Triacetin production using SiO$_2$-H$_3$PO$_4$ catalysts derived from bamboo leaf biomass waste for esterification reactions of glycerol and acetic acid

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Abstract. Increasing the demand for renewable fuels especially for biodiesel has the effect of increasing by products during biodiesel production. Therefore, the efforts made to make biodiesel by products in the form of glycerol become more economic value, then further processing is carried out into biofuel additives. One of the biofuel additives that can be synthesized from glycerol is triacetin. In this study, the production of triacetin compounds was carried out through an esterification reaction using calcined SiO$_2$-H$_3$PO$_4$ catalyst originating from bamboo leaf biomass waste so that glycerol conversion, concentration and selectivity of the best triacetin products from various reaction variables were obtained. The esterification process is carried out by reacting glycerol and acetic acid with a mass ratio of glycerol: acetic acid which is 1 : 9 at a temperature of 100 ± 5°C to produce the main product triacetin. The influence of various process variables such as catalyst type, catalyst weight, and reaction time on glycerol conversion was observed in this study. The best conditions produced in this study were the highest conversion of 100% glycerol, the concentration of triacetin products 18.53%, and selectivity of triacetin products 22.84% with catalyst type SiO$_2$-H$_3$PO$_4$ 1 : 2 (M/M), catalyst weight 5% from glycerol weight, reaction time of 4 hours, and stirring speed of 300 rpm.

1. Introduction

Biodiesel is one of the renewable fuels that can replace diesel fuel due to the similarity of physicochemical properties between the two [1][2]. At present, biodiesel is produced globally because the demand for renewable fuels is increasing and is estimated to reach 37 million tons by 2020 [1][3]. Generally, biodiesel is produced through transesterification reactions from vegetable oils, animal fats, or oil waste using alcohol (especially methanol) and the presence of alkaline catalysts [4][5][6]. Increasing biodiesel production capacity is increasing from year to year causing more and more by products of biodiesel production in the form of glycerol which will increase and increasingly cause a decrease in the price of glycerol [3]. Glycerol formed as a by-product of biodiesel production also reaches 10% by weight of the biodiesel produced [1][3]. Therefore, efforts are needed to increase the economic value of glycerol as a by-product of biodiesel production, one of which can be converted into biofuel additives [3].

This glycerol can actually be used as a raw material for making biofuel additives which can be done through several chemical reactions such as through esterification, acetylation, etherification, transesterification, hydrogenolysis, and carbonylation reactions. The esterification and acetylation process is an interesting reaction to convert glycerol to biodiesel production by-products [7].
Esterification of glycerol using acetic acid will produce chemical compounds that can be used as biofuel additives called triacetyl glycerol compounds or triacetin [7][8]. Triacetin has a wide range of applications in the industry, some of which can be used in the cosmetics, pharmaceuticals [9], as fuel additives to increase the octane number in gasoline [7], do not have an adverse effect on fuel quality, even can be used as a substance additives on biodiesel up to 10% by weight of biodiesel as cetane booster [10][11].

In the process of making triacetin compounds through esterification reactions of glycerol and acetic acid generally use homogeneous catalysts such as sulfuric acid (H$_2$SO$_4$), phosphoric acid (H$_3$PO$_4$), and hydrochloric acid (HCl). However, the use of homogeneous catalysts corrodes material [12], production of toxic compounds, difficulties in terms of separation from major products [13], waste disposal problems, and is expensive [14]. Therefore, to overcome this problem, then to create green processes in the glycerol esterifcation reaction, the liquid acid catalyst was replaced with a solid acid catalyst [15]. Solid acid catalysts can be easily separated through the filtration process, do not corrode the reactor in the reaction system, can be reused, and are environmentally friendly. So that the selection of solid acid catalysts is an attractive alternative to replace liquid acid catalysts in research and applications in the industry [16].

Some examples of solid acid catalysts that have been reported by Lacerda et al (2015) for esterification of glycerol and acetic anhydride are Amberlyst-15 resin in the molar ratio of acetic anhydride : glycerol = 3 : 1 and reaction time of 120 minutes to obtain 98% triacetin selectivity and conversion by 100% [9]. Costa et al (2016) used variations of solid acid catalysts such as SBA-15, Pr-SO$_3$H-SBA-15, H-ZSM-5 Zeolite, and H-Beta in the esterification of glycerol and acetic acid at a 1 : 6 molar ratio, catalyst weight 4wt%, and variations in reaction time 30, 60, 90, 120, 150, 180, 210, 240, and 270 minutes. The best results were obtained using the Pr-SO$_3$H-SBA-15 catalyst. Glycerol conversion reached 96% with selectivity of 87% at 150 minutes reaction time [13]. In addition, Chamack et al (2018) have also reported the production of fuel additives from glycerol and acetic acid with a 1 : 12 molar ratio, reaction temperature of 105°C, stirring speed of 700 rpm, and catalyst amount of 12 g/L with variation of reaction time 2, 6, and 20 hours. The desired product selectivity (TAG and DAG) reached 91% with perfect conversion using the H$_3$PW$_{12}$O$_{40}$ catalyst at 20 hours reaction time [17].

Based on studies conducted by previous researchers using various types of solid acid catalysts for the production of triacetin compounds. However, research on the use of SiO$_2$–H$_3$PO$_4$ catalysts derived from bamboo leaves for the glycerol esterification reaction has not been reported. In Indonesia, bamboo leaves tend to be seen as agricultural waste by the community which is generally burned in an uncontrolled way. This has a negative impact on the environment [18][19]. In addition, Indonesia also has 143 types of bamboo trees and almost 40 million bamboo clumps capable of producing silica with percentage of 75.90 – 82.86%. This amount is the second highest level of silica material after rice husk ash of 93.20% [20]. Based on relatively abundant of silica content, bamboo leaves were very potential to be used as a source of silica for the synthesis of solid acid catalysts. So, this study tried to examine the used of SiO$_2$–H$_3$PO$_4$ as solid acid catalyst from bamboo leaf waste impregnated with H$_3$PO$_4$ so that glycerol conversion was obtained and the concentration and selectivity of the highest triacetin products from various reaction variables were carried out. The influence of various process variables such as catalyst type and catalyst weight was observed in this study.

2. Method
2.1. Material
In this study, the materials used are glycerol (C$_3$H$_6$O$_3$), acetic acid (CH$_3$COOH), bamboo leaf, phosphoric acid (H$_3$PO$_4$), sodium hydroxide (NaOH), and hydrochloric acid (HCl).

2.2. Equipment
The main equipment used in this study are furnace, triple neck flask, hot plate, magnetic stirrer, and condenser reflux.
2.3. Procedure catalyst synthesis
Synthesis of solid acid catalysts from bamboo leaves was first cleaned the bamboo leaves, and then mashed and calcined for 3 hours at 600°C. Bamboo leaves ash was then silica extracted by sodium hydroxide (NaOH) solution 1 M with a ratio of bamboo leaf ash and NaOH solution of 1 : 20 (w/v). Extraction was carried out at 80°C for 3 hours. The extraction result was filtered and the filtrate solution was cooled to room temperature. The cooled filtrate was added with HCl solution 0.6 M dropwise to form a hydrogel. The formed hydrogel was filtered and dried to get silica powder. The obtained silica powder was impregnated with phosphoric acid (H₃PO₄) solution with a ratio of SiO₂-H₃PO₄ 1 : 2, 1 : 3, and 1 : 4 (M/M). Silica was impregnated at 80°C for 2 hours and then dried at 200°C until finally calcined at 600°C for 5 hours. The silica extraction process from bamboo leaf ash and silica impregnation process can be seen in the following figure 1.

![Silica extraction process from bamboo leaf ash](image1)
![Silica impregnation process with phosphoric acid](image2)

**Figure 1.** (a) Silica extraction process from bamboo leaf ash, (b) Silica impregnation process with phosphoric acid.

2.4. Procedure catalyst experiments
Triacetin production was carried out by esterification reaction between glycerol and acetic acid with a main variable in the form of a reaction time of 4 hours by sampling every 1 hour to determine the conversion of glycerol every hour, reaction temperature 100 ±5°C, stirring speed 300 rpm, and mass ratio of glycerol : acetic acid 1 : 9. While the variable changes in the form of variations catalyst weight by 3%, 5%, 7% (wt) of the weight of glycerol and the type of catalyst SiO₂-H₃PO₄. The type of SiO₂-H₃PO₄ catalyst 1 : 2 was coded SP1, SiO₂-H₃PO₄ catalyst 1 : 3 was coded SP2, and SiO₂-H₃PO₄ catalyst 1 : 4 was coded SP3. The series of research equipment can be seen in figure 2.

![Series of triacetin production equipment](image3)

**Figure 2.** Series of triacetin production equipment.
2.5. Analysis of esterification reaction products

The results from esterification glycerol and acetic acid using SiO$_2$-H$_3$PO$_4$ catalyst in various variations of SiO$_2$ : H$_3$PO$_4$ molar ratio were analyzed of glycerol conversion, triacetin concentration formed, and triacetin selectivity using Gas Chromatography Mass Spectrometry (GCMS). GCMS instrumentation used is GCMS-QP2010S SHIMADZU with column Rtx 5 MS, length 30 meters, ID 0.25 MM, film 0.25 micrometer, helium carrier gas, and ionizing El 70 Ev. The conversion of glycerol to the esterification process of glycerol and acetic acid can be calculated using following equation:

$$\text{Glycerol Conversion (\%)} = \frac{\text{Amount of Converted Glycerol}}{\text{Total Amount of Initial Glycerol}} \times 100\%$$  \hspace{1cm} (1)

While the selectivity of triacetin can be calculated using the following equation:

$$\text{Triacetin Selectivity (\%)} = \frac{\text{Amount of Glycerol Converted to a Product (Triacetin)}}{\text{Total Amount of Converted Glycerol}} \times 100\%$$  \hspace{1cm} (2)

3. Result and discussions

The results obtained in this study will be discussed in 3 subsections which include the effect of catalyst weight and SiO$_2$-H$_3$PO$_4$ catalyst type on glycerol conversion, the effect of catalyst weight and SiO$_2$-H$_3$PO$_4$ catalyst type on triacetin concentration, and the effect of catalyst weight and catalyst type on triacetin selectivity.

3.1. Influence of catalyst weight and SiO$_2$-H$_3$PO$_4$ catalyst type on glycerol conversion

In this study, various variations of SiO$_2$-H$_3$PO$_4$ catalysts in the molar ratio of SiO$_2$-H$_3$PO$_4$ were catalytically tested for the esterification of glycerol and acetic acid. The relationship between the influence of catalyst weight and type of catalyst on glycerol conversion can be shown figure 3.

Figure 3. Influence of catalyst weight and catalyst type on glycerol conversion.

In figure 3, it can be seen the influence of catalyst weight and catalyst type on the esterification reaction of glycerol and acetic acid on glycerol conversion. The glycerol conversion value obtained at the weight influence of the catalyst tends to fluctuate along with the increase in catalyst weight in each type of SiO$_2$-H$_3$PO$_4$ catalyst used. In this study, glycerol conversion was achieved for the used of SP1 catalyst types (SiO$_2$-H$_3$PO$_4$ 1 : 2) in the variation of catalyst weight 3%, 5%, and 7% respectively 99.66%; 100%; and 97.98%. In the used of SP2 catalyst types (SiO$_2$-H$_3$PO$_4$ 1 : 3) in the variation of catalyst weight 3%, 5%, and 7%, respectively were 99.57%; 99.44%; and 99.48%. Whereas in the used of SP3 catalyst type (SiO$_2$-H$_3$PO$_4$ 1 : 4) in the variation of catalyst weight 3%, 5%, and 7% respectively
were 99.32%; 99.38%; and 99.25%. Based on figure 2, the highest glycerol conversion reaches 100% conversion in the use of catalyst weight 5% of glycerol weight in SP1 catalyst type (SiO$_2$-H$_3$PO$_4$ 1 : 2). Overall, the conversion of glycerol in each esterification of glycerol and acetic acid to the ratio of catalyst weight and catalyst type showed a high average conversion of the data reported by several researchers.

Goncalves et al (2008) [21] have reported that in the esterification of glycerol using various solid acid catalyst, the glycerol conversion data was obtained at 97% after 30 minutes and the selectivity of triacetin formed by 13% using Amberlyst-15 resin catalyst. In addition, Goncalves et al (2008) also reported that the use of K-10 montmorillonite as a catalyst resulted in a conversion of 90% after a reaction time of 30 minutes. However, the selectivity of triacetin formed is only 5% and this result is smaller than that of using Amberlyst-15 resin catalyst [21]. When compared with the results obtained in this study, the value of glycerol conversion in this study was higher than previous studies. This indicates that the SiO$_2$-H$_3$PO$_4$ catalyst successfully catalyzes and converts glycerol with a higher conversion value.

The influence of the weight of the catalyst used in this study is enough to influence the value of glycerol conversion. This is can be shown by figure 3. However, with increasing catalyst weight used, the conversion of glycerol obtained tends to fluctuate in each type of SiO$_2$-H$_3$PO$_4$ catalyst. Dosuna-Rodriguez (2012) [22] stated that the higher the amount of catalyst used, the higher the rate of esterification to achieve reaction equilibrium. This phenomenon can be explained by the availability of higher active sites that allow simultaneous protonation of more acetic acid molecules. Using a lower amount of catalyst will cause a longer reaction time. However, the advantages of a catalyst cause solid waste which does not promote an increase in the rate of the reaction and cause the density of the solids of the catalyst in the solution to be large enough to reduce the contact area between the catalyst and the reactants. This is an important reason for determining the optimal amount of catalyst used in a reaction, namely maximizing the reaction rate but avoiding solid waste [22].

### 3.2. Influence of catalyst weight and catalyst type on esterification of glycerol and acetic acid against triacetin concentration

In this study, the products of the esterification reaction of glycerol and acetic acid using SiO$_2$-H$_3$PO$_4$ catalysts of various variations in weight and type of catalyst were analysed using Gas Chromatography Mass Spectrophotometry (GCMS) instrumentation. The influence of catalyst weight and catalyst type on the esterification reaction of glycerol and acetic acid can be seen in figure 4.

![Figure 4. Influence of catalyst weight and catalyst type on triacetin concentration.](image-url)
In figure 4, it can be seen the influence of catalyst weight and type of catalyst on the concentration of triacetin formed. Seen in figure 3 the triacetin concentration fluctuated with increasing catalyst weight for each type of SiO$_2$-H$_3$PO$_4$ catalyst used. In this study, the concentration of triacetin formed for the use of SP1 catalyst type (SiO$_2$-H$_3$PO$_4$ 1 : 2) in the variation of catalyst weight 3%, 5%, and 7% respectively was 11.16%; 18.53%; and 7.28%. In the use of SP2 catalyst types (SiO$_2$-H$_3$PO$_4$ 1 : 3) in the variation of catalyst weight 3%, 5%, and 7% respectively were 11.86%; 9.7%; and 10.73%. Whereas in the use of SP3 catalyst types (SiO$_2$-H$_3$PO$_4$ 1 : 4) in the variation of catalyst weight 3%; 5%; and 7% respectively were 9.42%; 10.13%; and 8.53%. So that the highest triacetin concentration was obtained using the SP1 catalyst type (SiO$_2$-H$_3$PO$_4$ 1 : 2) with a catalyst weight of 5%. The triacetin concentration obtained reached 18.53%. However, the lowest triacetin concentration was also obtained in the use of SP1 catalyst type (SiO$_2$-H$_3$PO$_4$ 1 : 2) with a catalyst weight of 7% where the triacetin concentration obtained was only 7.28%. The difference in triacetin concentration obtained in each variation using the SiO$_2$-H$_3$PO$_4$ catalyst type and the weight of the catalyst used is closely related to the mechanism of the reaction that occurs during the esterification process.

The reaction mechanism of calcined SiO$_2$-H$_3$PO$_4$ catalyst which occurred in the esterification reaction of glycerol and acetic acid began with the diffusion process of the reactants consisting of glycerol and acetic acid towards the surface of calcined SiO$_2$-H$_3$PO$_4$ catalyst. The second stage is the process of adsorption of glycerol and acetic acid on the surface of the catalyst. The third stage is a reversible reaction on the surface of the catalyst to produce the product. The fourth stage is the desorption of triacetin and glycerol products from the surface of the catalyst. The last stage is the diffusion of triacetin products from the pore to the outer surface of the catalyst. The reactions that occur can be seen in figure 5.

![Acid-catalyzed reaction mechanism of glycerol esterification with acetic acid](image)

**Figure 5.** Acid-catalyzed reaction mechanism of glycerol esterification with acetic acid [23].

On the influence of the use of catalyst weight and SiO$_2$-H$_3$PO$_4$ catalyst type on the glycerol esterification reaction in this study it can be concluded that the use of the optimum SiO$_2$-H$_3$PO$_4$ catalyst used was 5% of the glycerol weight used and SP1 catalyst type (SiO$_2$-H$_3$PO$_4$ 1 : 2). This is because in a reaction, the product will produce a high concentration if the use of the catalyst used is considered sufficient and not excessive [24].

### 3.3. Selectivity of triacetin compounds results of esterification of glycerol and acetic acid using SiO$_2$-H$_3$PO$_4$ catalyst

The result of the analysis of the product of esterification of glycerol and acetic acid using Gas Chromatography Mass Spectrophotometry (GCMS) then calculated the selectivity value of triacetin formed. The selectivity value of triacetin formed on the product of the reaction can be seen in figure 6. In figure 6, it can be seen the selectivity value of triacetin formed in the variation of catalyst weight and catalyst type. It can be seen in figure 4 that the selectivity of triacetin fluctuates with increasing catalyst weight for each type of SiO$_2$-H$_3$PO$_4$ catalyst used. When compared with figure 4, there are similarities in trend lines that occur in figure 6. In this study, the selectivity of triacetin was formed for the use of SP1 catalyst types (SiO$_2$-H$_3$PO$_4$ 1 : 2) in the variation of catalyst weight 3%, 5%, and 7% each is 15.24%; 22.84%; and 11.75%. In the use of SP2 catalyst types (SiO$_2$-H$_3$PO$_4$ 1 : 3) in the variation of catalyst weight 3%, 5%, dan 7% respectively were 15.68%; 13.44%; and 14.38%. Whereas in the use of SP3
catalyst types (SiO$_2$-H$_3$PO$_4$ 1 : 4) in the variation of catalyst weight 3%, 5%, and 7% respectively are 13.05%; 13.80%; and 11.99%. In this study, the highest selectivity of triacetin was obtained using 5% catalyst weight with SP1 catalyst type (SiO$_2$-H$_3$PO$_4$ 1 : 2) where the selectivity value reached 22.84%. While the lowest triacetin selectivity was obtained using 7% catalyst weight with SP1 catalyst type (SiO$_2$-H$_3$PO$_4$ 1 : 2) where the triacetin selectivity value was 11.75%.

Figure 6. Influence of catalyst weight and catalyst type on triacetin selectivity.

The selectivity of triacetin is the percentage of the triacetin product to the total reaction product [17]. Jagadeeswariah et al (2010) reported that the selectivity value did not significantly influence the change in the weight of the catalyst used [24]. In addition, Dosuna-Rodriguez et al (2011) [22] reported that the lower the acid site density, the higher the catalytic activity on a catalyst assuming that there is a nucleophilic attack by the hydroxyl glycerol group to acetic acid adsorbed on the catalyst surface to determine the esterification reaction rate. In addition, Dosuna-Rodriguez et al (2011) [22] also reported that the distribution of esters was determined by the equilibrium of the reaction especially with respect to the reactant concentration and reaction temperature. However, it is not affected by the catalyst used [25]. It can be concluded that the influence of the use of catalyst weight and SiO$_2$-H$_3$PO$_4$ catalyst type on triacetin selectivity tends to have no effect which can be seen in fluctuating Figure 6.

4. Conclusions

Based on the research that has been done on the operating conditions of esterifications of glycerol and acetic acid for the mass ratio of glycerol and acetic acid used 1 : 9, reaction time for 4 hours, variation of SiO$_2$-H$_3$PO$_4$ catalyst type, and variation in catalyst weight used for each type of catalyst optimum conditions were obtained using SP1 catalyst type (SiO$_2$-H$_3$PO$_4$ 1 : 2 (M/M)) at catalyst weight 5% of glycerol weight. The results achieved in the use of the type and weight of this catalyst are the conversion of the resulting glycerol 100% with the concentration of triacetin formed at 18.53% and the selectivity of triacetin reaching 22.84%. So, it can be concluded that the use of SiO$_2$-H$_3$PO$_4$ catalyst derived from bamboo leaf biomass waste is able to catalyze and convert glycerol and acetic acid to triacetin.

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