

# HASIL CEK5\_60181174

*by* 60181174 Teknik Kimia

---

**Submission date:** 09-Feb-2022 11:26AM (UTC+0700)

**Submission ID:** 1758258369

**File name:** Teknik Kimia\_60181174\_Shinta\_Paper 5 - Shinta Amelia.pdf (814.98K)

**Word count:** 2206

**Character count:** 11918

## Esterification of Glycerol with Acetic Acid in Bioadditive Triacetin with $\text{Fe}_2\text{O}_3$ /Activated Carbon Catalyst

Zahrul Mufrodi<sup>1, a</sup> and Shinta Amelia<sup>1, b\*</sup>

<sup>1</sup>Department of Chemical Engineering, Faculty of Industrial Technology, Universitas Ahmad Dahlan, Kragilan, Tamanan, Bantul, Yogyakarta, Indonesia

<sup>a</sup>zahrul.mufrodi@che.uad.ac.id, <sup>b</sup>shinta.amelia@che.uad.ac.id

**Keywords:** Activated Carbon, Biodiesel, Glycerol, Triacetin.

**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. 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-SiO<sub>2</sub>), and SO<sup>4</sup> / ZrO<sub>2</sub>-TiO<sub>2</sub>. 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 H<sub>2</sub>SO<sub>4</sub> 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 Fe<sub>2</sub>O<sub>3</sub> / 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 <sub>BET</sub> )	[m <sup>2</sup> /gram]	1165
Micropore area (S <sub>mic</sub> )	[m <sup>2</sup> /gram]	1076
Percentage of Micropore area (%S <sub>mic</sub> )	[%]	92.36
Total pore volume	[cm <sup>3</sup> /gram]	0.55
Micropore volume (V <sub>mic</sub> )	[cm <sup>3</sup> /gram]	0.42
Percentage of Micropore volume (% V <sub>mic</sub> )	[%]	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 m<sup>2</sup>/gram with a total pore volume of 0.55 cm<sup>3</sup>/gram.

The process of making  $\text{Fe}_2\text{O}_3$  / 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  $\text{Fe}_2\text{O}_3$ /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  $\text{Fe}_2\text{O}_3$  / 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  $90^\circ\text{C}$  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- $\text{SiO}_2$ ) 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.

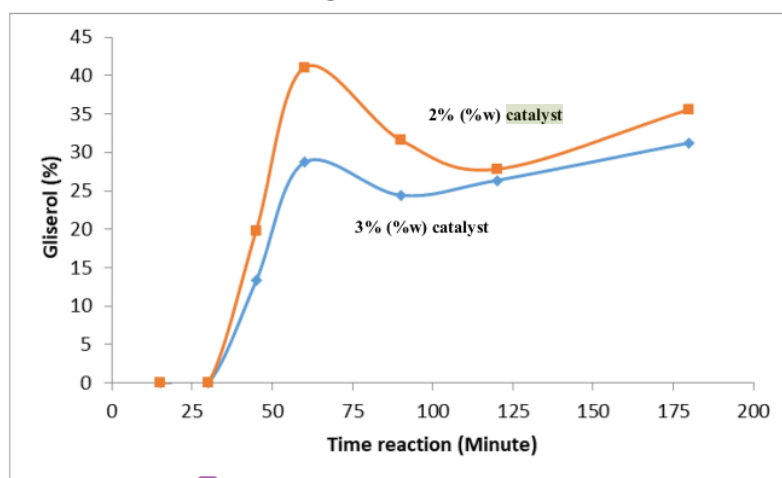


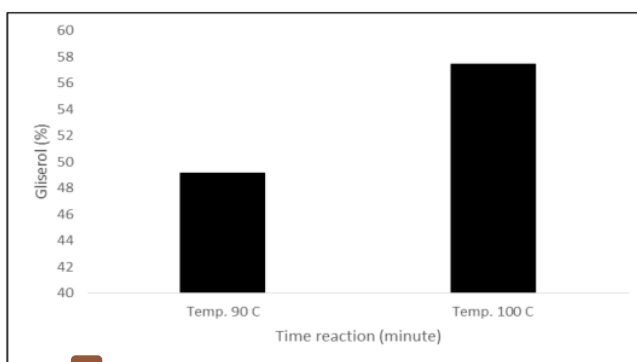
Fig. 2. Effect of catalyst mass on glycerol conversion

9

### 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.



19

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.

### Acknowledgement

The author would like to thank the students who helped this research namely Tita Griya Melyta and Dhenok Widiastuti. And thanks to the Research and Development Institute, Universitas Ahmad Dahlan, Yogyakarta, which has provided an internal research grant to fund this research.

### References

- [1] Mufrodi, Z., Rochmadi, Sutijan, dan Budiman, A., (2013), Continuous Process of Reactive Distillation to Produce Bio-additive Triacetin From Glycerol. *Modern Applied Science* 7(10) 70-78.
- [2] Jontib, N., Prommuak, C., Goto, M., Sasaki, M., and Shotipruk, A., (2011), Effect of Co-solvents on Transesterification of Refined Palm Oil in Supercritical Methanol, *Engineering Journal* 15 (3) 49-58.
- [3] Khayoon, M.s., dan Hameed, B.H., (2011), Acetylation of Glycerol to Biofuel additives Over Sulfated Activated Carbon Catalys. *Elsevier Bioresource Technology Journal*: 102.9225-9235

- 
- [4] Rahmat, N., Abdullah, A.Z., dan Mohamed, A.R., (2010), Recent progress on innovative and potential technologies for glycerol transformation into fuel additives: A critical review. *Renewable and Sustainable Energy Reviews*, 14(3) : pp. 987-100
- [5] Rao, P. V., and Rao, B. V. A., (2011), Effect of adding Triasetin additive with Coconut oil methyl ester (COME) in performance and emission characteristics of DI diesel engine, *Int. J. of Thermal Tech.*, 1, pp. 100-106.
- [6] Ferreira, P., Fonseca, I. M., Ramos, A. M., Vital, J., and Castanheiro, J. E., (2009), Esterification of glycerol with acetic acid over dodecamolybdophosphoric acid engaged in USY Zeolite, *Catal. Commun.*, vol. 10, pp. 481-484.
- [7] Zang, M., and Yuan, X., (2001), Synthesis of Glycerol Triacetate Catalized by Phosphotungstic Acid, *Hecheng Huaxue*, 9(5), 469-472.
- [8] Cahyono, R. B., Mufrodi, Z., Hidayat, A., and Budiman, A., (2016), Acetylation of Glycerol for Triacetin Production using Zr-Natural Zeolite Catalyst, *ARPN Journal of Engineering and Applied Sciences*, Vol. 11, No. 8.
- [9] Liu, Y. Lu, and Gong, S., (2007), Study on synthesis of glycerol triacetate using acidic functional ionic liquid as catalyst, *Hebei Gongye Keji*, 24 (1) 21-23.
- [10] Liao, X., Zhu, Y., Wang, S. G., Chen, H., and Li, Y., (2010), Theoretical elucidation of acetylating glycerol with acetic acid and acetic anhydride, *Appl. Catal. B: Environ.*, vol. 94, pp. 64-70.
- [11] Rodríguez, D. and Gaigneaux, E.M., (2012), Glycerol acetylation catalysed by ion exchange resins, *Catal. Today*, vol. 195, pp. 14- 21.
- [12] Molero, A., Grieken, R. V., Morales, G., and Paniagua, M., (2007), Acidic mesoporous silica for the acetylation of glycerol: Synthesis of bioadditives to petrol fuel, *Energy and Fuels*, vol. 21, pp. 1782-1791.

## ORIGINALITY REPORT

18%

SIMILARITY INDEX

12%

INTERNET SOURCES

17%

PUBLICATIONS

4%

STUDENT PAPERS

## PRIMARY SOURCES

1	<a href="https://ccsenet.org">ccsenet.org</a> Internet Source	3%
2	Shinta Amelia, R. Septiani Muflikhah, Ustinah. "Role of The Concentration of Fe/C Catalysts on Heterogeneous Fenton Degradation Remazol Yellow FG", IOP Conference Series: Materials Science and Engineering, 2021 Publication	2%
3	<a href="http://umpir.ump.edu.my">umpir.ump.edu.my</a> Internet Source	2%
4	Gita Indah Budiarti, Dika Fajariyanto, Okta Hendratno. "Quality Improvement of Recycled Paper with Extracted Xylan from Corncobs", Key Engineering Materials, 2020 Publication	2%
5	S Amelia, M Maryudi, A Aktawan, E Astuti. "Effect of absorbance for gas purification unit in biomass gasification process with downdraft method", IOP Conference Series: Materials Science and Engineering, 2020 Publication	1%

6	<a href="http://journal.unnes.ac.id">journal.unnes.ac.id</a> Internet Source	1 %
7	<a href="http://media.neliti.com">media.neliti.com</a> Internet Source	1 %
8	H Dewajani, A R Hakim, M A I Iswara, T Susanti, D Pratiwi. "The effect of concentration and acid types on the acidification process for improving the glycerol concentration and its application as a bio additive", IOP Conference Series: Materials Science and Engineering, 2020 Publication	1 %
9	María Pilar Pico, Juana María Rosas, Sergio Rodríguez, Aurora Santos, Arturo Romero. "Glycerol etherification over acid ion exchange resins: effect of catalyst concentration and reusability", Journal of Chemical Technology & Biotechnology, 2013 Publication	1 %
10	Anjali Patel, Sukriti Singh. "A green and sustainable approach for esterification of glycerol using 12-tungstophosphoric acid anchored to different supports: Kinetics and effect of support", Fuel, 2014 Publication	1 %
11	<a href="http://www.ijcmas.com">www.ijcmas.com</a> Internet Source	1 %



12	<a href="http://bpi.uad.ac.id">bpi.uad.ac.id</a> Internet Source	1 %
13	<a href="http://engj.org">engj.org</a> Internet Source	1 %
14	Zahrul Mufrodi, Erna Astuti, Mochamad Syamsiro, Sutiman, Suryo Purwono. "Triacetin Synthesis as Bio-Additive from Glycerol Using Homogeneous and Heterogeneous Catalysts", Key Engineering Materials, 2020 Publication	<1 %
15	Bart. "Valorisation of the glycerol by-product from biodiesel production", Biodiesel science and technology, 2010 Publication	<1 %
16	Gabriel Alejandro Bedogni, Cristina Liliana Padró, Nora Beatriz Okulik. "A combined experimental and computational study of the esterification reaction of glycerol with acetic acid", Journal of Molecular Modeling, 2014 Publication	<1 %
17	<a href="http://www.slideshare.net">www.slideshare.net</a> Internet Source	<1 %
18	<a href="http://www.tandfonline.com">www.tandfonline.com</a> Internet Source	<1 %
19	Vishnu P. Yadav, Sunil K. Maity, Debaprasad Shee. "Etherification of Glycerol with Ethanol	<1 %

over Solid Acid Catalysts: Kinetic Study Using Cation Exchange Resin", Indian Chemical Engineer, 2016

Publication

---

20

Yadollah M. Gorji, Hassan S. Ghaziaskar. "Optimization of Solketalacetin Synthesis as a Green Fuel Additive from Ketalization of Monoacetin with Acetone", Industrial & Engineering Chemistry Research, 2016

Publication

---

<1 %

---

Exclude quotes      On

Exclude matches      Off

Exclude bibliography      On