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Esterification of Glycerol with Acetic Acid in Bioadditive Triacetin with Fe₂O₃/Activated Carbon Catalyst

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Abstract. Esterification and transesterification processes for biodiesel production generate glycerol which is possible to be converted into triacetin. It is an attractive bioadditive for increasing octane number of fuel. The production of this bioadditive in a biodiesel plant also increases the revenue as raw material comes from biodiesel process production as by-product. This study examines the effects of catalyst concentration and temperature on triacetin production using glycerol from esterification process and acetic acid at volume ratio of 1:3 as raw materials. An activated charcoal as catalyst is activated with sulfuric acid at concentration of 2% and 3% (w/w). The esterification temperatures are varied at 90 and 100°C and the reaction time is set for 3 hours. The samples are taken frequently at certain interval times of 15, 30, and 60 minutes for chemical analysis using Gas Chromatography Mass Spectrometry. It is observed that using 2% and 3% (w/w) of catalysts at 90°C and 60 minutes reaction time converts 41.037% and 57.441% of glycerol respectively.

Introduction

The energy needs of oil derived from fossil fuels are increasing while inventory is low. The development of alternative fuels from renewable natural resources is one option that is expected to overcome this situation. Alternative fuel that is currently used is biodiesel [1]. Biodiesel can be made from various plants such as oil palm [2], soybean oil and microalgae.

The increase in oil energy needs leads to the increase in fossil fuels production. Glycerol is a by-product of the transesterification process of making biodiesel. If the production of biodiesel increases, the glycerol by-product equivalence will also increase. Glycerol is produced approximately 10% of the total volume of the product [3]. If later biodiesel is produced in larger quantities to replace fossil fuels, unless processed into more useful material, the amount of glycerol industrial waste will cause many problems. For this reason, it is necessary to explore the possibility of processing glycerol waste to become products with more economic value.

When esterified with acetic acid, glycerol will form triacetin, or glycerol triacetin. The use of triacetin is very good for food and non-food purposes. For food, triacetin can be used as a scent in candy, soft drink and chewing gum. On the other hand, in the field of non-food, triacetin can be used as solvents in perfumes, printing inks, solvents on scents, solvents and plastisizers [3, 4]. In addition, triacetin is a promising alternative chemical to be converted into additive fuel [5, 6]. Mixing 10% (w/w) of triacetin for biodiesel can provide better engine performance compared to pure biodiesel [7]. With the potential as an additive to increase the octane value of gasoline, triacetin compounds have the potential to be developed, moreover the raw materials used come from biodiesel waste.

However, so far the use of liquid catalysts requires a difficult separation process. The use of solid catalysts has also been carried out but it still uses expensive synthetic catalysts. Solid catalysts commonly used are aminosulfonates, phosphotungstic, mesoporous silica with sulfonic acid groups, p-toluenesulfone, amberlyst-15 or SAC-13 (Nafion-SiO₂), and SO₄²⁻ / ZrO₂-TiO₂. In this study, activated charcoal from coconut shells is used as a catalyst because of its abundant availability in the wild and not yet used optimally.

In addition, other studies using solid catalysts were also examined using natural Zeolite [8], phosphotungstic, p-toluenesulfone [9], Amberlyst-35 [10] and using ion exchange resins [11]. In this study, the use of glycerol as a by-product of biodiesel into triacetin through the esterification of

glycerol and acetic acid with a mole ratio of 1:3 reaction using activated charcoal from coconut shell catalyst was activated with sulfuric acid with a catalyst mass of 2% and 3% (% w) from the mass of acetic acid with esterification time of 3 hours with variations in temperature of 90°C, and 100°C. This study aims to determine the the proper mass fraction of catalyst and esterification temperature of glycerol conversion.

Methodology

Materials

The material used in this study was 2% Fe catalyst with coconut shell carbon carrier. While in the reaction of making triacetin, glycerol (93% analytical grade, P & G Chemicals) and acetic acid (98% analytical grade, Chang Cun Petrochemical) were used as reactants. Ultraviolet/Visible (UV-Vis) spectrophotometer (Shimadzu Mini 1240) is used to analyze the concentration of triacetin every 15 minutes.

Catalyst Preparation

As much as 2% and 3% (% w) of catalysts and 250 ml H₂SO₄ solutions were included in three neck flasks. Then the mixture was stirred by heating at 90°C for 4 hours. After that the mixture is cooled then filtered to separate between the solid and the filtrate. After separating the solids then neutralizing.

The process of making triacetin bioadditive

Glycerol and acetic acid are prepared with a 1: 3 mole ratio. After that, 2-3%-w (mass of catalyst/mass of acetic acid) were put into the reactor and heated at 90°C. Furthermore, glycerol is added to the reactor containing acetic acid and catalyst with temperature variations of 90°C and 100°C. A total of 2 ml of sample solution was taken every 15 minutes for 3 hours. Furthermore, the concentration of triacetin in solution (C) every time interval was analyzed by Gas Chromatography Mass Spectrometry (GCMS) at the Integrated Laboratory of Pharmacy Faculty of Universitas Ahmad Dahlan.

Results and Discussion

Characterization of Fe₂O₃ / activated carbon catalysts

Coconut shell carbon which has been modified by adding iron salt is then characterized using the Brunauer-Emmett-Teller (BET) analysis. The characterization results are shown in Table 1.

Table 1. Characterization of catalyst

Characteristic	Unit	Value
Specific surface area (S _{BET})	[m ² /gram]	1165
Micropore area (S _{mic})	[m ² /gram]	1076
Percentage of Micropore area (%S _{mic})	[%]	92.36
Total pore volume	[cm ³ /gram]	0.55
Micropore volume (V _{mic})	[cm ³ /gram]	0.42
Percentage of Micropore volume (% V _{mic})	[%]	76.9
Average pore diameter	[nm]	1.89

Table 1 shows that the coconut shell porous carbon that has been modified by the addition of iron salt is micropore carbon (IUPAC classification) with an average diameter of 1.89 nm. While the specific surface area produced by activated carbon as catalyst carrier is 1165 m²/gram with a total pore volume of 0.55 cm³/gram.

The process of making Fe_2O_3 / activated carbon catalyst begins with impregnation of the catalyst precursor, i.e. Fe into the carbon pore surface. In terms of the size of iron ions (194 pm, hydrate), these ions can enter the carbon-based biomass pores. The impregnation process begins by contacting the metal solution on the carbon surface. The next process is drying and calcination for iron oxide formation. The distribution of iron oxides on the surface of carbon is an important aspect in the process of impregnation of iron oxide on the carbon surface. The distribution of metals evenly distributed on the surface of the carbon will maximize the reaction process. The results of the morphological analysis of the catalyst using Scanning Electron Microscopy (SEM) can be seen in Fig. 1.

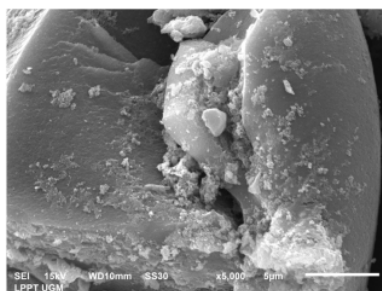


Fig. 1. SEM results for Fe_2O_3 /activated carbon catalysts

Effect of mass of catalyst on glycerol conversion

After the preparation and characterization of the catalyst, the next step of the research is done by reacting glycerol and acetic acid with the help of Fe_2O_3 / activated carbon catalyst. This research was carried out by varying the mass of the catalyst which was equal to 2% and 3% of the mass of acetic acid on glycerol conversion. The results showed that with the same temperature, namely 90°C conversion of glycerol with a catalyst mass of 2% (% w) was better than the one with catalyst mass of 3% (% w). This can be due to the increasing number of catalysts allowing agglomeration during the reaction formation of triacetin. If agglomeration occurs, the contact area of the catalyst with the bond becomes reduced so the possibility of the reaction becomes smaller. This is what causes the conversion of glycerol with the catalyst mass of 3% (%w) is less than the one with catalyst mass of 2% (% w). Meanwhile, the use of the Amberlyst-15 or SAC-13 (Nafion- SiO_2) catalyst was tried by Molero [12] and resulted in a conversion of about 90% to glycerol. Graph of the effect of catalyst mass on glycerol conversion is shown in Fig. 2.

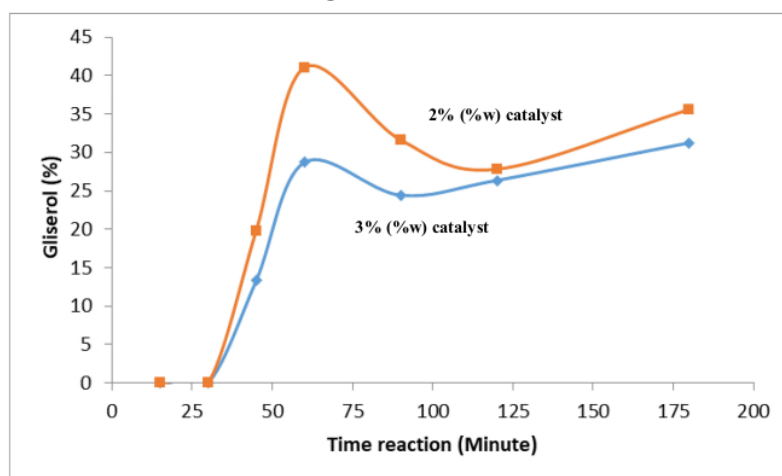


Fig. 2. Effect of catalyst mass on glycerol conversion

Effect of temperature on glycerol conversion

In addition to seeing the effect of variations in the mass of the catalyst, this study also carried out variations in the temperature of the reaction formation of the triacetin. The temperature used is 90°C and 100°C. Based on Figure 3 below, it can be seen that there is a significant increase in conversion at the reaction temperature of 100°C at the reaction time of 180 minutes. However, at the initial reaction time the conversion at 90°C was higher than 100°C. This can be caused by temperature shock in the reaction of the formation of triacetin at the beginning at the reaction temperature of 100°C while at the reaction temperature of 90°C it is relatively more stable resulting in a higher conversion at the beginning of the triacetin formation reaction.

In addition to seeing the effect of variations in the mass of the catalyst, in this study also carried out variations in the temperature of the reaction formation of the triacetin. The temperature used is 90°C and 100°C. Based on Figure 3 below, it can be seen that at the same reaction time that is 180 minutes the conversion at the reaction temperature of 100°C is higher when compared to the temperature of 90°C. This is in accordance with the theory in the Arrhenius equation, namely the higher the temperature the reaction rate increases. So that the conversion of triacetin produced at the reaction temperature of 100°C is higher when compared to the temperature of 90°C.

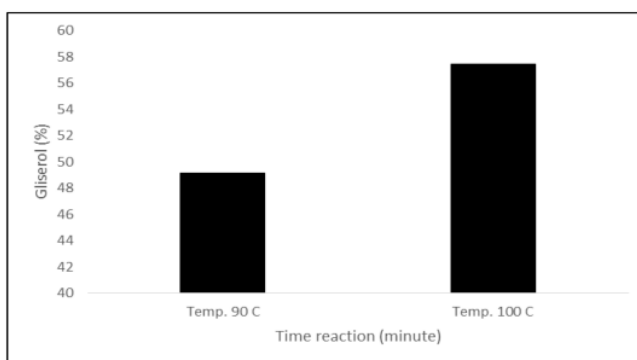


Fig. 3. Effect of temperature of reaction on glycerol conversion

Conclusion

A lower catalysts concentration and at higher reaction temperature performs higher conversion of glycerol. The maximum concentration is attained for 60 minutes reaction time at various catalyst concentrations and reaction temperatures.

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