Soedarto, SH Road, Tembalang-Semarang, INDONESIA

Email: * hady.hadiyanto@gmail.com

Abstract. Glycerol is a by-product of biodiesel production. So far, glycerol has not been used optimally. An alternative product that can be produced from glycerol is triacetin through the esterification process. Research on the review of reaction kinetics to determine the optimum conditions of the reaction still limited. Previous study also reported that the esterification process requires quite a long reaction time. Therefore, in this study ultrasonic technology will be used to accelerate the reaction of glycerol esterification with acetic acid using sulfuric acid catalyst. The purpose of this study is to study the effect of ultrasonic technology on the conversion of esterification of glycerol/acetic acid, and to observe the kinetic study of triacetin production. To answer this goal, this study uses a set of ultrasonic devices as a substitute for the esterification of conventional models. The greatest conversion results are obtained when the reaction temperature is 100°C with a mole ratio of glycerol/mole of acetic acid 1/8. The use of ultrasonic technology in theory should have a greater impact on conversion results. The reaction order obtained is order 2 with the largest k value in the mole ratio of glycerol: acetic acid 1: 8 which is 0.0006 (L.mol⁻¹.min⁻¹). Due to the variation of moles ratio, the ratio at 1/6 and 1/4 did not show significant changes of reaction rate, the changes are constant for both first and second order reaction. But at the mole ratio of 1/8, the reaction rate constant shows a significant different for temperature changes.

1. Introduction

Glycerol (1,2,3 propanetriol) is a liquid that is colorless, odorless and is a thick liquid which has a sweet taste [1]. Glycerol is used widely as a solvent, as a sweetener, in cosmetics and in liquid soaps, as a fermentation culture in the production of antibiotics, and in pharmaceuticals. Thus, the biodiesel industry is rapidly expanding, a way to overcome the abundance of glycerol is needed. One option that can be done is to convert glycerol into products that have added value. One of the derivative products of glycerol conversion is TAG (Triacyl-Glycerol)/Triacetin. In this study, the process of TAG
production was carried out by reacting glycerol and acetic acid by esterification. Triacetin can be produced from the reaction of glycerol and acetic acid using a catalyst. Triacyl-Glycerol (TAG) or Triacetin with molecular formula \((\text{CH}_3\text{COO})_3\text{C}_3\text{H}_5\) is made from the esterification process between glycerol and acetic acid with the help of a catalyst. TAG is used as food additives, such as flavor enhancers, plasticizers, solvents, fuel additives to reduce engine knocking (increasing octane value) and can be used as biodiesel additives [2]. In biodiesel, triacetin is used as an additive which increases the cetane rate to reduce nitrogen oxide emissions to an acceptable emission level. The addition of 10% triacetin in biodiesel can cause an increase in engine performance compared to pure biodiesel [3]. Previous researchers found that triacetin can be used to improve the cooling properties and viscosity of the final fuel quality [4]. Maneechakr et al., conducted a study on the interesterification reaction, this process goes through long stages resulting in low energy efficiency and high energy consumption, the cost of producing triacetin increases [5]. Therefore, ultrasonic technology could possibly use to maximize the energy efficiency of the process.

Ultrasonic waves are acoustic waves with a frequency greater than 18 kHz. Because the frequency is outside the threshold of human hearing ability. Therefore, Ultrasound technology is applied to sonicate a material without generating increase of temperature. The waves that propagate into the solution make the molecules compress and stretch under the force of pressure. This phenomenon automatically increases most of the temperature in the sample container and also increases the desired chemical reaction and increase the quality of triacetin production [6].

Due to low energy efficiency of conventional esterification, this study aimed to optimized the esterification process using ultrasonic technology with the variation of feed temperature, sonification time, and ratio of glycerol/acetic acid on ultrasonic technology to produce triacetin with sulphate acid as a catalyst. As far the author could acknowledge, the study that consider the use ultrasonic technology on producing TAG through esterification process is still limited. Also, the kinetic rate coefficient of TAG production is still limited, this research also going to develop the study in kinetic rate coefficient of TAG production.

2. Experimental

2.1. Materials
Glycerol that used in this research was collected from byproduct of PT. Willmar Nabati, Gresik, East Java, Indonesia. Other materials were supplied and collected from E-Merck company with following catalog number: Acetic Acid (CH\(_3\)COOH 100%) 100063; Sulfate Acid (H\(_2\)SO\(_4\) 98%) (112080); phenolphthalein (107233); Natrium Hydroxide (NaOH 98%) (106462).

2.2 Production of Triacetin
Acetic Acid with a Sulfuric Acid (6.639 ml) as catalyst and Glycerol was heated in the separated container with various of mole ratio of Glycerol/Acetic Acid (1/8; 1/6; 1/4) until it reaches the desired temperature (60°C; 80°C; 100°C) wit. Hence, the temperature of ultrasonic reactor was fixed at 80°C. Once the required temperature was reached, mix the 3 ingredients into one solution to continue to ultrasonic process. The samples were sonicated using Sonification Reactor with the similar wave frequency 18 kHz with varied operation time (60; 90; 120 minutes).

2.3 Triacetin Analysis
Triacetin is analyzed by calculate the conversion of the mole of glycerol that reacted on the process (by subtracting the initial mole of glycerol with the remaining mole of glycerol after reaction) and the mole of glycerol before reacted. The method used to calculate of glycerol conversion (Xa) was normalization (Acid-Alkaline) Titration with following formula to calculate the glycerol conversion:
Glycerol Conversion \((X_a) = \frac{\text{mole of reacted glycerol}}{\text{mole of glycerol before reacted}}\) (1)

2.4 Order Reaction and Kinetic Rate Coefficient \((k)\)
The order reaction is determined using a linear graph between \(-\ln (1-X_a)\) versus time \((t)\) for first order reaction and \(-\ln (C_B/C_A)\) versus time \((t)\) for second order reaction. Then calculate the regression of the graph, the highest number of regressions was determined as the number of order reaction.

Then the kinetics reaction was determined from conversion of glycerol in both first order reaction and second order reaction with various variable on the research. The stoichiometry of the three stages and overall, for the acetylation of glycerol with acetic acid is as follows:

\[
\text{Gliserol} + CH_3COOH \xrightarrow{k_1/k_4} \text{MAG} + H_2O
\]

\[
\text{MAG} + CH_3COOH \xrightarrow{k_2/k_5} \text{DAG} + H_2O
\]

\[
\text{DAG} + CH_3COOH \xrightarrow{k_5/k_6} \text{TAG} + H_2O
\]

Where:
- MAG: Monoacylglycerol
- DAG: Diacylglycerol

Overall reaction:

\[
\text{Glycerol} + 3CH_3COOH \xrightarrow{k_7/k_8} \text{TAG} + 3H_2O
\]

\[
C_3H_8O_3 + 3CH_3COOH \xrightarrow{k_7/k_8} (CH_3COO)_3C_3H_5 + 3H_2O
\]

From the above stoichiometry, the reaction rate can be determined as follows:

\[
-\frac{dC_A}{dt} = k_7C_A^wC_B^y - k_8C_C^wC_D^z
\] (2)

Where \(C_A, C_B, C_C\) and \(C_D\) are the concentrations of glycerol, concentrations of acetic acid, TAG, and H\(_2\)O. Whereas \(w, x, y,\) and \(z\) are the reaction orders. \(k_7\) and \(k_8\) are kinetic constants for the reaction towards the products and towards the reactants.

Assuming that the use of the molar ratio of acetic acid to glycerol is greater than the other components, so it could decrease the value of \(k_8\). Therefore, the value of \(k_8\) can be ignored due to way smaller value than \(k_7\) so the formula could be described as \(k' = k_7C_B^y\). Where \(k'\) is the constant rate of the modification reaction. The equation become:

\[
-\frac{dC_A}{dt} = k'C_A^w
\] (3)

Then the equation above was integrated as follows:

\[
\ln \frac{C_A}{C_{A0}} = -k't
\] (4)

If \(C_A = C_{A0}(1 - X_a)\) then the formula become as follows:

\[
\ln (1 - X_a) = -k't
\] (5)

Then the coefficient of kinetic reaction is determined using graph method by plotting \(-\ln (1-X_a)\) and \(\ln (C_B/C_A)\) as vertical axis and time \((t)\) as horizontal axis. The slope of the graph is considered to be the coefficient of kinetic reaction or the formulas could derivates as follows:

\[
k(\text{first order reaction}) = -\frac{\ln(1-X_a)}{t}
\] (6)

\[
k(\text{second order reaction}) = \frac{\ln(C_B/C_A)}{t}
\] (7)

Where:
- \(C_{A0}\): the concentration of glycerol before the reaction (mole)
- \(C_A\): the concentration of glycerol after the reaction (mole)
- \(X_a\): the conversion of glycerol
- \(C_B\): the concentration of acetic acid (mole)
- \(t\): time (minutes)
3. Result and Discussion

3.1. Effect of Ultrasonic Technology
Triacetin production is carried out with three variables of molar ratio of glycerol and acetic acid. Table 1 and figure 1 (a), 1 (b) and 1 (c) are the results of the conversion of triacetin against time at various mole ratios.

| Variable | Xa 60 minutes | Xa 90 minutes | Xa 120 minutes |
|----------|---------------|---------------|----------------|
| (1/8)    |               |               |                |
| 60 °C    | 0.016         | 0.027         | 0.031          |
| 80 °C    | 0.018         | 0.038         | 0.053          |
| 100 °C   | 0.040         | 0.054         | 0.070          |
| (1/6)    |               |               |                |
| 60 °C    | 0.029         | 0.038         | 0.048          |
| 80 °C    | 0.030         | 0.044         | 0.050          |
| 100 °C   | 0.027         | 0.050         | 0.058          |
| (1/4)    |               |               |                |
| 60 °C    | 0.019         | 0.029         | 0.038          |
| 80 °C    | 0.025         | 0.032         | 0.042          |
| 100 °C   | 0.026         | 0.041         | 0.051          |

Figure 1. The conversion of glycerol towards reaction time: (a) mole ratio 1/8 (b) mole ratio 1/6 (c) mole ratio 1/4
Table 1 shows the result on sonification of TAG production where the conversion was increased due to the longer time reaction of esterification of glycerol/acetic acid using sonification. The best of reaction time was found at 120 minutes and this condition was chosen to calculate the best temperature and mole ratio of TAG production condition. Ultrasonic technology has an impact on the esterification reaction of acetic acid with glycerol, which is a wave that propagates into the solution making the molecules compressed and stretched by pressure. This phenomenon increases most of the temperature and also increases the chemical reaction so that the reaction time can be more effective and the resulting conversion can be greater than the conventional esterification process [7].

The result also shows in figure 1, where the conversion of glycerol was increased during the higher of feed temperature and moles ratio of glycerol/acetic acid. Based on the results, the best conversion of triacetin is found at 100°C and on first variable with 1/8 of glycerol and acetic acid moles ratio as shown on figure 1. This is because the higher the reaction temperature, the kinetic rate will increase as well, in accordance to the Arrhenius equation:

\[ k = A e^{-\frac{E_A}{RT}} \]  

(8)

From Figure 1a, 1b, and 1c, it can be known that the conversion value from the first minute to 120 minutes has increased. This is because the longer the reaction time, the greater the conversion due to there is a bigger chance for the particles to collide with each other [8].

3.2. Determination of Reaction Order and Reaction Kinetic Rate (k)

The relationship between -ln (1-Xa) with time (t) in the first order and the relationship between ln \( C_B/C_A \) and time (t) in the second order are carried out at a 1/8 mole ratio of glycerol/acetic acid at temperature of 100°C, with 0.98 N sulfuric acid as a catalyst.

By using the first-order and second-order esterification reaction kinetics approaches, kinetics calculation are carried out using the graph method of the relationship between concentration and time (t), then the K value is taken from the slope of the graph. The results for the first-order is shown on figure 3 and for the second order is shown on figure 4.

\[ y = 0.0006x + 2.3043 \quad R^2 = 0.9955 \]

\[ y = 0.0003x + 0.605 \quad R^2 = 0.996 \]

Figure 2. Kinetic study using graph method: (a) -ln (1-Xa) vs time in first order reaction; (b) ln \( C_B/C_A \) vs time in second order reaction

The comparison of reaction kinetic (k) value and \( R^2 \) value in first order and second order between variables can be seen from table 2.
Table 2. Comparison of reaction kinetic (k) and $R^2$ value

| Variable | 1st Order | 2nd Order |
|----------|-----------|-----------|
|          | $k$ (minute$^{-1}$) | $R^2$ | $k$ (L/mole.minute) | $R^2$ |
| (1/8)    | 60 °C | 0.0003 | 0.9905 | 8.00E-05 | 0.9907 |
|          | 80 °C | 0.0005 | 0.987 | 0.0002 | 0.978 |
|          | 100 °C | 0.0006 | 0.9955 | 0.0003 | 0.996 |
| (1/6)    | 60 °C | 0.0004 | 0.9895 | 0.0002 | 0.99 |
|          | 80 °C | 0.0004 | 0.9516 | 0.0002 | 0.9527 |
|          | 100 °C | 0.0005 | 0.9792 | 0.0003 | 0.9799 |
| (1/4)    | 60 °C | 0.0003 | 0.9918 | 0.0005 | 0.9917 |
|          | 80 °C | 0.0004 | 0.9843 | 0.0003 | 0.9844 |
|          | 100 °C | 0.0004 | 0.9851 | 0.0003 | 0.9851 |

Table 2 shows that the variation of moles ratio at 1/6 and 1/4 did not show significant changes of reaction rate, the changes are constant for both first and second order reaction. But at the mole ratio of 1/8, the reaction rate constant shows a significant different for temperature changes.

Based on the result that shows in figure 2 and table 1, overall variable of mole ratio of glycerol/acetic acid (1/8; 1/6; and 1/4) has a regression value that is close to 1. As seen on Table 1, the largest value of k is found at the 1/8 mole ratio of glycerol/acetic acid, which is 0.0006 (minute$^{-1}$). Based on the theory, a large concentration of reactants contains a larger number of particles, so that the particles are more densely arranged. Particles that have a dense arrangement will collide more frequently so that the chance of the reaction to occur is bigger [10].

4. Conclusion

Ultrasonic technology gives impact to esterification process of the production of triacetin. Triacetin with best conversion is indicated by high kinetic rate that can be found on temperature of 100°C and on moles ratio of glycerol/acetic acid 1/8. The triacetin produced in this study still give a very small conversion in comparison to other literatures.

From this study, it can be known that overall reaction on esterification process of glycerol/acetic acid using sulfuric acid as a catalyst has the highest k value is obtained on moles ratio of glycerol/acetic acid 1/8 with value of 0.0006 (minute$^{-1}$) on first order reaction, although the reaction still works in second order reaction due to the higher of regression value.

Acknowledgement

The authors greatly acknowledge the financial support of Chemical Engineering Department of Diponegoro University. The authors would like also thank through Central of Biomass and Renewable Energy Laboratory and Advance Laboratory of Diponegoro University for providing the necessary facilities in this research project.

References

[1] P Mario and R Michele The future of glycerol: new uses of a versatile raw material 2008 RSC Green Chemistry Book Series Ed.2 chapter 1 pg.1
[2] L J Konwar, P M Arvela, P Begum, N Kumar, A J Thakur, J P Mikkola, R C Deka and D Deka 2015 Shape selectivity and acidity effects in glycerol acetylation with acetic anhydride: selective synthesis of triacetin over Y-zeolite and sulfonated mesoporous carbons J. Catal. 329 pg. 237-47
[3] P Ferreira, I M Fonseca, A M Ramos, J Vital and J E Castanheiro 2011 Acetylation of glycerol over hetero polyacids supported on activated carbon Catal. Commun. 12 573-76
[4] J Melero, R V Grieken, G Morales and M Paniagua 2007 Acidic mesoporous silica for the acetylation of glycerol: synthesis of bioadditives to petro fuel Energy and Fuels 21 pg.1782-91
[5] P Maneechakr, J Samerjit and S Karnjanakom 2015 Ultrasonic assisted biodiesel production from waste cooking oil over synthesis of novel sulfonic functionalized carbon spheres derived from cyclodextrin via one-step: a way to produce biodiesel at short reaction time RSC Adv. pg.1-22
[6] S Karnjanakom, P Maneechakr, C Samart and G Guan 2018 Ultrasound-assisted acetylation of glycerol for triacetin production over green catalyst: a liquid biofuel candidate Energy Cons. and Man. 173 262-70
[7] S Karnjanakom, P Maneechakr, C Samart and G Guan 2018 Ultrasound-assisted acetylation of glycerol for triacetin production over green catalyst: a liquid biofuel candidate Energy Cons. and Man. 173 262-70
[8] O Levenspiel 1999 Chemical reaction engineering Wiley ed.2
[9] S Karnjanakom, P Maneechakr, C Samart and G Guan 2018 Ultrasound-assisted acetylation of glycerol for triacetin production over green catalyst: a liquid biofuel candidate Energy Cons. and Man. 173 262-70
[10] J Poosumas, K Ngaosuwan, A T Quitain and S Assabumrungat 2016 Role of ultrasonic irradiation on transesterification of palm oil using calcium oxide as a solid base catalyst Energy Conv. and Man. 120 pg. 62-70
[11] S Kale, S B Umbarkar, M K Dongare, R Eckelt, U Armbruster and A Martin 2015 Selective formation of triacetin by glycerol acetylation using acidification-exchange resins as catalyst and toluene as an entrainer Appl Catal A 490 pg.10–6.
[12] J Sun, X Tong, L Yu and J Wan 2016 An efficient and sustainable production of triacetin from the acetylation of glycerol using magnetic solid acid catalysts under mild conditions Catal Today 264 pg. 115-22