

# The Utilization of Waste Biomass as Heterogeneous Catalyst for Triacetin Production

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## The Utilization of Waste Biomass as Heterogeneous Catalyst for Triacetin Production

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**Abstract:** The process of biodiesel transesterification produces crude glycerol as the main by-product, which accounts for about 10% by weight of biodiesel production. Utilization of crude glycerol can increase added value as well as provide benefits for the survival of biodiesel industri, utilizing crude glycerol as a raw material for making triacetin. The purpose of this study was to produce triacetin from crude glycerol byproduct of the biodiesel industry and to utilize waste biomass as a heterogeneous catalyst, namely orange peel, pineapple leaf and palm peel in the process of esterification reaction. The method started from the preparation of the catalyst material, extraction of the catalyst, purification of crude glycerol and the esterification process. The results of which were then carried out with a GC-MS test to determine the selectivity of triacetin. The highest glycerol conversion using orange peel catalyst was 94.89%, for palm peel 87.07% and pineapple leaf 89.75% with triacetin selectivity of 100% with reactant volume ratio treatment of 1: 9. Triacetin production using SiO<sub>2</sub> catalyst derived from Biomass, especially heterogeneous catalysts derived from orange peel, palm peel and pineapple leaf, can be recommended for use in the esterification process to obtain high glycerol conversion values and triacetin selectivity.

**Keywords** - Crude glycerol, Conversion, GC-MS, Silica, Triacetin.

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### I. INTRODUCTION

Biodiesel is generally produced from the transesterification process of vegetable oils (triglycerides) and methanol with the help of a catalyst. The process of biodiesel transesterification produces glycerol crude oil as the main by-product, which accounts for about 10% by weight of biodiesel production [1]. Biodiesel is a promising renewable energy. When its production increases, so does the production of the main by-product, namely crude [2]. Utilization of crude glycerol can increase added value as well as provide benefits for the survival of biodiesel.

The increase in biodiesel production will be followed by an increase in the amount of glycerol produced as a by-product, therefore an effort is needed to utilize glycerol as a raw material for the manufacture of other chemicals. Tri Acetyl Glycerol or triacetin is a glycerol derivative product which can be used in various industries, such as emulsifiers, plasticizers, additives in the coating and paint industries, and can also be used as an additive in liquid fuels (octane boosters). The use of triacetin as an octane enhancer is considered very promising because it comes from renewable and environmentally friendly raw materials [3]. The reuse of biomass waste will have a significant impact on reducing the waste generated so that the environmental impact is reduced [4].

The triacetin production process generally uses a homogeneous catalyst. The disadvantage is that homogeneous catalysts are difficult to separate from the product. Homogeneous catalysts can be replaced with heterogeneous catalysts which are environmentally friendly because they are made from biomass and are easily separated from the reaction products and can be reused [5]. It provides a shorter reaction time and can provide quality products [6].

Biomass feedstock can be used as a source of new materials in the manufacture of heterogeneous catalysts. In current developments, the natural potential which can be used as raw material for heterogeneous catalysts is agricultural biomass waste such as orange peel, pineapple leaf and palm peel. The catalyst obtained

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from pineapple leaf waste, waste of orange peel and palm peel waste meets commercial silica catalyst standards so that it can be applied to the biodiesel industry [7].

The famous pineapple leaf plant in South Kalimantan itself are from Barito Kuala Regency, and the orange peel used from oranges which grow in South Kalimantan has been confirmed as a national superior variety [8]. The palm skin is from kolang kaling industry in Pingaran Village, Astambul District.

The purpose of this study was to produce triacetin from crude glycerol byproduct of the biodiesel industry and to utilize waste biomass as a heterogeneous catalyst, namely orange peel, pineapple leaf and palm peel in the esterification reaction process.

## II. RESEARCH METHODS

### II.1. Preparation of Catalyst Material Source from Biomass

Biomass waste of orange peel, palm fruit peel and pineapple leaf were selected which were still in good condition. The next stage, each of the pineapple leaf waste, palm fruit peel and orange peel was washed with running water and cut. Waste orange peel, palm fruit peel and pineapple leaf were dried in the sun until the water content was 10%. then crushed and sieved 80 mesh. Then it would be in the furnace to be made into ashes. The furnace process was carried out for 4 hours at a temperature of 800°C. Then the ash from the furnace was ground and sieved to produce uniform ash using an 80 mesh sieve.

### II.2. Making Extraction As Catalyst

The sifted ash was mixed using 3M NaOH in a ratio of 1: 4 (w/v), the reflux method was extracted at 90°C for 12 hours, then the filtrate and residue were separated using filter paper. The results of filtering the filtrate were then added little by little 1M HCl until a white precipitate was formed and reached a neutral pH (6.5-7). In the next step, the precipitate was washed with water and dried at 80°C for 4 hours to form dry silica gel. The serogel was then pulverized to obtain white silica powder and then calcined at 700°C for 3 hours to obtain silica crystals.

### II.3. Glycerol Crude Refining

Crude glycerol as much as 400 grams was added with distilled water with 2:3 (v/v). To remove the color on crude glycerol used activated carbon 5% of the total weight of crude glycerol and aquadest. The sample mixture and activated carbon were stirred for 30 minutes, then left for 24 hours. After 24 hours the sample was filtered using filter paper. The sample was put into evaporation using a rotary evaporator type REV-4L with a temperature of 100°C for 4 hours which had been set at a vacuum pressure and a temperature of 60°C. To increase the purity of glycerol, then the physical and chemical properties were analyzed.

### II.4. Esterification Stage

The purified glycerol was put into a three-necked flask as much as a predetermined volume and heated to a temperature of 115°C. Acetic acid was separately heated from glycerol at a temperature of 115°C, the volume of acetic acid was in accordance with the ratio of the specified volume ratio, the ratio of the volume of glycerol: acetic acid was 1: 9. Glycerol and acetic acid which had reached a temperature of 115°C were mixed into a three-neck-rounded flask and added with silica catalyst as much as 3% by weight of glycerol. The magnetic stirrer was run at 700 rpm, after the inclusion of silica catalyst from pineapple leaf, palm fruit peel and orange peel, the time was recorded as the start of the reaction until the set time was 180 minutes, every 60 minutes a sample was taken for analysis of glycerol conversion using the acid-base titration method. The results from the esterification process were then separated from the catalyst by filtering it using Wathman filter paper and tested using GC-MS Type GCMS QP2010 Plus, Shimadzu.

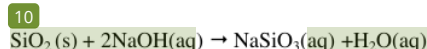
## III. RESULTS AND DISCUSSION

### III.1. Catalyst Extraction Results from Biomass Sources

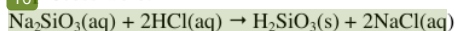
The raw materials for making heterogeneous catalysts from biomass sources were waste of orange peel, pineapple leaf and palm fruit peel. After the materials were carried out in the furnace, orange peel ash, pineapple leaf and palm fruit peel were extracted using 3 M NaOH and titrated with HCL until a precipitate was formed (pH 6.5-7). The yield obtained from orange peel was 0.12%, pineapple peel was 42,% and the catalyst yield of palm fruit peel was 0.03%. This was proven in the extraction process using NaOH able to penetrate the capillaries of the ash sample from the calcination of biomass waste and form silica solubility where sodium

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silicate ( $\text{Na}_2\text{SiO}_3$ ) was formed. [4]. The percentage of  $\text{SiO}_2$  yield of palm fruit peel was smaller than that of orange peel and pineapple leaf. This could be because the 3M NaOH did not penetrate the cell walls of the palm skin, the cell walls between the leaf and the skin could be different. The concentration of the alkaline solution would affect the solubility of the solute. The greater the concentration of the alkaline solution (NaOH) was, the greater the yield produced [9]. The reactions which occurred in the extraction process were:



The resulting filtrate, namely sodium silicate ( $\text{Na}_2\text{SiO}_3$ ), was dripped little by little with HCl until the exchange of  $\text{Na}^+$  ions with  $\text{H}^+$  produced a gel-shaped solid which would separate the silica particles. The reactions which occurred in the catalyst synthesis process were:



#### III.2. Glycerol Crude Refining Results

The raw material for crude glycerol was purified by adding 5% activated carbon and aquades in a ratio of 2:3 (v/v). The purpose of adding aquades was to increase the density of glycerol so that it was hoped that the absorption of impurities with activated carbon would be better. This activated carbon could absorb black pigment dissolved in glycerol [10].

Crude glycerol used for the manufacture of triacetin which had to first be purified to remove impurities being still contained in it in this study purification was carried out using activated carbon. Chemical properties analysis performed on crude glycerol and purified glycerol in this study included analysis of density, water content and ash content.

##### III.2.1. Density

The density of crude glycerol which had not gone through the purification stage looked lower than the density of crude glycerol after purification. This purification process resulted in this purification process producing glycerol with a higher density than crude glycerol which before being purified was  $1.224 \text{ gml}^{-1}$  and after purification the density was obtained  $1.257 \text{ gml}^{-1}$  (Figure 1).

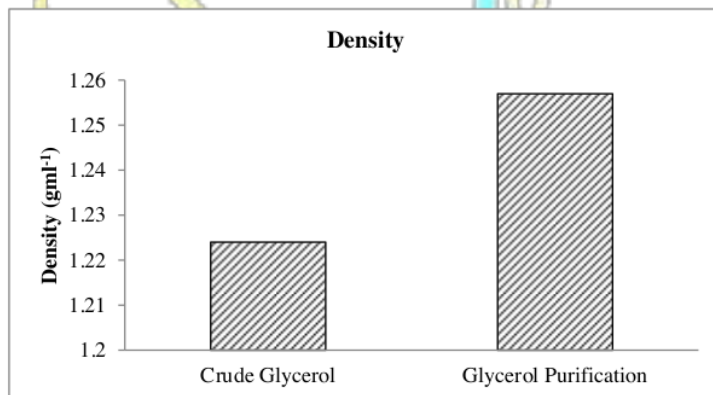


Figure 1. Density comparison of crude glycerol and purified glycerol

The increase was influenced by the loss of water content in crude glycerol [11]. Density was influenced by the water content contained in the product. The higher the water content, the lower the density, and vice versa, the lower the water content, the density would also increase. This statement is in accordance with several previous studies where after purification the density increased as it could be seen in Table 1.

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Table 1. Comparison of crude glycerol and purified glycerol in several studies

Crude glycerol (gml <sup>-1</sup> )	Purified glycerol (gml <sup>-1</sup> )	Reference
1,224	1,257	Research
1,151	1,262	[12]
1,140	1,231	[13]

#### III.2.2. Water content

The water content of crude glycerol before purification was higher because in the process of making biodiesel there was a washing process. The water content of purified glycerol produced a lower water content than crude glycerol because evaporation of water content occurred during the high evaporation process. It was because crude glycerol from biodiesel production plants did not consist only of glycerol but also many other chemicals, such as water, organic, inorganic salts, alcohols, trace mono, di-glycerides and vegetable colors [14]. The purified crude glycerol and glycerol obtained an average water content of 13.52% to 2.33%. The decrease was influenced by the evaporation process during purification. The water content could be seen in Figure 2.

#### III.2.3. Ash Content

The ash content could be seen in Figure 2. Crude glycerol before purification was higher at an average of 4.54%, while the ash content of purified glycerol was an average of 4.35%. Through this adsorption process, the impurities in the glycerol were bound to the outer surface of the activated carbon so that a clear glycerol solution was obtained [15]. Ash content indicated the content of inorganic matter in glycerol such as potassium salt derived from the catalyst used in the transesterification process [13].

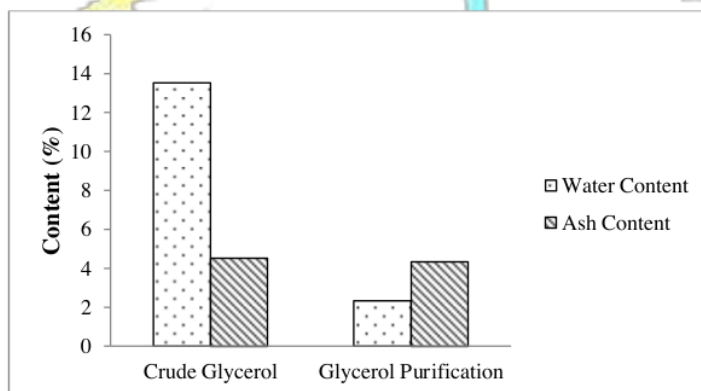


Figure 2. Comparison of chemical properties of crude glycerol and purified glycerol

#### III.2.4. Color

It could be seen from the picture below (Figure 3) that the color of crude glycerol changes from copper red (#C57B4A) to solitude (#E4E8E9). The addition of activated carbon produced the color of the purified glycerol to be whiter and clearer. This activated carbon could absorb black pigment dissolved in crude glycerol [10]. Through this adsorption process, the impurities in the glycerol were bound to the outer surface of the activated carbon so that a clear glycerol solution was obtained [15].

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Figure 3. Color comparison between crude glycerol and purified glycerol using a color palette

#### III.3. Esterification Process Results

SiO<sub>2</sub> catalyst which had been obtained from biomass waste, namely palm peel, pineapple leaf and orange peel then applied for the esterification reaction of glycerol and acetic acid. The reaction conditions in the esterification reaction process were heterogeneous catalyst weight of 3% by weight of glycerol. A reaction time of 3 hours was used, the reaction temperature was 115°C and the stirring speed used was 700 rpm. This was because the stirring speed affected the esterification reaction process [16]. The higher the stirring speed was, the greater the chance of collisions between reactants and reactants thereby increasing the reaction rate [17].

The results of the acid titration carried out showed different glycerol conversion values, from these results were taken three samples of the product producing the highest glycerol conversion from products using catalysts from pineapple leaf, orange peel and palm fruit peel to be analyzed using GC-MS to show the compounds contained in the esterification reaction of glycerol and acetic acid, so that the percentage of triacetate compounds formed in the resulting product could also be known.

In this study, the esterification process was analyzed by the acid-base method to determine the results of the glycerol conversion. In the esterification process for the formation of triacetin, glycerol from purification was used with a ratio of reactant volume of glycerol: acetic acid which was 1:9. Three types of SiO<sub>2</sub> catalysts were used, namely 3% orange peel, 3% pineapple leaf and 3% palm fruit peel.

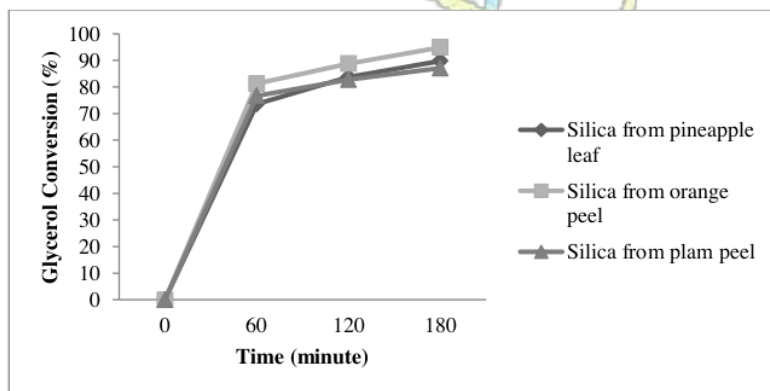


Figure 4. Conversion of glycerol for each change in reaction time

Figure 4 showed that the longer the esterification process lasted, the higher the glycerol conversion value obtained with increasing glycerol conversion over time. Other factors affecting the conversion of glycerol were temperature, reactant ratio. The greater the concentration of reactants was, the greater the number of

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particles, the more densely arranged particles would collide more often so that the possibility of a reaction was greater [18].

Conversion of purified glycerol with reactant ratio was of 1:9 (purified glycerol: acetic acid) 3% orange peel catalyst with 94.98% conversion in 180 minutes. The results of the conversion of glycerol obtained from 3% palm fruit skin was a ratio of 1:9 (purified glycerol: acetic acid) with a conversion of 87.07% in 180 minutes and the conversion of glycerol obtained from pineapple leaf peel 3% ratio of 1:9 (glycerol purification: acetic acid) with a conversion of 89.75% at 180 minutes. It could be seen from the results of esterification that higher conversion was obtained in the orange peel catalyst. This result was in line with the study of mesoporous silica nanoparticles which stated that SiO<sub>2</sub> orange peel extract had a larger surface area [4]. Catalysts which have a larger surface area could produce greater glycerol conversion and greater catalyst activity because they had more contact area with reactant molecules [19]. Based on the analysis using Gas Chromatography-Mass Spectrometry (GC-MS) on products with catalyst treatment of pineapple leaf, palm peel and orange peel were able to produce triacetin with 100% selectivity. From the results of research which had been done obtained high conversion and selectivity. This could be compared with the results of several previous studies as shown in Table 2.

Table 2. Glycerol Conversion and Selectivity of Triacetin from Several Studies

Catalyst	Ratio reactants	Time; temperature	Glycerol Conversion (%)	Triacetin Selectivity (%)	Reference
Zn/Zr-5.5 wt%	1 : 7	240 minute; 115°C	46.41	14.69	[20]
Glycerol-based carbon 2 wt%	1 : 3	180 minute; 110°C	99	88 (combined DAG, TAG)	[21]
HSiW/ZrO <sub>2</sub>	1 : 10	240 minute; 120°C	100	93.6 (combined DAG, TAG)	[22]
CsPWA 7 wt %	1 : 10	120 minute; 85°C	98.2	16	[23]

From Table 2 it could be seen that reaction parameters such as temperature, reactant concentration and amount of catalyst could shift the reaction to product formation [21]. The use of heterogeneous catalysts from the utilization of biomass waste based on the ability of the catalyst to convert glycerol and the ability to obtain selectivity values could be measured against the results of triacetin in the esterification reaction process. Utilization of biomass waste as a catalyst allowed to know the conversion value and selectivity of triacetin produced in the esterification process.

#### IV. CONCLUSION

Utilization of SiO<sub>2</sub> catalyst from waste biomass in the esterification reaction for triacetin production causes the highest glycerol conversion using orange catalyst, namely 94.89%, for palm fruit peel 87.07% and pineapple leaf 89.75% with triacetin selectivity of 100% with volume ratio treatment reactants 1: 9. Production of triacetin using SiO<sub>2</sub> catalyst derived from biomass, especially heterogeneous catalysts derived from orange peel, palm peel and pineapple leaf, can be recommended for use in the esterification process to obtain high glycerol conversion value and triacetin selectivity.

#### V. ACKNOWLEDGMENTS

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