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PRODUCTION OF FUEL ADDITIVE (TRIACETIN) FROM GLYCEROL AND ACETIC ACID USING ESTERIFICATION PROCESS WITH SULPHURIC ACID CATALYST

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ABSTRACT

Biodiesel is an alternative energy that can replace fossil fuel diesel. Biodiesel production by transesterification reaction produces glycerol. This study aims to form triacetin by reacting glycerol with acetic acid through an esterification reaction. The total volume of glycerol and acetic acid used in this study was 240 ml. Stirring speed was carried out at 100 rpm. The weight of the catalyst was varied at 5, 7, 9, 11, and 13% by weight of glycerol. The ratio of glycerol to acetic acid was varied at 1:4; 1:6; 1:8; 1:10; and 1:12. The content of triacetin was analyzed using GCMS. The results showed that the best operating conditions were obtained at a mole ratio of 1:12 glycerol and acetic acid, 13% catalyst weight, 80˚C reaction temperature and 60 minutes reaction time. The conversion obtained is 88.5%.

KEYWORDS: glycerol; acetic acid; esterification; triacetin; conversion

1. INTRODUCTION

Biodiesel is a mono alkyl ester derived from long chain fatty acids (triglycerides) found in vegetable oils or animal fats. Biodiesel is one of the renewable energy sources and is used to fuel diesel engines (Ejikeme et al., 2010). The esterification reaction is the formation of fatty acids in the presence of alcohol and a catalyst at a certain temperature to form fatty acid alkyl esters (FAAE) and glycerol. (Buchori et al., 2022). Biodiesel production can be done by transesterification reaction between triglycerides and alcohols such as methanol or ethanol. This reaction proceeds slowly, therefore a catalyst is used in the biodiesel production process. The catalyst used can be a homogeneous or heterogeneous catalyst.

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Glycerol is a by-product of biodiesel production from the transesterification reaction. Glycerol is an inorganic compound and has the chemical formula C3H8O3. Glycerol is a group of alcohol compounds consisting of a three-carbon chain with a hydroxyl group attached to each carbon. This compound is classified as a polar compound due to it has several OH groups. Glycerol has various benefits in many areas of everyday life. The benefits of glycerol in the cosmetic field include being an emollient, which functions as a moisturizer to reduce scaly skin and improve skin appearance. Another benefit is in the health sector, glycerol has a function as a humectant. Glycerol is usually also used as an admixture in the manufacture of polymers that provide plasticizer and stabilizer properties. In the food and beverage industry, glycerol can be used as a solvent, sweetener and preservative (Tan et al., 2013).

Glycerol when esterified with acetic acid will form triacetin. Triacetin is widely used in the cosmetic industry and as a fuel additive to improve fuel performance at low temperatures and is used as an anti-nocking agent for gasoline. Triacetin can be produced from the esterification of glycerol with acetic acid. The esterification reaction is the conversion of free fatty acids to esters. Esterification is done by reacting oil and alcohol. Suitable catalysts are catalysts of strong acid character. Sulfuric acid, sulfonic acid or strong acid cation exchange resins are catalysts commonly used in industry. Short chain alcohol reactants, such as methanol must be added in very large quantities and water as a by-product must be removed from the reaction phase, i.e. the oil phase. Through appropriate combinations of reaction conditions and water removal methods, the complete conversion of fatty acids to methyl esters can be completed within 1 hour (Veljković et al., 2006).

This research will examine the effect of the weight of the sulfuric acid catalyst and the mole ratio between acetic acid and glycerol on the resulting glycerol conversion. The results of this study are expected to show the weight of sulfuric acid catalyst and the best mole ratio of reactants between glycerol and acetic acid which results in the highest conversion of triacetin formation.

2. METHOD

2.1. Materials

The materials used are glycerol, acetic acid, sulfuric acid, NaOH and aquadest. As an approach, technical grade glycerol is used with a purity of 90% and a density of 1.25 gr/ml.

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2.2. Equipment

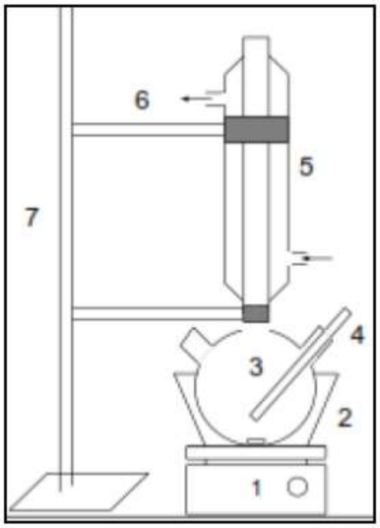

Figure 1. Hydrolysis equipment: (1) magnetic stirrer + heater; (2) water bath; (3) three neck flasks; (4) thermometer; (5) cooler; (6) klem; (7) stative

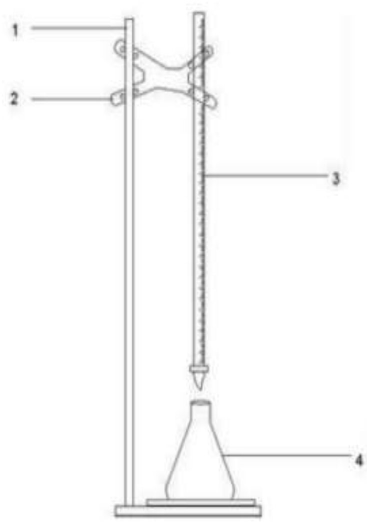

Figure 2. Titration equipment: (1) Stative; (2) klem; (3) burette; (4) erlenmeyer

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Figure 3. GCMS equipment

2.3 Procedure

The research was conducted by heating glycerol and acetic acid in a separate place with a certain temperature. After reaching the desired temperature, then the glycerol and acetic acid are put into a three-neck flask along with sulfuric acid and heated according to the desired temperature. Sampling is every 15 minutes until the 60 minutes. After that, the analysis process is carried out by means of qualitative and quantitative analysis. Qualitative analysis using GCMS to prove the presence of triacetin. While the quantitative analysis used the acid-alkali titration method with 0.45 N NaOH as the titrant to find the glycerol conversion value.

3. RESULTS AND DISCUSSION

3.1. Effect of Sulfuric Acid Catalyst Weight on Glycerol Conversion

Esterification research was carried out by testing the catalyst weight variable on the conversion of glycerol. The results are shown in Figure 4.

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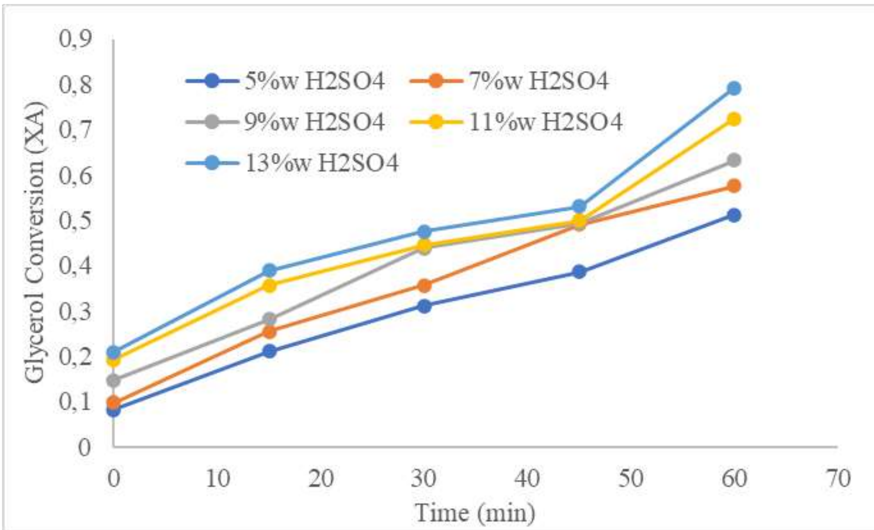

Figure 4. Effect of sulfuric acid catalyst weight and time (minutes) on glycerol conversion (X_A)

Based on Figure 4, the glycerol formed at a catalyst weight of 13% wt has the highest conversion, which is 0.792. In other variables, the resulting conversion is smaller than the catalyst variable 13% wt. At 5% wt catalyst has a conversion of 0.512; 7% wt has a conversion of 0.576; 9% wt has a conversion of 0.632; and 11% wt has a conversion of 0.724.

Based on Figure 4, it can be seen that the catalyst with a weight of 13%w has the highest percentage of glycerol conversion compared to other variables. These results indicate that the reaction that occurs is highly dependent on the amount of catalyst. According to Maquirriain et al. (2021), every increase in catalyst concentration will increase the conversion of the reaction. The weight of the catalyst, or the smallest concentration of catalyst, increases the reaction rate by a small amount. The results showed that the less amount of catalyst used in the esterification process, the less glycerol conversion. This is influenced by the reaction rate described by the Arrhenius equation that the reaction rate constant (k) increases with a decrease in activation energy (Ea). The addition of a catalyst makes it possible to lower the activation energy and increase the number of activated molecules (Mukhtar et al., 2015).

$$k = A.e^{(-Ea/RT)}$$

In the esterification reaction, the need for activation energy for ester formation can be minimized by the use of sulfuric acid catalyst. Figure 5 explains that in the Arrhenius equation, the catalyst does not change the initial energy of the reactants or products so that it does not change the equilibrium, but only affects the activation energy.

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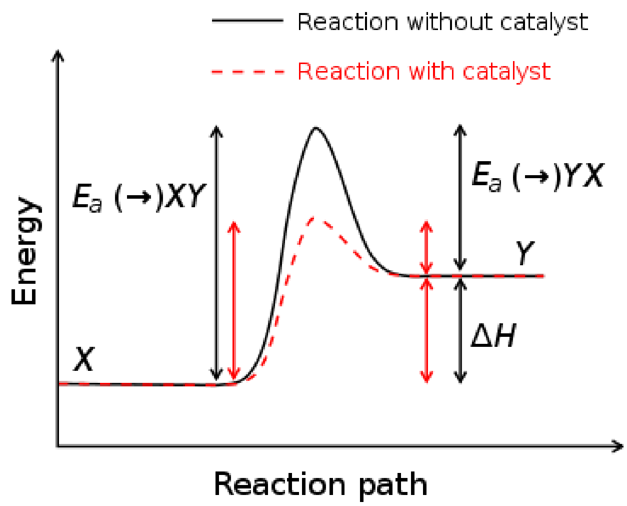

Figure 5. The relationship between activation energy and reaction direction

Activation energy is the energy that must be passed by a reaction for the reaction to take place. To speed up a chemical reaction, a catalyst is needed that can lower the activation energy. The catalyst is the factor that most influences the reaction rate conditions that occur in the reaction (Marchetti et al., 2007). The result of the research shows that it is in accordance with the existing theory, where the greater the catalyst concentration, the higher the glycerol conversion.

Farag et al. (2010) have conducted research on the esterification process using oil reactants (with a high acid content) and alcohol. The catalyst used is sulfuric acid. The research variable was sulfuric acid concentration, namely 3M, 4M, 5M, 6M, and 9M, respectively. The results showed that the largest conversion of oil to form esters and water was at a concentration of 9M with a final conversion of 95%. Meanwhile, at the concentration of 3M, it got 73% conversion, 4M with 78% final conversion, 5M with 82% final conversion, and 6M with 87.5% final conversion. The results of the research by Farag et al. (2010) are in accordance with the results of this study, where the greater the amount of catalyst used, the faster the reaction rate.

3.2. Effect of Molar Ratio of Acetic Acid to Glycerol-on-Glycerol Conversion

In this study, the variation of the molar ratio between acetic acid and glycerol was 1:04; 1:06; 1:08; 1:10; 1:12. The results of the study are presented in Figure 6.

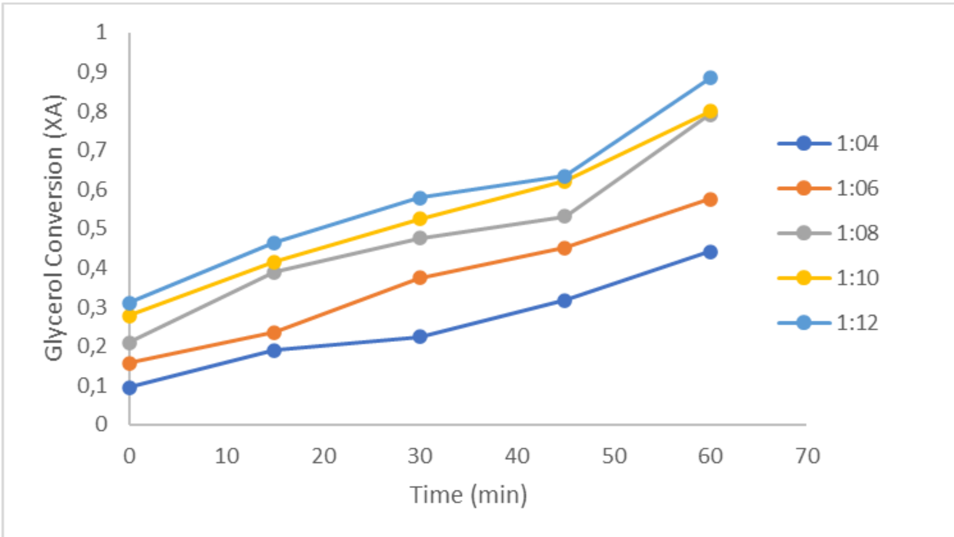

Figure 6. Effect of acetic acid molar ratio on glycerol conversion (XA) and time (min) on the esterification process

Based on Figure 6, it can be seen that the glycerol conversion tends to increase. At a 1:4 molar ratio, the conversion starts at 0.095 and ends at 0.442. Variable 1:6 gets a conversion of 0.575; variable 1:8 with a conversion of 0.799; the variable 1:10 obtains a conversion of 0.8; and the variable 1:12 attains a conversion of 0.885.

If it is seen from the experimental results that along with the increase in the molar ratio between acetic acid and glycerol, the conversion of glycerol that occurs also increases. This is due to the nature of the esterification reaction, where if one of the reactants is excess, the reaction will move towards the product, so that the conversion value will be even greater (Xie et al., 2021). The esterification reaction requires a minimum of one mole of acetic acid per one mole of glycerol (He et al, 2014). The results of the research by Nayak and Vyas (2019) showed that the product formed was difficult to separate into 2 phases and this could be avoided by increasing the molar ratio between glycerol and acetic acid. The increased conversion of glycerol at high molar ratios was due to the decrease in viscosity and the combined concentration of the sulfuric acid (H2SO4) catalyst. However, a high molar ratio has a negative effect, namely the possibility of formation of by-products. If the molar ratio exceeds the limit, it will reduce the conversion due to the limited concentration of glycerol and the possibility of a reverse reaction (Nayak et al., 2021). Research conducted by Setyaningsih et al. (2017) using glycerol and acetic acid with a Lewatit catalyst. The variables used in this study were the molar ratio of acetic acid to glycerol, namely 1:6; 1:7 and 1:8. The product of the reaction between glycerol and acetic acid is triacetin and water. The results of the experiment obtained the largest glycerol conversion at a ratio of 1:8, which was 73.16%. While the 1:6

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molar ratio find a conversion of 66.91% and 1:7 with a conversion of 73.36%. The results of this study are in accordance with the experimental results in this study.

3.3. GCMS Analysis Results *(Gas Chromatography Mass Spectrometry)*

The results of the analysis of the product composition of the esterification reaction of glycerol and acetic acid using Gas Chromatography Mass Spectrometry at a molar ratio of 1:12 with a sulfuric acid catalyst weight of 13%w are presented in Table 1 and Figure 7.

Table 1. Result of product composition analysis using GCMS

Peak	SI	Retention Time	Area	Area%	Height	Name
1	85	1,384	254954040	13,53	32174593	Hydrazine, 1,2-dimethyl- (CAS)
2	97	1,624	693779	0,04	629485	Butanoic acid (CAS)
3	76	6,149	1614720	0,09	753450	1,2-Ethanediol, diacetate (CAS)
4	88	6,955	229981749	12,20	14261275	1,2,3-Propanetriol, diacetate
5	78	7,01	49723125	2,64	15340812	1,2,3-Propanetriol, diacetate
6	70	7,09	93287220	4,95	16844749	1,2,3-Propanetriol, diacetate
7	74	7,155	53135240	2,82	17975838	2,6-D2-MS-INOSITOL
8	75	7,203	35738114	1,90	19193229	Nadolol tri-TMS derivative
9	91	7,898	492864020	26,15	41993170	1,2,3-Propanetriol. Triacetate (CAS)
10	96	8,179	11558939	0,61	2813231	n-Decanoic acid
11	96	9,961	476992262	25,31	31096891	Dodecanoic acid (CAS)
12	92	13,205	77803524	4,13	2384080	9-Octadecenoic acid (Z)- (CAS)
13	92	14,258	43705867	2,32	1760276	9-Octadecenoic acid (Z)- (CAS)
14	74	15,207	16269973	0,86	2502387	Myristin, 2,3-diaceto-1- (CAS)
15	72	15,945	3986261	0,21	904327	2-HYDROXY-3-(TETRADECANOYLOXY)PROPYL MYRISTATE#
16	89	16,234	4760544	0,25	1344199	Myristin, 2,3-diaceto-1- (CAS)
17	86	17,266	18210962	0,97	2056810	Hexadecanoic acid, 2,3-bis(acetyloxy)propyl ester (CAS)
18	75	18,07	5287485	0,28	553583	9-Octadecenoic acid (Z)-, 2,3-bis(acetyloxy)propyl ester (CAS)
19	82	18,406	11494255	0,61	1560109	9-Octadecenoic acid (Z)-, 2-(acetyloxy)-1-[(acetyloxy)methyl]ethyl ester (CAS)
20	78	18,72	2723756	0,14	525356	Stigmast-5-en-3-ol, oleate
			1884785835	100	206667850	

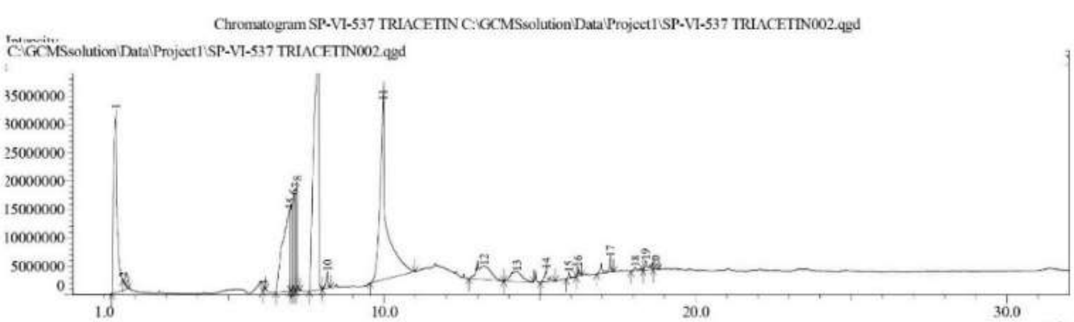

Figure 7. GCMS analysis results

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Figure 7 shows that biodiesel obtained from glycerol esterification contains 2 types of methyl esters, the largest being triacetin and lauric acid. Based on the composition, it shows that glycerol contains high amounts of unsaturated fatty acids. These fatty acids are generally found in glycerol which has the potential to be used as triacetin. Figure 7 also does not identify the presence of free fatty acids, so the esterification process in glycerol can minimize the free fatty acid content (Al-Sakkari et al., 2020).

The desired compound, triacetin, has a Similarity Index (SI) of 91 out of 100 with a retention time of 7,898 minutes. In addition, through the chromatogram data, it can be seen that the composition of triacetin in GCMS is 26.15%.

4. CONCLUSION

This study shows that the heavier the sulfuric acid catalyst used, the greater the glycerol conversion that occurs. This is because the presence of a catalyst will increase the number of reacting molecules and reduce the activation energy. In the mole ratio of acetic acid and glycerol, the higher the molar ratio, the greater the glycerol conversion. This is due to the nature of the esterification reaction which is reversible (back and forth). GCMS analysis results prove that the esterification reaction produces triacetin compounds and is the largest compound compared to other compounds.

REFFERENCE

Al-Sakkari, E. G., Abdeldayem, O. M., El-Sheltawy, S. T., Abadir, M. F., Soliman, A., Rene, E. R., Ismail, I. 2020. Esterification of high FFA content waste cooking oil through different techniques including the utilization of cement kiln dust as a heterogeneous catalyst: A comparative study. *Fuel*, 279(118519) : 1-11.

Buchori, L., Widayat, W., Hadiyanto, H., Satriadi, H., Chasanah, N., Kurniawan, M.R. 2022. Modification of magnetic nanoparticle lipase catalyst with impregnation of Activated Carbon Oxide (ACO) in biodiesel production from PFAD (Palm Fatty Acid Distillate). *Bioresource Technology Reports*, 19(101137): 1-7.

Ejikeme, P.M., Anyaogu, I.D., Ejikeme, C.L., Nwafor, N.P., Egbuonu, C.A.C., Ukogu, K., Ibemesi, J.A. 2010. Catalysis in biodiesel production by transesterification processes-an insight. *E-Journal of Chemistry*, 7(4): 1120-1132.

Farag, H.A., El-Maghraby, A., Taha, N.A. 2011. Optimization of factors affecting esterification of mixed oil with high percentage of free fatty acid. *Fuel Processing Technology*, 92(3): 507-510.

He, B., Deng, T., Li, J., Yan, F., Wang, H., Huang, Y., Peng, C. 2014. An innovative auto-catalytic esterification for the production of phytosterol esters: Experiment and kinetics. *RSC Advances*, 4: 64319–64327.

Maquirriain, M.A., Querini, C.A., Pisarello, M.L. 2021. Glycerine esterification with free fatty acids: Homogeneous catalysis. *Chemical Engineering Research and Design*, 171: 86–99.

Marchetti, J.M., Errazu, A.F. 2008. Esterification of free fatty acids using sulfuric acid as catalyst in the presence of triglycerides. *Biomass and Bioenergy*, 32(9): 892–895.

Mukhtar, A., Shafiq, U., Khan, A.F., Qadir, H.A., Qizilbash, M. 2015. Estimation of parameters of Arrhenius equation for ethyl acetate saponification reaction. *Research Journal of Chemical Sciences*.5(11) : 46-50.

Nayak, M.G., Vyas, A.P. 2019. Optimization of microwave-assisted biodiesel production from Papaya oil using response surface methodology. *Renewable Energy*, 138: 18–28.

Nayak, S.N., Nayak, M.G., Bhasin, C.P. 2020. Microwave-assisted transesterification of kusum oil: Parametric, kinetic and thermodynamic studies. *Asian Journal of Chemistry*, 32(11) : 2893–2903.

Setyaningsih, L., Siddiq, F., Pramezy, A. 2018. Esterification of glycerol with acetic acid over Lewatit catalyst, *MATEC Web of Conferences*, 154(01028): 1-4.

Tan, H.W., Aziz, A.R.A., Aroua, M.K. 2013. Glycerol production and its applications raw material: A review. *Renewable and Sustainable Energy*. 27(3): 118-127.

Veljković, V.B., Lakićević, S.H., Stamenković, O.S., Todorović, Z.B., Lazić, M.L. 2006. Biodiesel production from tobacco (Nicotiana tabacum L.) seed oil with a high content of free fatty acids. *Fuel*, 85(17-18): 2671-2675.

Xie, L., Zhang, T., Karrar, E., Xie, D., Zheng, L., Jin, J., Wang, X., Jin, Q. 2021. *Highly efficient synthesis of 4,4-dimethylsterol oleates using acyl chloride method through esterification*. *Food Chemistry*, 364(130140): 1-8.