Synthesis of Acetin: Bio-Based Additive for Low Sulfur Petrodiesel

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ABSTRACT

Valorisation of glycerol as a by-product of biodiesel production is the main reason researchers to synthesis acetin. It is known as a cold flow improver and emission CO reducer of petrodiesel. Generally, it can be applied as a supplement to diesel and biodiesel. Another route to synthesis it is trans-esterification of glycerol with ethyl acetate. In this work, the product has been synthesized by simple reflux methods. The conversion of glycerol to the product of acetin was 85.82%. Although the result is not significant, this research revealed that acetin are potentially synthesized from renewable feedstock using a simple method.

Keywords: Bio-Additive, Acetin, Low sulphur diesel.

1. INTRODUCTION

With the growth of the economic sector in Indonesia, consumption of petrodiesel is predicted will increase by 3.19% every year until 2025 [1]. However, petrodiesel has produced hydrocarbon gas emission, CO, NOx, and particulate matter [2], [3]. To overcome these issues, desulphurization treatment has performed. On the other hand, it caused the loss of lubricity properties. The addition of Fatty Acid Methyl Ester (FAME) into it also has caused the number of problems. The abundance of unsaturated fatty acids in FAME was susceptible to oxidized. Since saturated fatty acids content does not have good cold flow properties [4], researchers have been developed additive to eliminate the problems.

Transformation of glycerol as a by-product of biodiesel production into oxygenated compounds have been becoming attention researchers [5]–[10]. This effort has been able to increase the efficiency of biodiesel production and turn glycerol into chemical more valuable. Sandesh et al., [9], [10], Veluturla et al., [11], Reinoso et al., [12] have synthesized acetin using esterification of glycerol with acetate acid. Another route to synthesis acetin through trans-esterification of glycerol with methyl or ethyl acetate [13]–[15]. Nda Umar et al., [16], Casas et al., [17] stated that di- and triacetin as cold improver additive of diesel and biodiesel. Thus, the researchers have used esterification and trans-esterification to transform glycerol to petrodiesel or biodiesel additive. The catalyst was also used varied namely homogenous and heterogeneous catalysts [18].

Based on the efforts of researchers to address the problems above, the methods have used are not simple. It is a necessary special apparatus and reaction condition although using renewable feedstock (acetate acid or ethyl acetate). Hence, this study aims to show how to produce acetin from renewable feedstock by means reflux method. Then, the produced product is evaluated by Thin Layer Chromatography (TLC) and Gas Chromatography-Mass Spectrometry (GCMS) method.

2. METHOD

2.1. Chemicals

Glycerol, ethyl acetate, and sulfuric acid were for analysis grade. Sulfuric acid was purchased from Smart Lab Indonesia while Glycerol and ethyl acetate from Merck.


2.2. Experimental Setup

The glycerol ester or acetin was synthesized by the reflux method only. The amount of glycerol and ethyl acetate was heated at 70°C in the reactor. The molar ratio of glycerol to ethyl acetate was chosen 1:10. After this time was achieved, sulfuric acid as a catalyst was introduced to the reactor. The system was allowed to 74°C for 10 hours. The products consist of the target compound, glycerol, and ethyl acetate unreacted were separated using ethyl acetate 2 x 100 mL, NaHCO3 3 x 20 mL, and NaCl solution 15 mL in separating funnel. This mixture was settled overnight. Two layers will be formed. The organic layer was removed and evaporated.

The product was analysed by TLC before GCMS using chloroform and methanol 5:1 as eluent. The injection port of GCMS was adjusted to 250°C and column flow 1.23 mL/min. From 40°C to 180°C with 5°C/min, the column temperature was kept for 5 minutes. This temperature was increased to 220°C with 10°C/min and maintained for 10 minutes. The conversion of glycerol to the product can be calculated by the equation below,

\[
\% \text{ conversion} = \frac{\text{weight of the product}}{\text{weight of initial glycerol}} \times 100
\]  

(1)

3. RESULT AND DISCUSSION

3.1. Result

Acetin can be synthesized by excess of ethyl acetate to more acetin are formed. The molar ratio of glycerol to ethyl acetate is 1:10. The produced product from this study was monitored by TLC. Two Spots of the product are formed far above glycerol. A spot of glycerol is observed from mixture glycerol-product (see Figure 1). It demonstrated that there is unreacted glycerol from the system. These spots were investigated further using GCMS. Peaks of the obtained product have been identified at 17 and 21 minutes (Figure 2). Reactant was identified earlier than products.

3.2. Discussion

Peaks at 17 and 21 minutes (Figure 2) was investigated further its mass spectra. Monoacetin and triacetin identified based on M+ 134 and 218 respectively. Monoacetin and triacetin fragmented into a molecule with m/z 43 (base peak). The other peaks of monoacetin observed in m/z 103 and 117. While triacetin peaks characteristic appeared in m/z 103 and 145 (Figure 3).

Figure 1 Spots of glycerol (Gly), ethyl acetate (EA), product (P) and mixture of glycerol-product (Gly+P) on TLC plate.

Figure 2 The Chromatogram of obtained product of trans-esterification ethyl acetate with glycerol. (a) glycerol; (b) monoacetin; (c) triacetin.

Figure 3 Mass spectrum of: (a) monoacetin, (b) triacetin.
Acetin has been synthesized by means of trans-esterification of ethyl acetate with glycerol and homogeneous acid catalyst. The basic principle of this reaction is addition-elimination (see Figure 4). Glycerol was added to the ethyl acetate molecule and ethanol released from it. Thus, ethanol produced in the system.

In this study, the condition of the reaction was sufficient to produce acetin. The conversion of glycerol into acetin in this study was 85.82%. This conversion indicated that there is glycerol not yet unreacted. It is in line with the spots on TLC plate. There is a spot of glycerol in a mixture of product-glycerol spots (Figure 1). Why was it happen? In this work, the system’s pressure was not performed reduction. It causes the temperature cannot be raised anymore. Though, the temperature has an important role in accelerating the reaction rate. It is the other researchers’ reason in which reflux system was reduced pressure [14], [19] or under autogenous pressure [20], [21]. Meireles et al., [14] reported that acetin could be synthesized successfully at 90°C for 9 hours. The obtained acetin in this study could be possibly increased by increasing the reaction time, and the system should be oxygen-free [22]. So, the higher system’s temperature can be reached.

![Figure 4 Reaction mechanism of monoacetin formation from glycerol and homogeneous acid-catalyst. Adapted from Meireles et al., [14]](image)

4. CONCLUSION

In this study, the conversion of raw material into the product was 85.82% through a simple reflux method. This conversion can be increased by expelling oxygen and reducing the pressure of the reflux system. This research also revealed that glycerol and ethyl acetate as renewable feedstock can be used to produce bio-based additive for low sulfur petrodiesel.

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REFERENCES

[1] Akhmad and Amir, “Study of fuel oil supply and consumption in Indonesia,” Int. J. Energy Econ. Policy, vol. 8, no. 4, hal. 13–20, 2018.

[2] A. Shirneshan, “HC, CO, CO2 and NOx Emission Evaluation of a Diesel Engine Fueled with Waste Frying Oil Methyl Ester,” Procedia - Soc. Behav. Sci., vol. 75, no. x, hal. 292–297, 2013.

[3] K. Tucki, R. Mruk, O. Orynycz, K. Botwinska, A. Gola, and A. Baczyk, “Toxicity of exhaust fumes (CO, NOx) of the compression-ignition (diesel) engine with the use of simulation,” Sustain., vol. 11, no. 8, hal. 1–15, 2019.

[4] P. Verma, M. P. Sharma, and G. Dwivedi, “Evaluation and enhancement of cold flow properties of palm oil and its biodiesel,” Energy Reports, vol. 2, hal. 8–13, 2016.

[5] P. Mukhopadhyay and R. Chakraborty, Effects of Bioglycerol Based Fuel Additives on Diesel Fuel Property, Engine Performance and Emission Quality: A Review, vol. 79. Elsevier B.V., 2015.

[6] E. E. Oprescu, R. E. Dragomir, E. Radu, A. Radu, S. Velea, I. Bolocan, E. Stepan, P. Rosca, “Performance and emission characteristics of diesel engine powered with diesel-glycerol derivatives blends,” Fuel Process. Technol., vol. 126, hal. 460–468, 2014.

[7] C. Saengarun, A. Petsom, and D. N. Tungasmita, “Etherification of glycerol with propylene or 1-butene for fuel additives,” Sci. World J., vol. 2017, 2017.

[8] F. Frusteri, C. Cannilla, G. Bonura, L. Spadaro, A. Mezzapica, C. Beatrice, G. Di Blasio, C. Guido, “Glycerol ethers production and engine performance with diesel/ethers blend,” Proc. Catal., vol. 56, no. 1–8, hal. 378–383, 2013.

[9] S. Sandesh, P. Manjunathan, A. B. Halgeri, and G. V. Shanbhag, “Glycerol acetins: Fuel additive synthesis by acetylation and esterification of glycerol using cesium phosphotungstate catalyst,” RSC Adv., vol. 5, no. 126, hal. 104354–104362, 2015.

[10] S. Sandesh, P. K. R. Kristachar, P. Manjunathan, A. B. Halgeri, and G. V. Shanbhag, “Synthesis of biodiesel and acetins by transesterification reactions using novel CaSn(OH)6 heterogeneous base

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catalyst,” *Appl. Catal. A Gen.*, vol. 523, hal. 1–11, 2016.

[11] S. Veluturla, A. Narula, S. R. D, and S. P. Shetty, “Kinetic study of synthesis of bio-fuel additives from glycerol using a heteropolyacid,” *Resour. Technol.*, vol. 3, no. 3, hal. 337–341, 2017.

[12] D. M. Reinoso and G. M. Tonetto, “Bioadditives synthesis from selective glycerol esterification over acidic ion exchange resin as catalyst,” *J. Environ. Chem. Eng.*, vol. 6, no. 2, hal. 3399–3407, 2018.

[13] G. Morales, M. Paniagua, J. A. Melero, G. Vicente, and C. Ochoa, “Sulfonic acid-functionalized catalysts for the valorization of glycerol via transesterification with methyl acetate,” *Ind. Eng. Chem. Res.*, vol. 50, no. 10, hal. 5898–5906, 2011.

[14] B. A. Meireles and V. L. P. Pereira, “Synthesis of bio-additives: Transesterification of ethyl acetate with glycerol using homogeneous or heterogeneous acid catalysts,” *J. Braz. Chem. Soc.*, vol. 24, no. 1, hal. 17–25, 2013.

[15] A. Shafiei, H. Rastegari, H. S. Ghaziaiskar, and M. Yalpani, “Glycerol transesterification with ethyl acetate to synthesize acetins using ethyl acetate as reactant and entrainer,” *Biofuel Res. J.*, vol. 4, no. 1, hal. 565–570, 2017.

[16] U. I. Nda-Umar, I. B. Ramli, E. N. Muhammad, N. Azri, U. F. Amadi, and Y. H. T. Yap, “applied sciences Influence of Heterogeneous Catalysts and Reaction Parameters on the Acetylation of Glycerol to Acetin,” vol. 10, 2020.

[17] A. Casas, J. R. Ruiz, M. J. Ramos, and Á. Pérez, “Effects of triacetin on biodiesel quality,” *Energy and Fuels*, vol. 24, no. 8, hal. 4481–4489, 2010.

[18] B. A. Meireles and V. L. P. Pereira, “Synthesis of bio-additives: Transesterification of ethyl acetate with glycerol using homogeneous or heterogeneous acid catalysts,” *J. Braz. Chem. Soc.*, vol. 24, no. 1, hal. 17–25, 2013.

[19] U. Chandrakala, R. B. N. Prasad, and B. L. A. Prabhavathi Devi, “Glycerol valorization as biofuel additives by employing a carbon-based solid acid catalyst derived from glycerol,” *Ind. Eng. Chem. Res.*, vol. 53, no. 42, hal. 16164–16169, 2014.

[20] J. A. Melero, R. van Grieken, G. Morales, and M. Paniagua, “Acidic mesoporous silica for the acetylation of glycerol: Synthesis of bioadditives to petrol fuel,” *Energy and Fuels*, vol. 21, no. 3, hal. 1782–1791, 2007.

[21] J. Sun, X. Tong, L. Yu, and J. Wan, “An efficient and sustainable production of triacetin from the acetylation of glycerol using magnetic solid acid catalysts under mild conditions,” *Catal. Today*, vol. 264, hal. 115–122, 2016.

[22] G. A. Bedogni, M. D. Acevedo, F. Aguzín, N. B. Okulik, and C. L. Padró, “Synthesis of bioadditives of fuels from biodiesel-derived glycerol by esterification with acetic acid on solid catalysts,” *Environ. Technol. (United Kingdom)*, vol. 39, no. 15, hal. 1955–1966, 2018.