

Process Optimization of Glycerol-to-Triacetin Conversion in Clean Technology Applications: In Situ Water Removal for Enhanced Reaction Performance in Sustainable Biodiesel Byproduct Valorization

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ARTICLE INFO

Received: 2 Oct 2025
Received in revised: 21 Mar 2026
Accepted: 30 Mar 2026
Published online: 19 Jun 2026
DOI: 10.32526/ennrj/24/20250278

Keywords:

Chemical reaction/ Glycerol/
Acetic acid/ Water/ Zero-waste
process

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ABSTRACT

Increasing biodiesel production generates excess glycerol, which has a declining economic value. Converting glycerol into triacetin, a value-added fuel additive, offers a promising solution. However, the reversible nature of the esterification reaction and the formation of water reduce selectivity. Therefore, this study was conducted to evaluate the effect of in situ water removal on reaction performance in terms of acetic acid conversion and the resulting triacetin product. Experiments were conducted in a batch reactor through three clearly defined stages. In Stage 1, the optimal glycerol-acetic acid molar ratio (1:3-1:5) was determined at 100°C and 700 rpm, using a 5% natural zeolite catalyst (based on acetic acid mass), and a reaction time of 4 h with in situ water removal. In Stage 2, residual water was removed by fractional distillation at 105°C until bubbling ceased. Stage 3 comprised the main reaction, where the distillate containing monoacetin, diacetin, triacetin, and glycerol was reacted with fresh acetic acid at the optimal ratio, while in situ water removal continued to enhance triacetin formation. Acetic acid conversion was analyzed by acid-base titration using 0.5 N NaOH, and triacetin was identified by GC-MS. This innovation showed excellent results, achieving 94.00% conversion of acetic acid with 85.58% selectivity for triacetin at 110°C and a 1:5 glycerol-to-acetic acid molar ratio. These results showed that in situ water removal intensified esterification by shifting the equilibrium, enhancing triacetin conversion and selectivity. This strategy advances glycerol valorization and supports the production of sustainable fuel additives within integrated biorefinery systems.

HIGHLIGHTS

- In situ water removal boosts triacetin synthesis efficiency and selectivity.
- Three-stage esterification enhances acetic acid conversion up to 94.00%.
- Optimal at 110°C and 1:5 molar ratio, achieving 85.58% triacetin selectivity.
- Kinetic study fits a second-order model with strong correlation ($R^2 \geq 0.94562$).

1. INTRODUCTION

Biodiesel production as a renewable energy source continues to increase and generates glycerol as a byproduct at approximately 10% of the total production capacity (Khan et al., 2025; Bansod et al., 2025). The accumulation of glycerol causes oversupply in the global market and reduces its economic value (Sriratchachawan et al., 2022), and it potentially becomes waste when the purification cost

is higher than its selling price. One strategy to increase its added value is to convert glycerol into triacetin as a biodiesel fuel additive to improve combustion performance and fuel viscosity stability (Singare et al., 2025; Guimarães et al., 2025). Triacetin is produced through an esterification reaction between glycerol and acetic acid, and the reaction rate can be accelerated by using porous solid catalysts (Figure 2)

Citation: Nuryoto N, Hanifah N, Hariani N, Bagaskara RNT. Process optimization of glycerol-to-triacetin conversion in clean technology applications: In situ water removal for enhanced reaction performance in sustainable biodiesel byproduct valorization. Environ. Nat. Resour. J. 2026;24(4):469-481. (<https://doi.org/10.32526/ennrj/24/20250278>)

(Sandid et al., 2024). This reaction is reversible and produces water as a byproduct, which can shift the equilibrium toward the reactants and reduce triacetin selectivity (Figure 1). Therefore, water control during the reaction becomes a crucial aspect. For the reaction to proceed effectively, the reactants, namely acetic

acid and glycerol, must reach the active sites of the catalyst, because the reaction can only occur efficiently at those sites. The stages of glycerol esterification with acetic acid using a porous solid catalyst are illustrated in Figure 2.

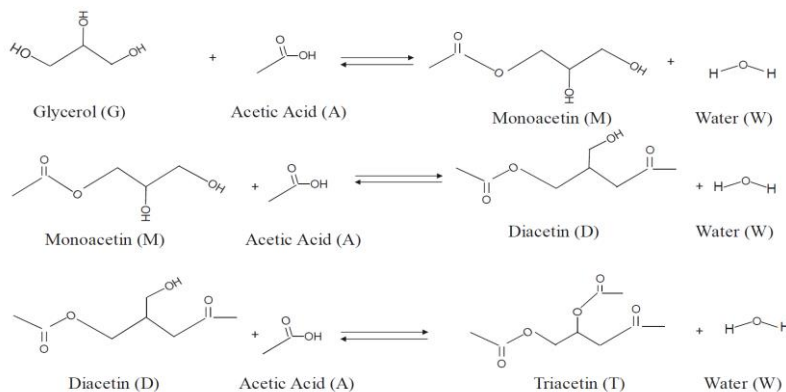


Figure 1. Esterification reaction steps of acetic acid and glycerol to produce triacetin

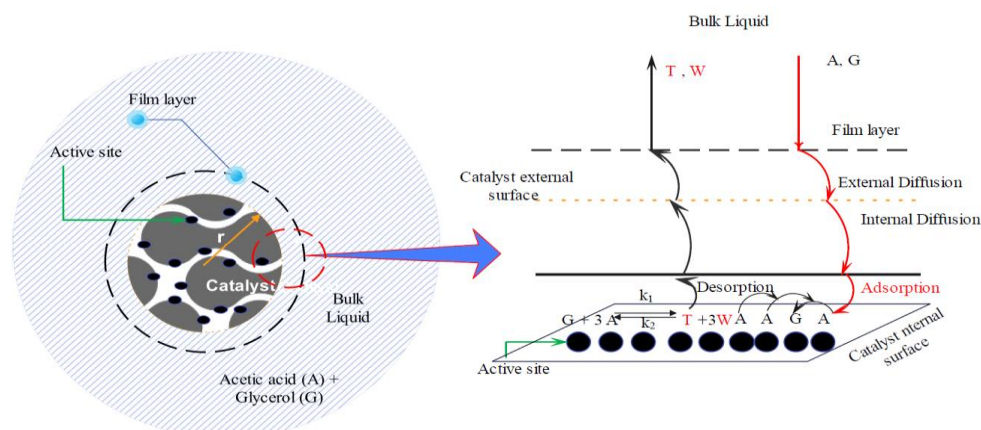


Figure 2. Illustration of the triacetin synthesis steps using a porous solid catalyst

Under steady-state conditions, the rates of external diffusion, internal diffusion, adsorption, desorption, and reaction are equal (Figure 2). Because this study adopted a steady state approach, the kinetic modelling was developed using an overall reaction rate approach, in which the adsorption rates of the reactants (glycerol and acetic acid), as well as the desorption rates of the products (triacetin and water), were not modeled as separate rate determining steps but were instead incorporated into the overall kinetic equation. As mentioned earlier, because this esterification reaction is reversible, the presence of water as a byproduct still affects the equilibrium position and indirectly influences the reaction rate as well as the triacetin produced (Sriratchachawan et al.,

2022). The stages of the esterification reaction between glycerol and acetic acid using a porous solid catalyst, under steady-state conditions, are illustrated in Figure 2 and presented in Equations (1) and (2) (Fogler, 2006).

$$N_{A \text{ ext}} = 3 N_{G \text{ ext}} = N_{A \text{ int}} = 3 N_{G \text{ int}} = \frac{dC_A}{dt} = 3 \frac{dC_G}{dt} \quad (1)$$

$$\begin{aligned} \frac{dC_A}{dt} &= k_{cA} (C_{A,b} - C_{A,s}) = D_{\text{eff},A} a_p \frac{dC_A}{dr} \\ &= k_1 C_A C_G - C_T C_W \end{aligned} \quad (2)$$

With, $N_{A \text{ ext}}$ and $N_{G \text{ ext}}$ =external diffusion rates of acetic acid and glycerol (mol/(dm³·s)); $N_{A \text{ int}}$ and $N_{G \text{ int}}$ =internal diffusion rates of acetic acid and glycerol (mol/(dm³·s)); C_A and C_G =concentrations of

acetic acid and glycerol at the catalyst active sites (mol/dm^3); C_T and C_W =concentrations of triacetin and water at the catalyst active sites (mol/dm^3); $C_{A,b}$ =concentration of acetic acid in the bulk liquid (mol/dm^3); $C_{A,s}$ =concentration of acetic acid at the external catalyst surface (mol/dm^3); k_{CA} =volumetric mass transfer coefficient of acetic acid ($1/\text{s}$); dC_A/dt and dC_G/dt =reaction rates of acetic acid and glycerol ($\text{mol}/(\text{dm}^3 \cdot \text{s})$); k_1 and k_2 =forward and reverse second-order rate constants ($\text{dm}^3/(\text{mol} \cdot \text{s})$); $D_{\text{eff},A}$ =effective diffusivity of acetic acid in the porous catalyst (dm^2/s); a_p =cross-sectional area available for diffusion within the particle pores (dm^2); dC_A/dr =radial concentration gradient of acetic acid inside the particle, from surface to center (mol/dm^4).

Research on triacetin has been conducted by many scholars and has advanced rapidly using a variety of methods. However, based on the literature reviewed, converting glycerol into triacetin is not straightforward. Even with different catalysts, the resulting selectivity for triacetin remains low. A sulfonated biochar catalyst derived from palmyra shell waste yielded only 4.20% triacetin selectivity (Jagadish et al., 2025), and a phosphate-silica catalyst from bamboo leaves produced just 24.00% triacetin selectivity (Manurung et al., 2022). A combination of porous alumina with Co/Ni/Mg metals achieved better triacetin selectivity of 53.00% (Bezerra et al., 2022). Microwave-irradiation studies using a Pd/activated carbon catalyst produced a high glycerol conversion of 96.64%, but the triacetin selectivity was very low at only 0.23% (Azmi et al., 2023). An interesterification system using babassu oil also yielded only 22.00% triacetin (Priebe et al., 2024). Increasing the temperature from 90°C to 110°C did increase acetic acid conversion, but triacetin selectivity remained very low at only 6.73% (Nuryoto et al., 2025). Some studies have achieved relatively high reactant conversion and triacetin selectivity (though still classified as low because they are below 70.00%), such as using mesoporous sulfonated carbon catalyst, which gave 97.00% glycerol conversion and 66.50% triacetin selectivity (Nda-Umar et al., 2020). A KIT-6 catalyst modified with $-\text{SO}_3\text{H}$ groups also showed reasonably good performance with 99.00% glycerol conversion, but triacetin selectivity was only 35.00% (Baingam et al., 2025). Referring to Figure 1, producing triacetin requires three reaction steps (formation of monoacetin, then diacetin, and finally triacetin), and each step generates water. Theoretically, the presence of water in the reaction

system tends to shift the equilibrium toward the reactants, preventing the reaction from proceeding fully to produce triacetin in significant amounts. Moreover, water has the simplest molecular structure compared with other substances (acetic acid, glycerol, monoacetin, diacetin, and triacetin), which have more complex structures and therefore larger molecular sizes than water. Because water molecules are smaller than the other compounds, they can diffuse more easily into the catalyst pores and occupy active sites, making it difficult for reactants such as glycerol and acetic acid to enter and react optimally within the catalyst. This condition hinders the esterification of glycerol and acetic acid to triacetin, as reflected by the consistently low triacetin selectivity. The low selectivity suggests that the reaction tends to remain at the intermediate stages, yielding mainly monoacetin and diacetin rather than proceeding further to triacetin. Even when esterification is conducted at a high molar ratio of up to 1:9 glycerol to acetic acid, triacetin selectivity remains low (Baingam et al., 2025). Therefore, an innovation is needed to address the problem of low triacetin selectivity. Studies on the esterification of glycerol and acetic acid have in fact been widely reported, but most of them still focus on catalyst development and the search for suitable reaction systems, so water control as a byproduct has not yet become a primary strategy for improving triacetin selectivity. This study proposes an innovation through in situ water removal as a process intensification and optimization strategy to increase the driving force of the reaction by shifting the equilibrium toward the products. Theoretically, this innovation has strong potential to improve the selectivity of the triacetin produced. To verify the success of this innovation, this study was conducted to evaluate the effect of in situ water removal on reaction performance in terms of acetic acid conversion and the resulting triacetin product. The findings can complement previous studies, enabling the development of an effective, efficient, and economical triacetin synthesis process that can be scaled up commercially and integrated with the biodiesel industry.

2. METHODOLOGY

2.1 Material and equipment

The main raw materials used in this study were technical-grade acetic acid (96%) and technical-grade glycerol (99%), both purchased from the Shopee Indonesia marketplace. The catalyst used was natural

clinoptilolite zeolite obtained from Lampung, Indonesia (LNZ) (Nuryoto et al., 2025; Hadi and Ilim, 2025; Hauli et al., 2025). Prior to use, the zeolite underwent pretreatment with 6 N H₂SO₄. This pretreatment was carried out to remove impurities, increase acidity, and enlarge the zeolite's surface area.

It is expected that, after pretreatment of the LNZ, diffusion-reaction processes in triacetin synthesis will proceed more rapidly, thereby maximizing triacetin yield. The equipment used for triacetin synthesis is illustrated in Figure 3.

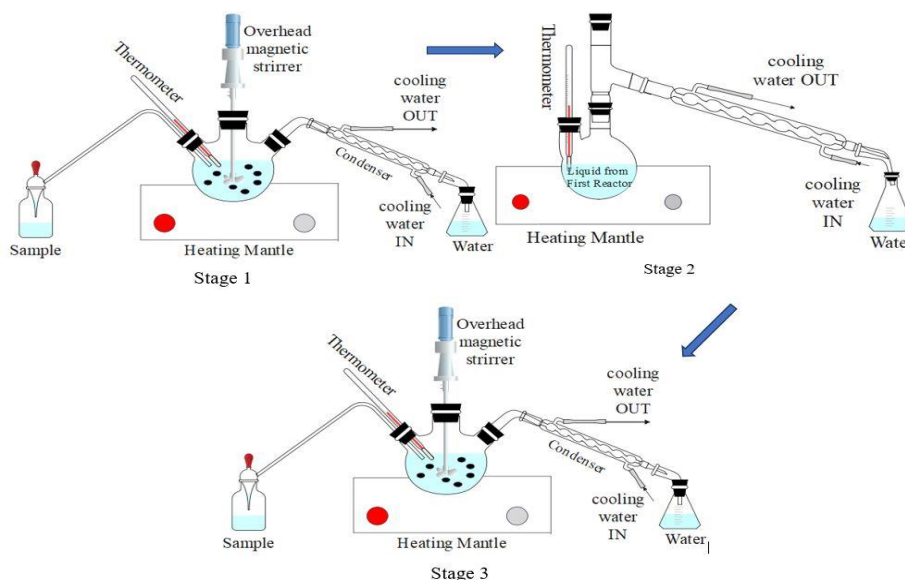


Figure 3. Schematic illustration of triacetin synthesis with in situ water removal

2.2 Natural zeolite catalyst preparation

Natural clinoptilolite zeolite from Lampung, Indonesia (LNZ), with a particle size of -45+60 mesh, was activated using a 6 N sulfuric acid solution, prepared by diluting 98% Merck sulfuric acid in distilled water to the desired volume, at a ratio of 10 g zeolite per 100 mL acid solution. The activation was carried out at 110°C for 2 h with stirring at 600 rpm (Nuryoto et al., 2025). The activated zeolite was then filtered and washed with distilled water until the pH of the wash water matched that of the distilled water. Next, the zeolite (LNZ) was drained and placed in an oven at 200°C for 2 h (Nuryoto et al., 2025). After cooling to room temperature, it was ready for use as a catalyst. To confirm that the activation had proceeded properly and that the zeolite was suitable for catalytic use, the LNZ was characterized before and after activation by X-ray diffraction (XRD) to observe changes in its crystal structure.

2.3 Esterification procedures

2.3.1 Stage 1 (preliminary reaction)

Glycerol and acetic acid in specified volumes, corresponding to reactant ratio of 1:3-1:5 mol glycerol

per mol acetic acid, were heated separately, with acetic acid in a beaker and glycerol in the reactor, until they approached the desired reaction temperature of 100°C (Sandid et al., 2024; Nuryoto et al., 2025). Cooling water was circulated through the condenser to condense the water vapor generated during the reaction, thereby ensuring that the removed water did not interfere with the experiment. Once both reactants reached a temperature close to the reaction set point of 100°C, the acetic acid was added to the reactor. The reaction temperature was then maintained at 100°C while overhead stirrer operated at 700 rpm (Nuryoto et al., 2025). After the mixture appeared homogeneous, a sample was collected for initial acid analysis (A_0) using 0.5 N NaOH, which was taken as the start of the reaction ($t_0=0$ h). The catalyst was then added to the reactor at 5% of the acetic acid mass (Sandid et al., 2024; Nuryoto et al., 2025). Subsequent samples were taken every hour for residual acid analysis (A_t) until the total reaction time reached 4 h. Acetic acid conversion was then calculated using Equation (3).

$$\% A = \frac{(A_0 - A_t)}{A_0} \times 100\% \quad (3)$$

With, %A=acetic acid conversion (%); A_0 =concentration of acetic acid at $t=0$ hours (mg/dm^3); A_t =concentration of acetic acid at time t hours (mg/dm^3).

2.3.2 Stage 2 (evaporation)

For Stage 2, the liquid product obtained from the preliminary reaction in Stage 1 under the optimal conditions was transferred to a two-necked flask and heated to evaporate the residual water from the mixture. The evaporation was carried out at 105°C and stopped when no more bubbles were observed, indicating that the residual water had evaporated.

2.3.3 Stage 3 (main reaction)

When the evaporation process was completed, the experiment proceeded to Stage 3, which was the main reaction, conducted at reaction temperatures of 90 , 100 , and 110°C . At this stage, the liquid from Stage 2, containing residual glycerol, acetic acid, monoacetin, diacetin, and triacetin, was further reacted with acetic acid using the optimal reactant ratio determined in the preliminary reaction. Samples were collected every hour over a total reaction time of 4 h. The sampling procedure and the method used to analyze and calculate acetic acid conversion were the same as those used in the preliminary reaction. In Stage 3, the triacetin product was analyzed by Fourier Transform Infrared Spectroscopy (FTIR) and validated by Gas Chromatography-Mass Spectrometry (GC-MS). The repeated reaction under water free conditions in Stage 3 was intended to promote the conversion of monoacetin, diacetin, and the remaining glycerol into triacetin (Figure 1).

2.4 Characterization of zeolite and analysis of the triacetin product

Characterization of the natural zeolite (LNZ) was carried out using a Bruker D8 ADVANCE X-ray Diffraction (XRD) instrument operated over a 2θ range of approximately 3° to 150° to identify changes in crystal structure. The product obtained from the main reaction (Stage 3) was analyzed by Fourier Transform Infrared Spectroscopy (FTIR) using an Alpha II instrument from Bruker, Germany, to identify changes in functional group peaks by comparison with standard references. This analysis served as an initial confirmation of whether the reaction had occurred and produced the expected product. Once the FTIR results indicated product formation, GC-MS analysis was performed for validation and to determine the percentage of triacetin produced. The GC-MS used was a thermo scientific instrument consisting of a

Trace 1,310 gas chromatograph and a Trace ISQ7000 mass spectrometer to identify triacetin and its byproducts, namely monoacetin and diacetin.

2.5 Mathematical model testing

To obtain more comprehensive information, this study also included reaction-kinetics calculations using a simple mathematical model, namely a pseudo-homogeneous model that was previously shown to be suitable for describing the reaction behavior, although the earlier study did not involve in situ water removal (Nuryoto et al., 2025). The use of the same mathematical model in this study was intended to test whether it remains valid under different conditions. If the model remains valid under different operating conditions, it may be used for reactor design and to predict conversion and product yield within specified operating ranges. The mathematical model was formulated based on several assumptions: (a) The catalyst particles were assumed to be small and uniform in size; (b) acetic acid was present in excess, so the reverse reaction was neglected; (c) the reaction rate was based on the change in acetic acid concentration; and (d) external and internal diffusion, as well as adsorption and desorption, were assumed to occur rapidly without significant resistance, so the reaction step was taken as the rate controlling step of the overall process. Based on these assumptions and the pseudo-homogeneous model, the concentrations of reactants and products in Equation (2) are taken to be equal to those in the bulk liquid phase, thus Equation (2) can be simplified into Equation (4).

$$\frac{dC_A}{dt} = k C_A^n \quad (4)$$

Where; dC_A/dt =acetic acid reaction rate ($\text{mol}/(\text{dm}^3 \cdot \text{h})$); k =reaction rate constant ($1/\text{h}^n$); n =reaction order; C_A =acetic acid concentration at a certain time (mol/dm^3).

This study employed reaction orders $n=1$ and $n=2$, which are commonly applied in chemical reactions, with $n=1$ or 2 . Equation (4) can be rewritten as Equations (5) and (6).

$$-\frac{dC_A}{dt} = k C_A \quad (5)$$

$$-\frac{dC_A}{dt} = k C_A^2 \quad (6)$$

Equations (5) and (6) can be integrated to obtain Equations (7) and (8).

$$\ln C_A = \ln C_{A0} + k t \quad (7)$$

$$\frac{1}{C_A} = \frac{1}{C_{A0}} + k t \quad (8)$$

The parameter (k) was determined by fitting the experimental data to first- and second-order kinetic models. The model with an R^2 value close to 1 is considered suitable for predicting acetic acid conversion under different operating conditions and for future reactor design.

3. RESULTS AND DISCUSSION

3.1 LNZ catalyst characterization

The XRD diffraction pattern of the natural zeolite (LNZ) before activation showed higher peak intensities than after activation using 6 N H_2SO_4 (Figure 4, green circled area). This decrease in peak intensity indicates that changes in the crystalline structure occurred as a result of the dealumination process. The observed changes in intensity and crystalline structure in Figure 4 show that the pretreatment of LNZ with H_2SO_4 altered the aluminosilicate framework of the zeolite. This

phenomenon is consistent with what is illustrated in Figure 5, where protons from H_2SO_4 attack the aluminosilicate framework and cause the release of Al atoms from the tetrahedral structure of the zeolite. Thus, Figure 4 provides structural evidence, while Figure 5 explains the chemical mechanism underlying these changes, so the two figures complement each other in supporting the occurrence of dealumination. This dealumination process contributes significantly to the increase in the Si/Al ratio, which is directly associated with the enhancement of the acidity of the LNZ catalyst. Referring to the study by Nuryoto et al. (2025), which used the same type of zeolite and activation conditions, treatment with 6 N H_2SO_4 increased the specific surface area from 57.230 m^2/g to 98.738 m^2/g and also showed stronger acidity characteristics based on TPD NH_3 analysis, with desorption peaks detected up to 400°C. The increase in surface area and acidity indicates that the activated LNZ has better catalytic potential when used in the esterification reaction.

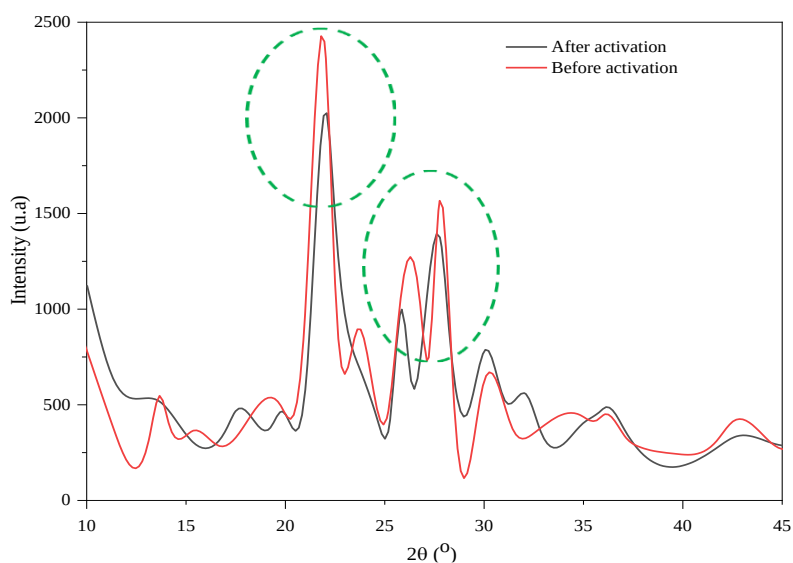


Figure 4. XRD characterization of LNZ zeolite before and after activation with 6 N H_2SO_4

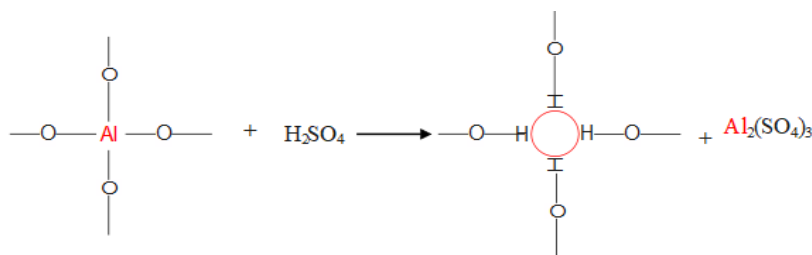


Figure 5. Illustration of dealumination reaction of natural zeolite using H_2SO_4 (Feng et al., 2019)

3.2 Effect of reactant ratio

Increasing the reactant ratio led to an increase in acetic acid conversion (Figure 6). At glycerol-to-acetic acid molar ratios of 1:3, 1:4, and 1:5, the acetic acid conversions after 4 h were 92.00%, 94.40%, and 97.60%, respectively. Theoretically, increasing the amount of acetic acid beyond the stoichiometric requirement increases its concentration in the reaction system, which can enhance mass transfer and adsorption at the catalyst active sites, thereby increasing the overall reaction rate (Equations 1 and 2). From a thermodynamic perspective, the phenomenon shown in Figure 6 is logical. As the reactant ratio increases, the reaction equilibrium constant (K_e) also increases (Equation 9) (Fogler, 2006). An increase in acetic acid concentration (C_A) proportionally raises k_1 and thereby increases K_e . A

higher k_1 leads to higher acetic acid conversion and greater product formation.

$$K_e = \frac{k_1}{k_2} = \frac{C_A^3 C_G}{C_W^3 C_T} \quad (9)$$

With, C_A , C_G , C_T , and C_W =concentrations of acetic acid, glycerol, triacetin and water (mol/dm³); 3=stoichiometry coefficient (dimensionless); K_e =equilibrium constant (dimensionless).

Thus, increasing the moles of acetic acid relative to glycerol, as shown in Figure 6, creates reaction conditions that drive the reaction toward product formation while minimizing the reverse reaction (Figure 1). Under these conditions, the forward reaction rate becomes dominant over the reverse reaction, resulting in higher overall reactant conversion (Hilmioğlu, 2022).

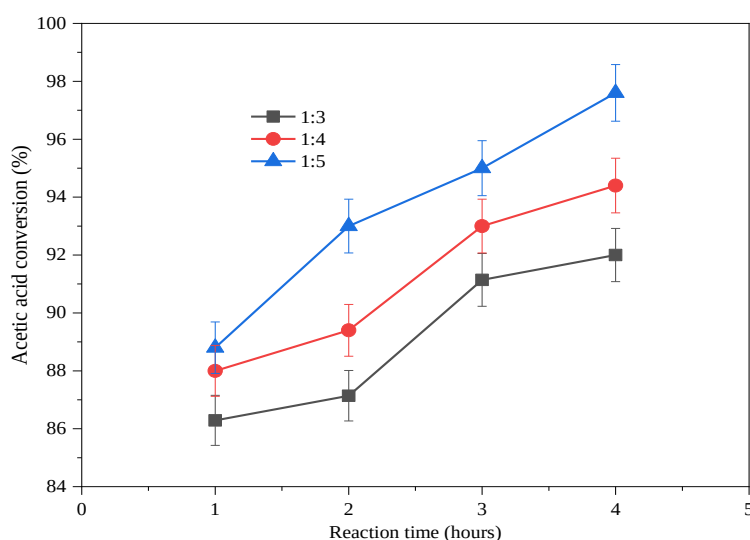


Figure 6. Effect of reactant ratio (mol glycerol/mol acetic acid) at a reaction temperature of 100°C (preliminary reaction)

Table 1 shows that increasing the reactant ratio (mol glycerol/mol acetic acid) leads to higher glycerol conversion. However, although glycerol conversion is relatively high, exceeding 90.00%, triacetin selectivity remains low, at only 8.00% and 36.40% (Baingam et

al., 2025; Doukeh et al., 2025). This phenomenon is likely due to the presence of water in the reaction system, which shifts the equilibrium and limits triacetin formation.

Table 1. Effect of reactant ratio (mol glycerol/mol acetic acid) on triacetin synthesis from acetic acid and glycerol

No.	Operation condition	Reactant conversion-triacetin selectivity	Reference
1	Reactant ratios of 1:3, 1:6, and 1:9, a reaction temperature of 115°C, a reaction time of 8 h.	Glycerol conversions were 91.0%, 99.0%, and 100.0%, with triacetin selectivity of 36.4% (overall reactant conversion reached 100%).	Baingam et al. (2025)
2	Reactant ratios of 1:3 and 1:3.6 (mol/mol) at 100°C for 4 h, using an SnFe ₂ O ₄ catalyst.	Glycerol conversion increased from 55.0% to 90.0%, while triacetin selectivity rose from 1.0% to 8.0%.	Doukeh et al. (2025)
3	Reactant ratios of 1:6 and 1:9, a reaction temperature of 110°C, and a reaction time of 150 min.	Glycerol conversion increased from 78.0% to 87.0%.	Petchsoongsakul et al. (2025)

3.3 Effect of reaction temperature

Acetic acid conversion increased as the reaction temperature increased. At 90, 100, and 110°C after 4 h of reaction, the conversions were 85.00%, 90.00%, and 94.00%, respectively (Figure 7). This behavior can be attributed to the increase in molecular kinetic energy at higher temperatures, which leads to more frequent and energetic collisions between reactant molecules. As a result, the reaction rate increases, leading to higher acetic acid conversion. The effect of temperature on collision frequency and reaction rate is described by Equations (10) and (11) (Fogler, 2006).

$$k = A e^{-\frac{E_a}{RT}} \quad (10)$$

$$A = p N_a \pi d^2 \sqrt{\frac{8 k_B T}{\pi \mu}} \quad (11)$$

With, k =reaction rate constant (first order=1/h; second order= $\text{dm}^3/\text{mol}\cdot\text{s}$); A =collision frequency factor (first order=1/s ; second order= $\text{dm}^3/\text{mol}\cdot\text{s}$); E_a =activation energy (J/mol); R =universal gas constant (8.314 J/(mol·K)); T =temperature (K); p =probability factor (dimensionless); N_a =Avogadro's number (6.022×10^{23} 1/mol); π =3.14 (dimensionless); d =molecular diameter (dm); k_B =Boltzmann constant (1.3806×10^{-23} J/K); and μ =reduced mass of the two colliding molecules (kg).

According to Equations (10) and (11), together with Equation (2), increasing the reaction temperature has a positive effect on the reaction rate, but only up to a certain limit. For a liquid-liquid reaction such as that in this study, the reaction temperature should not exceed the boiling point of either reactant, particularly acetic acid at 118°C. At temperatures above this point, contact between glycerol and acetic acid can decrease sharply because the two reactants exist in different phases, with acetic acid in the vapor phase and glycerol in the liquid phase. As a result, molecular interactions between the reactants are greatly reduced, even though such interactions are essential for the reaction to occur. If the reaction is conducted well above the boiling point, sufficient interaction can only be maintained by using a high reactant ratio and operating under reflux. For example, a reaction temperature of 130°C can produce up to 99.00% glycerol conversion, but it requires a glycerol-to-acetic acid molar ratio of 1:9 (Sandid et al., 2024). However, such operating conditions have several drawbacks, including relatively high reactant consumption, greater separation loads, and the need for an additional condenser to return acetic acid vapor to the reactor under reflux. Therefore, a process employing both high reaction temperatures and high reactant ratios becomes uneconomical.

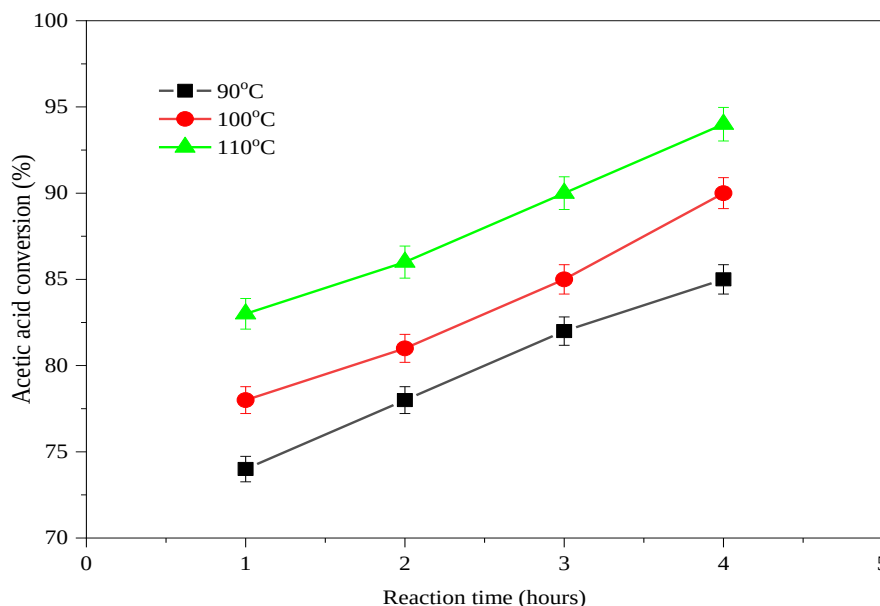


Figure 7. Effect of reaction temperature on acetic acid conversion (main reaction)

The trend observed in this study is consistent with previous research (Table 2), showing that increasing the reaction temperature leads to higher

reactant conversion. However, at lower temperatures below 90°C (25-65°C), glycerol conversion remains relatively low, at about 5-55%, while triacetin

formation remains limited to only 0-5% (Da Silva et al., 2025). This indicates that the reaction has not proceeded efficiently because the thermal energy is still insufficient to overcome the activation energy barrier effectively, so the reaction products are dominated by the intermediates monoacetin and diacetin rather than triacetin. When the reaction temperature is increased to 90-110°C under the specified operating conditions, with glycerol-to-acetic

acid molar ratio of 1:6, glycerol conversion increases significantly from 58.56% to 66.38% (Setyaningsih et al., 2018). This result confirms that, in addition to reactant ratio, reaction temperature is a key factor in triacetin synthesis. Higher temperatures increase the frequency of effective collisions between glycerol and acetic acid molecules, thereby increasing the esterification rate and driving the reaction toward triacetin formation.

Table 2. Effect of reactant ratio on triacetin synthesis from acetic acid and glycerol

No.	Operation condition	Reactant conversion-triacetin selectivity	Reference
1	Reaction temperatures of 25 to 65°C, catalyst $\text{Sn}_2\text{SiW}_{12}\text{O}_{40}$, glycerol-to-acetic acid molar ratio 1:3, catalyst loading 0.1 mol%, and reaction time of 6 h.	Glycerol conversions were 5%, 15%, 20%, 5%, and 55%, with triacetin formation of 0%, 0%, 0%, 3%, and 5%, respectively.	Da Silva et al. (2025)
2	Reaction temperatures of 90 to 110°C, reactant ratio 1:6 (mol glycerol/mol acetic acid), reaction time 90 minutes, catalyst concentration 3 wt%, and stirring speed 175 rpm.	Glycerol conversions were 58.56%, 66.91%, and 66.38% at 90, 100, and 110°C, respectively.	Setyaningsih et al. (2018)

3.4 Analysis of reaction products

Based on reference FTIR data for pure glycerol (National Institute of Standards and Technology, 2025a), glycerol exhibits a strong O-H absorption band in the range of 3,000-3,700 $1/\text{cm}$ (Akachat et al., 2025), with transmittance approaching 1%, and no distinct C=O absorption band characteristic of esters in the range of 1,702.42-1,740 $1/\text{cm}$ (Akachat et al., 2025; Aisyah et al., 2021). When glycerol was reacted with acetic acid in this study and analyzed by FTIR at 100°C and 110°C, the O-H absorption band in the range of 3,000-3,700 $1/\text{cm}$ became markedly weaker, with transmittance increasing from about 1% to

approximately 80% (Figure 8, orange circle). In addition, in the region 1,702.42-1,740 $1/\text{cm}$ (green circle), which is characteristic of esters, distinct peaks appeared in the samples obtained at 100°C and 110°C, with transmittance of around 20% (green circle). These results indicate the formation of esters products, namely monoacetin, diacetin, and triacetin. Compared with the standard FTIR spectrum (National Institute of Standards and Technology, 2025b), the FTIR results shown in Figure 8 are consistent with triacetin. The peak in the red circled region of Figure 8 (960-970 $1/\text{cm}$) is sharper at 110°C than at 100°C.

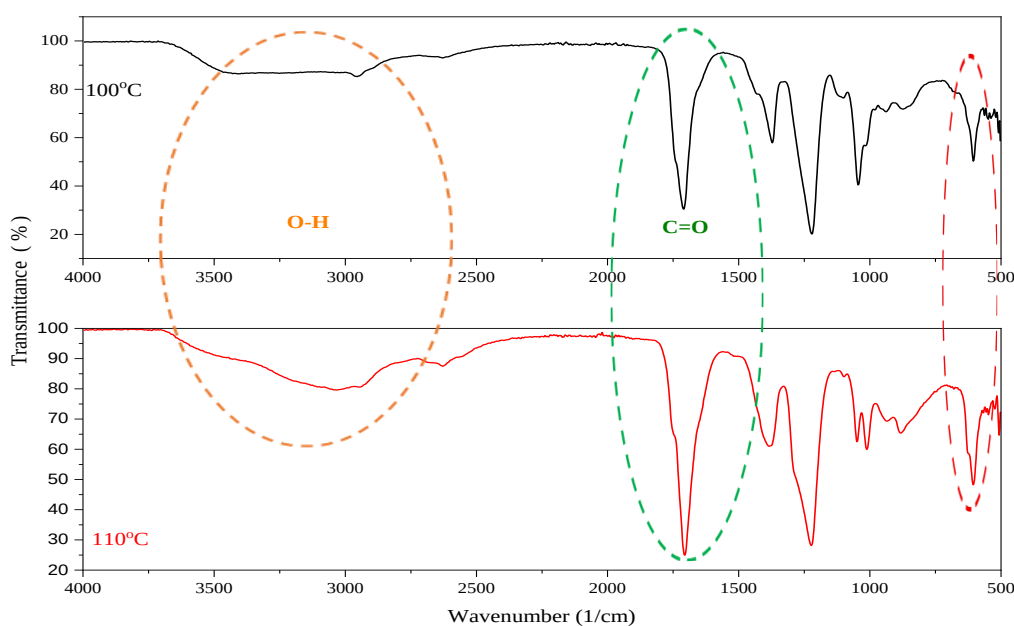


Figure 8. FTIR results at 100°C and 110°C for a 1:5 glycerol-to-acetic acid molar ratio

To validate the FTIR results, the contents of monoacetin, diacetin, and triacetin were analyzed using GC-MS (Figure 9(a) and Figure 9(b)). Triacetin selectivity relative to monoacetin and diacetin was 79.98% at a reaction temperature of 100°C (Figure 9(a)) and increased to 85.58% at 110°C (Figure 9(b)), representing an increase of 5.60%. These results indicate that increasing the reaction temperature at a reactant ratio of 1:5 mol acetic acid, together with in situ water removal during the reaction, promotes triacetin formation. Compared with a previous study

conducted without in situ water removal (Nuryoto et al., 2025), triacetin selectivity at 100°C was only 6.73%, whereas under the same temperature in this study it reached 79.98%. These findings support the hypothesis that the presence of water in the reaction system is a key factor limiting the esterification of glycerol and acetic acid to triacetin. Therefore, the in situ water removal strategy in this study proved effective, resulting in a substantial increase of 73.25% in triacetin selectivity compared with the previous study (Nuryoto et al., 2025).

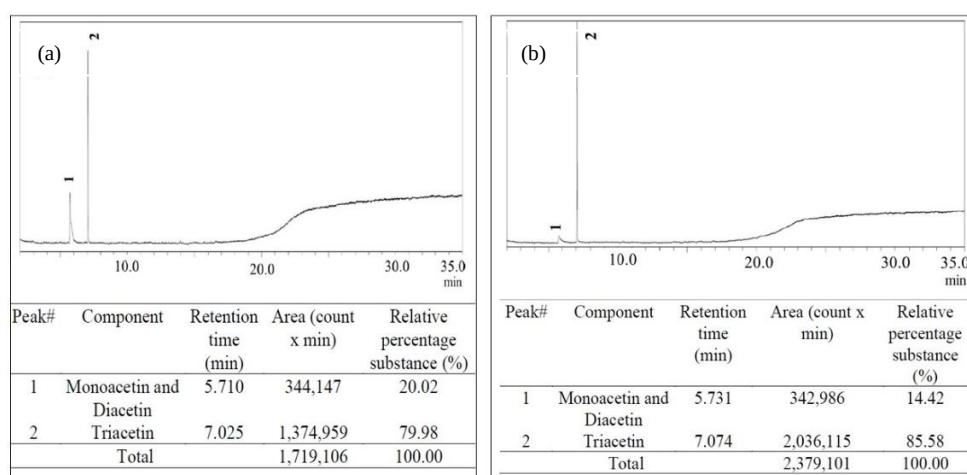


Figure 9. GC-MS results: (a) at 100°C and (b) at 110°C

3.5 Mathematical model testing

Based on Figures 10(a) and 10(b), the second-order mathematical model provides a better fit than the first-order model, as indicated by coefficients of determination (R^2) that are closer to 1. For the second-order model, the R^2 values are above 0.94562, whereas the highest R^2 for the first-order is only 0.84343. Therefore, the second-order kinetic model is more representative of the reaction behavior in the esterification of glycerol and acetic acid for triacetin synthesis. Previous research by Nuryoto et al. (2025) also showed that the second-order model performs better than the first-order model based on R^2 values. This indicates that the second-order pseudo-homogeneous model is suitable for predicting reactant conversion during operation and for reactor design. Using the best fit model (second-order pseudo-homogeneous), the reaction rate constant (k) at each temperature was determined (Table 3). The obtained k values and the corresponding temperatures (T) were then used to construct a plot of $\ln k$ versus $1/T$ according to the Arrhenius equation (Equation 10), as shown in Figure 11. This plot was used to determine

A (the molecular collision frequency factor) and E_a (the activation energy), since both parameters are important for reactor operation and design.

From the linearization of Table 3 (see Figure 11), Equation (12) was obtained.

$$\ln k = 17.89403 - \frac{7341.42499}{T} \quad (12)$$

Referring to Equation (12) and using the gas constant $R=8.314 \text{ J/ (mol} \cdot \text{K)}$, the collision frequency factor (A) was calculated to be $5.91 \times 10^7 \text{ dm}^3/(\text{mol} \cdot \text{h})$, and the activation energy (E_a) was $6.10 \times 10^4 \text{ J/mol}$. This E_a value is quite similar to that reported in a previous study by Nuryoto et al. (2011), which used a different catalyst, namely Indion 225 Na, without in situ water removal, and reported an E_a of $6.60 \times 10^4 \text{ J/mol}$. The observed difference may be attributed to differences in catalyst concentration and activity. In this study, the catalyst used was activated natural clinoptilolite zeolite at 5% relative to the acetic acid mass, whereas the previous study used an ion-exchange catalyst (Indion 225 Na) at 3% of the acetic acid mass (Nuryoto et al., 2011).

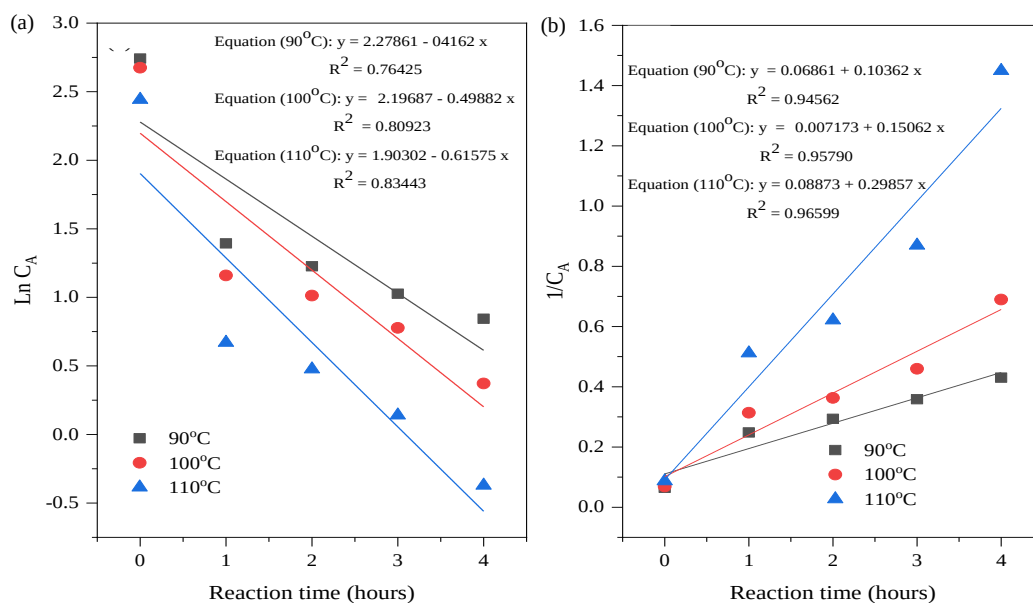


Figure 10. Model validation: (a) first-order pseudo-homogeneous model and (b) second-order pseudo-homogeneous model.

Table 3. Reaction rate constant (k) versus reaction temperature

No.	T (K)	k	1/T	ln k
1	363.15	0.10362	0.0027537	-2.26702
2	373.15	0.15062	0.0026799	-1.89300
3	383.15	0.29857	0.0026099	-1.20875

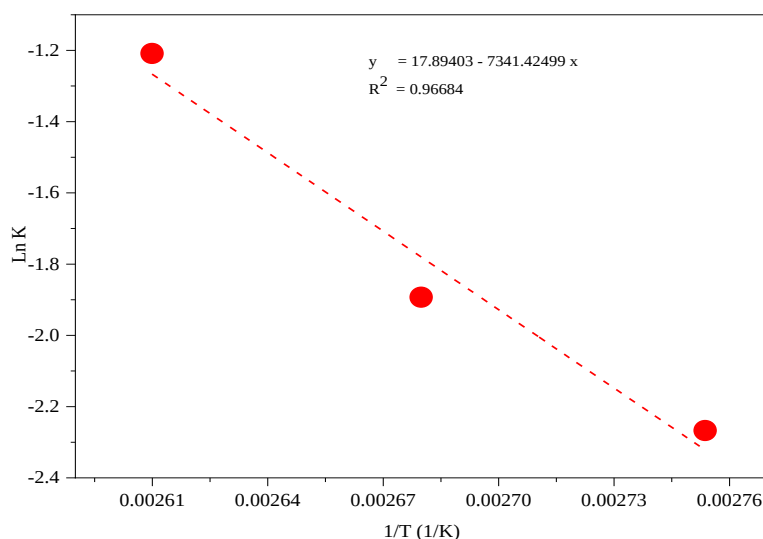


Figure 11. Linearization of $\ln k$ versus $1/T$ for the second-order model

3.6 Practical implication and implementation strategy

In general, the optimization results and kinetic modeling presented in this study provide a strong scientific basis for the development of triacetin synthesis through reaction intensification via in situ water removal. This approach enables the reaction

equilibrium to shift continuously toward product formation, thereby increasing glycerol conversion and triacetin selectivity without requiring extreme operating conditions. In the next stage of development, this research has the potential to be expanded to pilot scale by considering reactor design, long-term catalyst stability, and cyclic performance

evaluation of the water removal system. Techno-economic assessment (TEA) and life cycle assessment (LCA) are also needed to evaluate its commercial feasibility and environmental impact compared with conventional processes. From an industrial perspective, integration of this process into the biodiesel production chain has significant potential because it converts glycerol, the main byproduct, into value-added triacetin as a biodiesel fuel additive. Therefore, this study not only contributes to the development of kinetic models but also offers a direction for implementing a more efficient, economical, and sustainable.

4. CONCLUSION

This study shows that the in situ water removal strategy applied during the reaction through a three-stage esterification of glycerol with acetic acid, significantly improved reaction performance. The best operating conditions were obtained at glycerol-to-acetic acid molar ratio of 1:5 and a reaction temperature of 110°C, yielding 94.00% acetic acid conversion and 85.58% triacetin selectivity. These results indicate a shift in product distribution from monoacetin and diacetin toward the desired main product, triacetin, and confirm the importance of reaction temperature, reactant ratio, and water removal from the system in increasing both acetic acid conversion and triacetin selectivity. Kinetic analysis showed that the second-order pseudo-homogeneous model provided a better fit to the data than the first-order model, with R^2 values above 0.94562, a frequency factor (A) of $5.91 \times 10^7 \text{ dm}^3/(\text{mol} \cdot \text{h})$, and an activation energy (E_a) of $6.10 \times 10^4 \text{ J/mol}$. The results of this study strengthen the theoretical foundation while also providing guidance for reactor design and process operation. From an industrial application perspective, the conversion of glycerol into triacetin has the potential to increase added value within the biodiesel production chain while also supporting the implementation of green chemistry principles. Therefore, this research is worthy of further development at the pilot scale for process validation, although additional evaluation is still needed, including catalyst stability, energy efficiency analysis, and integration with biodiesel production units, in order to support commercialization readiness and contribute to reducing the carbon footprint.

ACKNOWLEDGEMENTS

The authors express their gratitude to the Department of Chemical Engineering-Universitas Sultan Ageng Tirtayasa for providing the facilities and support that made this research possible and enabled its publication. It is hoped that the results of this study will contribute to the advancement of science and technology and provide a tangible benefit to society at large.

AUTHOR CONTRIBUTIONS

Nuryoto Nuryoto: Conceptualization, methodology, supervision, visualization, and writing-original draft preparation and finishing; Nasywa Hanifah and Najiha Hariani: Investigation, validation, resources, and data curation; Rafiif Nur Tahta Bagaskara: Writing-review and editing.

DECLARATION OF CONFLICT OF INTEREST

The authors declare no conflict of interest.

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