



## Preparation and Characterization of Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Catalyst for Acetylation of Glycerol in a Fixed Bed Reactor Applied as an Octane Booster for Commercial Fuels

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### Abstract

Glycerol is a by-product of biodiesel production with the amount of 10% of the total biodiesel product. To increase the utility and economic value of glycerol, it can be processed into several derivative products. One of the glycerol derivative products is currently being developed through the acetylation process. Glycerol acetylation product has been investigated as a component that can be used to increase the octane number of commercial fuels, otherwise known as bio-additives or octane boosters. This study aims to convert glycerol from the by-product of biodiesel production through the acetylation process using a modified solid catalyst Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in a fixed bed reactor. The focus of this research is to study the effect of reactant flow rate and the mole ratio of glycerol to acetic acid on glycerol conversion. The variations used were flow rates of feed from 40, 60, 80 and 100 ml/minute, and the mole ratio of glycerol to acetic acid was 1:3, 1:5, 1:7, and 1:9. The experiment was carried out in several stages, namely: preparation and modification of the catalyst, the acetylation process and product application into commercial fuels. The acetylation reaction took place at a temperature of 100 °C and the mass of the catalyst used was 5% of the mass of glycerol. The results showed that the highest conversion of 74.24% was achieved under operating conditions with a reactant flow rate of 40 ml/min and glycerol to acetic acid mole ratio of 1:9. The utilization of acetylation products as bio-additives is carried out by adding reaction products to Pertamina fuel. The highest increase in octane number of Pertamina fuel at the addition of 8% volume of acetylation product from the initial octane number of 93 increased to 102 (increased by 10%).

### INTRODUCTION

Green energy policies have encouraged increased production of biodiesel as a biofuel to reduce the use of fossil fuels. In the biodiesel production process, the by-product in the form of glycerol is approximately 10% by weight (Meireles & Pereira 2013). Thus the utilization of excessive crude glycerol is becoming so necessary to convert glycerol into more valuable products and environmentally friendly (Silva et al., 2010). One of the promising routes to the conversion of glycerol is by esterification process into glycerol derivatives such as glycerol ester, acetyl glycerol and glycerol

acetal (Bagheri et al., 2015; Sun et al., 2016). The glycerol derivatives obtained from the acetylation reaction produce acetyl compounds (mono-, di- and tri-ester glycerol). which is widely used as a commercial fuel additive (Gryglewicz 1999; Meireles and Pereira 2013). Triacetin can be used as an additive to reduce the knocking properties of gasoline (Mou et al., 2021). Apart from that, acetyl compounds are also widely used in the food, cosmetic and pharmaceutical industries (Gholami et al., 2014; Mufrodi et al., 2018; Quispe et al., 2013). In previous studies, the glycerol acetylation process was mostly carried out using a homogeneous acid catalyst such as sulfuric acid

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(Meireles & Pereira 2013; Mufrodi et al., 2014). Reactions involving strong acids such as  $H_2SO_4$  will make the separation and purification of triacetin products more difficult (Kale et al., 2015). Furthermore, acidic solutions can damage the environment. Another type of catalyst that is often used in this reaction is a heterogeneous catalyst with a solid form. Solid catalysts have the advantage that they are easy to separate from the product, and can be used many times through catalyst regeneration (Ferreira et al., 2009).

There have been several attempts at acetylation of glycerol using solid acid catalysts in forms such as Amberlyst, niobatic acid, heteropoly acid, zeolite and others (Banu et al., 2020; Manurung et al., 2020; Sun et al., 2016). From previous studies it was explained that heterogeneous catalysts resulted in higher glycerol conversion and selectivity to the desired product. On the other hand, solid acid catalysts such as zeolite, amberlyst and heteropoly acid show good thermal stability and regeneration ability as well as specific surface area convenient for esterification reactions (Dewajani et al., 2019; Mufrodi et al., 2013; Okoye and Hameed 2016). In this study, the acid-solid catalyst properties were improved by modifying the catalyst using metal oxides so as to produce a catalyst that is more stable, easy to regenerate and has more active sites.

The  $Ni/\gamma-Al_2O_3$  catalyst is a metal supported catalyst consisting of metal and a support. The active side of the metal can use alkali metals and transition metals. The metal is in the form of a precursor salt such as Ni from the  $Ni(NO_3)_2 \cdot 6H_2O$  salt. Nickel is included in group VIII B which is often used as a heterogeneous acidic catalyst. The choice of Ni metal as a catalyst is because the bonds formed between Ni metal and the reactants are relatively weak, so that the reaction products are easily released from the surface of the catalyst (Savitri et al., 2016). The advantages of  $\gamma-Al_2O_3$  as a catalyst carrier are its large surface area and well-defined porosity (Murdijanto et al., 2010). The  $\gamma-Al_2O_3$  buffer has a large surface area, namely 150-300  $m^2/g$ , large pore size and volume, and its performance tends to be stable at high temperatures (Silva et al., 2010).

The reactor selection is one of the important considerations in research. Previous studies still used a simple batch reactor (Dewajani et al., 2019; Kale et al., 2015; Silva et al., 2010; Zhou et al., 2012) or a combination column

(Mufrodi et al., 2013). In a batch reactor there is no mass entering and leaving during the reaction, thus the concentration at all points is always the same or homogeneous. However, achieving high conversion takes a long time. This research was carried out using a fixed bed reactor to overcome the shortage of batch reactors. Fixed bed reactors have a fluid flow profile close to plug flow reactors which can result in higher conversion. This study aims to determine the effect of reactant flow rate and mole ratio of glycerol: acetic acid to glycerol conversion in the fixed bed reactor and to determine the performance of reaction products as commercial fuel bio-additives to increase the octane number of fuels.

## MATERIALS AND METHODS

### Materials

The raw material used in this research was crude glycerol with 87% purity obtained from the by-product of the Biodiesel Plant in Gresik, East Java, acetic acid glacial,  $\gamma-Al_2O_3$  catalyst, 5% (w/w) of  $Ni(NO_3)_2 \cdot 6H_2O$  solution, 0.1 N NaOH solution, and distilled water.

### Methods

This research was carried out in the following stages: 1. Preparation and activation of catalysts, 2. Modification of catalysts, 3. Characterization of catalysts, 4. Acetylation reactions, 5. Application of reaction products as additives in commercial fuels.

#### *Preparation and Activation Catalyst*

The  $\gamma-Al_2O_3$  catalyst was washed using distilled water to remove impurities. The washed  $\gamma-Al_2O_3$  catalyst was filtered and dried at 110 °C for 3 hours and followed by calcination at temperature of 500 °C for 4 hours.

#### *Catalyst Modification*

The catalyst modification was carried out using the wet impregnation method by adding of 5% (w/w) solution of  $Ni(NO_3)_2 \cdot 6H_2O$  solution into calcined  $\gamma-Al_2O_3$  catalyst followed by refluxing the mixture at 85°C for 3 hours. The impregnated catalyst was dried at 110 °C and calcined using a furnace at 500°C for 4 h then oxidized and reduced at 400 °C for 2 hours.

### Characterization of Catalysts

The modified Ni/ $\gamma$ - $\text{Al}_2\text{O}_3$  catalyst was characterized using BET, XRD and XRF analysis. BET analysis aimed to determine the surface area of the materials, pores distribution, and gas adsorption on the materials. XRD analysis was used to observe the characteristic of a solid's crystal structure. XRF analysis was used to determine the chemical composition and the concentration of catalyst constituent that had been through impregnation process.

### Acetylation Reaction

The glycerol acetylation process was taking place in a fixed bed reactor with the configuration shown in Figure 1. Glycerol with a volume of 100 ml and acetic acid with a mole ratio of 3:1, 5:1, 7:1 and 9:1 according to the specified mole ratio variable is entered into the feed tank. The Ni/ $\gamma$ - $\text{Al}_2\text{O}_3$  catalyst as much as 5% by weight of glycerol was introduced into the pipe reactor. The glycerol and acetic acid in the feed tank are heated to a temperature of 100 °C. The reactor containing the catalyst was heated to a constant temperature at 100 °C and then the reactant flow rate was adjusted according to the variables of 40, 60, 80 and 100 ml/min. Furthermore, the glycerol - acetic acid solution was flowed into the reactor containing the catalyst. The product stream leaving the reactor was recorded as the first pass and samples were taken for analysis of glycerol conversion using the 0.1N NaOH titration method. The titration results show the remaining unreacted of acetic acid in the

product, then through the stoichiometric calculation of the reaction, the glycerol conversion will be obtained. The esterification reaction was continued by flowing the first product into the reactor under the same reaction conditions and analyzing the conversion of glycerol into the second product. Prior to testing the physical properties, the acetylated product was purified by distillation at a temperature of 120°C to evaporate acetic acid.

### Application of Reaction Products as Additives in Commercial Fuels

The performance of the acetylation reaction product as a fuel additive was carried out by adding the product to commercial fuel to determine its effect on the octane number. Determination of the octane number of commercial fuels is carried out using a portable octane number device. Commercial gasoline fuels namely premium, pertalite and pertamax are mixed with acetylated products with variations of 0-8% (v/v). The sample was stirred until homogeneous and the octane number tool port is dipped into the sample until a constant number is read on the screen showing the octane number of the fuel being tested.

## RESULTS AND DISCUSSION

### Analysis of Catalyst Using BET-BJH

The initial and modified (Ni/ $\gamma$ - $\text{Al}_2\text{O}_3$ ) catalysts were tested using the BET (Brunaur,

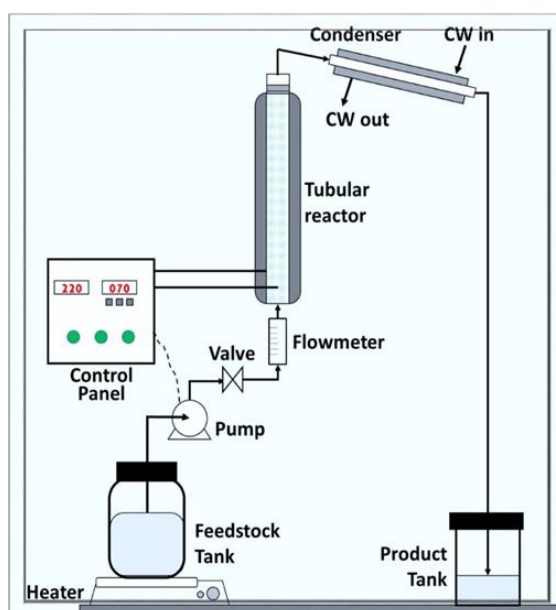


Figure 1. Schematic of apparatus fixed bed reactor for acetylation glycerol.

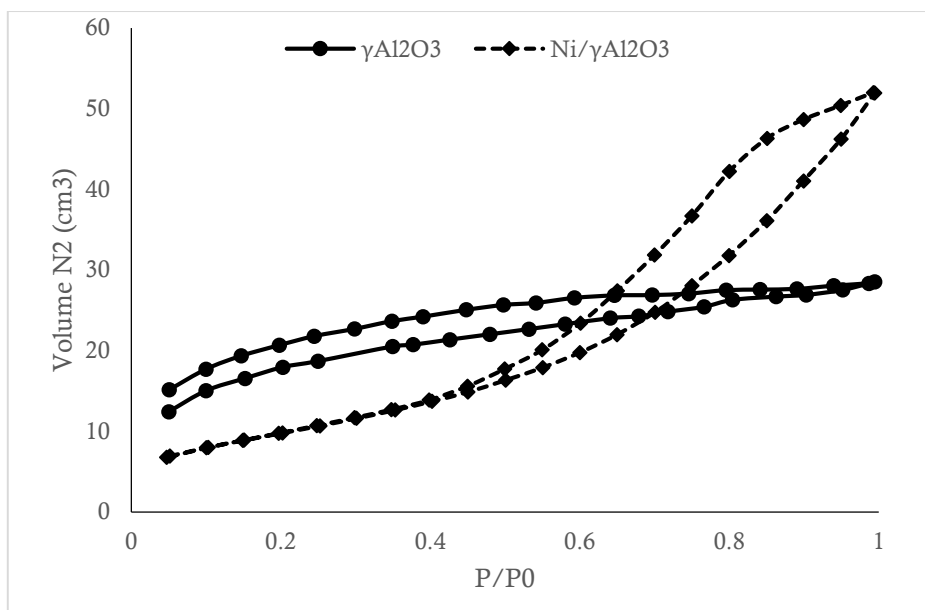


Figure 2. Isotherm curve of the adsorption-desorption of N<sub>2</sub>.

Emmett and Teller) method. Metal impregnation into the catalyst aims to increase the activity of the catalyst. The characteristics of catalysts can be predicted through isotherm curves of adsorption-desorption reaction which shows the interaction of the N<sub>2</sub> that was adsorbed into the catalyst pores during analysis. The pore characteristics can be estimated through the form of adsorption-desorption isotherm and hysteresis.

The adsorption-desorption isotherm curve is shown in Figure 2, depicting the interaction of N<sub>2</sub> gas that is absorbed into the pores of the catalyst during the analysis process. The pore distribution curve using the BJH (Barret-Joyner-Halenda) method as shown in Figure 3 was used to determine the average pore diameter, pore size distribution, and total pore volume. Table 1 shows the difference between surface area, pore distribution, and mean pore diameter for the catalyst before and after impregnation. In general, the surface area, pore distribution, and average diameter of the catalyst will decrease after the deposition of Ni metal.

The pore distribution of catalyst can be identified as shown in Figure 3 and Table 1. Mesopore catalysts with a pore diameter of 2 – 50 nm appeared dominant within the catalyst before and after the impregnation process. The size and the size distribution of catalyst pores were considered as important parameters in catalyst characteristics to ensure that the pore size of a catalyst is bigger than the size of the reactant particle because reactant can be bound to the active site of the catalyst.

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Table 1. Characteristics of Catalyst from BET Analysis.

Catalyst Characteristics	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Ni/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	
Surface area (m <sup>2</sup> /gr)	131.215	32.679	
Pore size distribution:			
Micropores volume (cm <sup>3</sup> /gr)	0.0000	0.00%	0.0000 0.00%
Mesopores volume (cm <sup>3</sup> /gr)	0.0360	90.95%	0.3809 88.24%
Macropores volume (cm <sup>3</sup> /gr)	0.0036	9.05%	0.0508 11.76%
Total pore volume (cm <sup>3</sup> /gr)	0.0395	0.4317	
Average pore diameter (nm)	24.0652	23.8722	

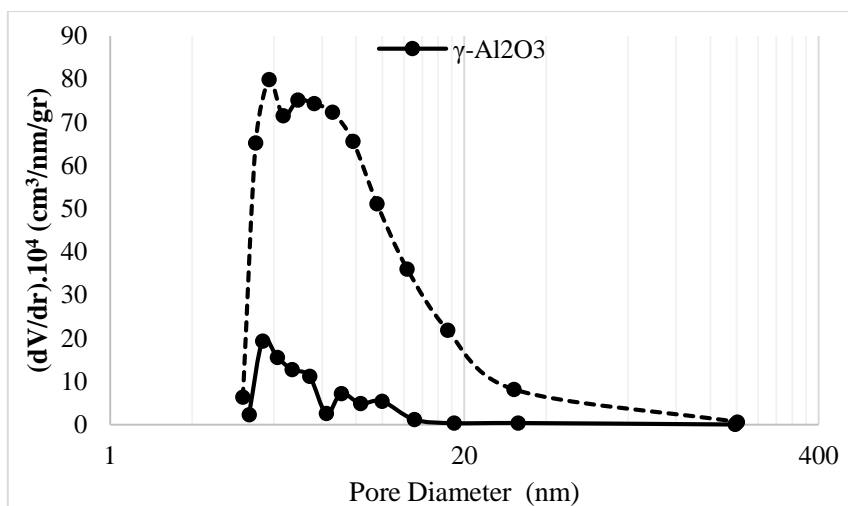


Figure 3. Pore size distribution of catalyst.

analysis showed that the surface area of  $\gamma\text{-Al}_2\text{O}_3$  catalyst was  $131.215 \text{ m}^2/\text{gram}$  slightly different from several previous studies, i.e  $131.046 \text{ m}^2/\text{gram}$  (Savitri et al., 2016). The surface area of the catalyst after impregnation of 7% Nickel is  $32.679 \text{ m}^2/\text{gram}$  which means that it shrinks by 75.09% of the area before impregnation. During the impregnation, calcination, reduction, and oxidation processes occur which are expected to open the pores of the catalyst to be larger. However, the metal deposition process also covered the entire surface of the catalyst, so that the decrease in pore diameter resulted in a decrease in the surface area of the catalyst.

**Analysis of Catalyst Using XRD and XRF**

XRD analysis was used to determine the characterization of the crystal structure of solid materials. The crystallinity of material can be seen through the diffractogram pattern. Table 2 showed that  $2\theta$  value of  $\gamma\text{-Al}_2\text{O}_3$  catalyst in the reference (Okamoto, 1998) and the samples were similar. The  $\gamma\text{-Al}_2\text{O}_3$  catalyst analysis which was done by Murdijanto et al. (2010) produced a peak  $2\theta$  value in  $32^\circ$ ;  $37.6^\circ$ ;  $45.48^\circ$ ; and  $68.81^\circ$ . In the catalyst

Table 2. The diffractogram patterns of  $\gamma\text{-Al}_2\text{O}_3$  and  $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$ .

$\gamma\text{-Al}_2\text{O}_3$ reference (Murdijanto et al., 2010)	$\gamma\text{-Al}_2\text{O}_3$	$\text{Ni}/\gamma\text{-Al}_2\text{O}_3$
$2\theta$	$2\theta$	$2\theta$
$37^\circ$	$14.45^\circ$	$16.29^\circ$
$45.86^\circ$	$26.65^\circ$	$37.31^\circ$
$60.02^\circ$	$28.25^\circ$	$44.63^\circ$
$67.03^\circ$	$38.36^\circ$	$45.54^\circ$
	$49.29^\circ$	$66.83^\circ$
	$67.05^\circ$	

production process by (Alviany et al. 2018) the XRD result showed a diffractogram pattern with  $2\theta$  peak value in  $39.59^\circ$ ;  $46.14^\circ$  and  $66.81^\circ$ . The shift in the  $2\theta$  value was influenced by the differences in the analyzed catalyst due to the composition of the catalyst.

**Analysis of Catalyst Using XRF**

XRF analysis was used to determine the chemical composition and concentration of the catalyst. The composition of the  $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$  catalyst after the impregnation process is presented in Table 3. From Table 3, it can be seen that Al or Alumina is the main constituent of the  $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$  catalyst, while Nickel is brought into the catalyst through the impregnation process. The presence of nickel composition indicated that the impregnation process was properly done.

Table 3. Composition of  $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$  catalyst.

Component	Composition (%)
Al	50.2
Ni	46.02
Y	2.4
P	0.71
Ca	0.47
Fe	0.17
Cr	0.078

**Conversion of Glycerol**

The conversion of glycerol in the variation of the flow rate and the mole ratio of the reactants is shown in Figure 4. From Figure 4 it can be seen that the higher the mole ratio of glycerol to acetic acid results in an increase in the conversion of glycerol. The glycerol esterification reaction is a reversible reaction, therefore if there is an excess in

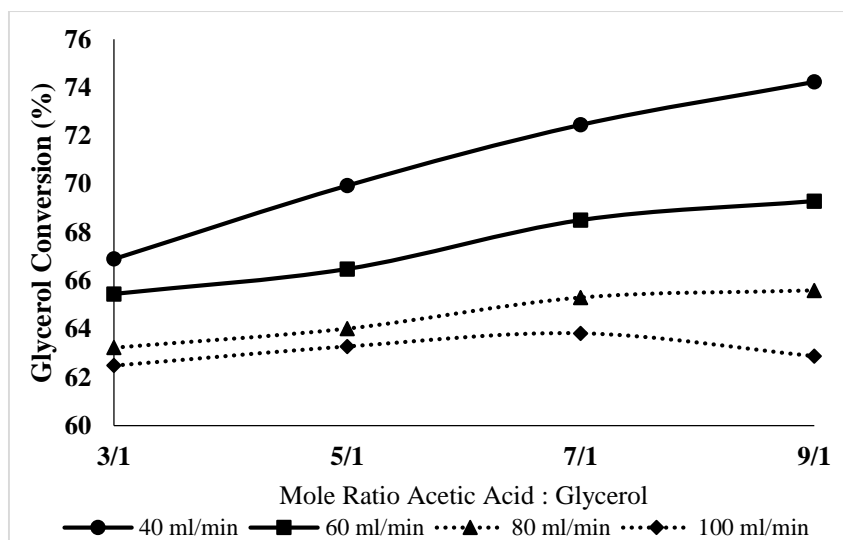


Figure 4. The conversion of glycerol in the variation of the flow rate and the mole ratio reactants.

one reactant, the reaction equilibrium will proceed towards the product, and the molecular collision process will increase resulting in a larger conversion. The result showed that glycerol concentration in the reactant is the main factor that significantly affected the reaction equilibrium because acetic acid is an excess reactant. The conversions of glycerol on various variables are shown in Figure 4. The highest conversion of 72.4% was obtained at the mole ratio of glycerol to acetic acid 1:9 at a flow rate of 40 ml/min. While the lowest conversion value of 62.66% was produced by a 1:3 ratio at a flow rate of 100 ml/min.

Previous research done by Silva et al. (2010) using a mole ratio of 1:9 using Fly Ash as catalyst resulted in 53.33% glycerol conversion, Zhou et al. (2012) using Amberlyst-15 catalyst resulted in 94.90% glycerol conversion, (Reinoso & Boldrini 2020) using Natural Zeolite catalyst resulted in a conversion of 94.3% while Gonçalves et al. (2008) using a 1:3 mole ratio of silica alumina catalyst resulted in a conversion of 71%.

The reactant flow rate affected the glycerol conversion in the acetylation reaction using a fixed bed reactor. When the flow rate was increased from 40 ml/min to 100 ml/min, the glycerol conversion value decreased due to a shorter contact time. The higher the reactant flow rate causes the conversion to increase at each mole ratio. However, at a mole ratio of 1:9 with a flow rate of 100 ml/min, it showed a decrease in glycerol conversion. In this variable, the volume of acetic acid was the highest so it took a longer reaction time to convert the reactants into products. This caused a decrease in

the contact time between the reactant and the catalyst so that only a small part of the reactants was converted into products. Previous studies have observed reaction times in batch systems with one reaction process. Research conducted by Banu et al. (2020) using Y-zeolite catalyst for 150 minutes resulted in a conversion of 98%. Research that has been done by Mou et al. (2021) using silica alumina with a reaction time of 150 minutes resulted in a conversion of 71%. Sun et al. (2016) carried out an acetylation reaction using Amberlyst-35 catalyst with a reaction time of 3 hours resulted in a conversion of 99%, and (Meiros & Pereira 2013) using a ZrO<sub>2</sub> catalyst with a reaction time of 3 hours resulted in a conversion of 86.32%.

#### Application of Reaction Products as Additives in Commercial Fuels

The performance of the product resulting from the acetylation reaction to increase the octane number was carried out by mixing it into Pertamina commercial fuel with concentrations of 2, 4, 6 and 8% (v/v). According to Quispe et al. (2013), the addition of triacetin to diesel fuel can increase the viscosity and cetane number and reduce the cloud point. Meanwhile, if added to gasoline, it can increase the octane number.

The Octane Number of the fuel was measured using a portable octane number device and it was known that the initial octane number of Pertamina was 93. Pertamina fuel has the best quality compared to Premium and Peralite fuels, because its components are lead-free and contain several hydrocarbon constituents that have performance

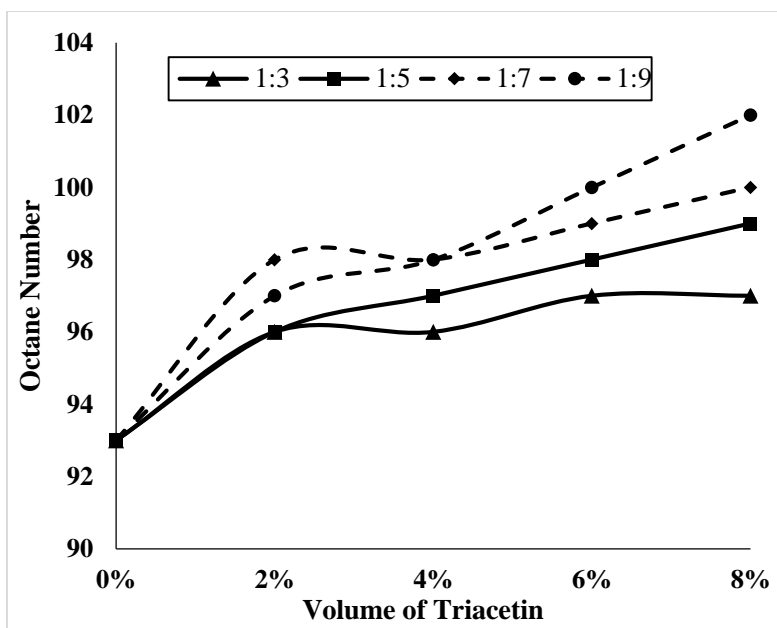


Figure 5. The octane number of Pertamina on the addition of reaction products in various mole ratio of reactants.

capabilities to produce higher Octane Number. The effect of the addition of the acetylation reaction on increasing the octane number of Pertamina fuel is presented in Figure 5. From this figure, it can be seen that at the same mole ratio between reactants, the higher the percentage volume of the added acetylation product results in an increase in the Octane Number.

The highest results were obtained at the mole ratio of glycerol to acetic acid 1:9 with the addition of 8 vol% bio-additives where the octane number of Pertamina reached 102 or an increase of 10% from its initial value. From a previous study conducted by Dewajani et al. (2019) on acetylation reactions using a Ni/Zelite catalyst in a batch reactor, the addition of the product into commercial fuel resulted in an increase in the octane number of a maximum of 8.5%. In this research, the acetylation products are added to commercial fuels in volumes ranging from 2 to 8% of fuels. The addition of more than 8% is not recommended because it forms a mixture with two layers that cannot be mixed homogeneously so that it will result in a decrease in fuel performance.

## CONCLUSION

Conversion of glycerol acetylation reaction in fixed bed reactor is influenced by reactant flow rate and mole ratio of reactant glycerol to acetic acid. From the research, it was concluded that the lower the reactant flow rate, the higher the reaction

conversion. The highest glycerol conversion of 74.24% was obtained at a flow rate of 40 ml/minute. The mole ratio of the reactants affects the conversion of glycerol, whereas increasing the mole ratio of the reactants leads to a higher conversion of glycerol. The highest glycerol conversion of 74.24% was obtained at a mole ratio of 1:9. The application of acetylated products as bio-additives is applied by adding glycerol acetylation products using a Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst can be used as bio-additives to increase the octane number of Pertamina-type commercial fuels. The highest of Octane Number is produced by adding 8% product from 1:9 mole ratio variable, flow rate 40 ml/min from the initial Octane Number 93 to 102.

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## REFERENCES

- Alviany, R., Marbun, M. P., Kurniawansyah, F., Roesyadi, A. 2018. Proses Produksi Katalis  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Menggunakan Metode

- Impregnasi. *Jurnal Teknik Kimia*. 12(2): 64–68.
- Bagheri, S., Julkapli, N. M., Yehye, W. A. 2015. Catalytic Conversion of Biodiesel Derived Raw Glycerol to Value Added Products. *Renewable and Sustainable Energy Reviews*. 41. 113–127.
- Banu, I., Bumbac, G., Bombos, D., Velea, S., Gălan, A. M., Bozga, G. 2020. Glycerol Acetylation With Acetic Acid Over Purolite CT-275. Product Yields and Process Kinetics. *Renewable Energy*. 148: 548–557.
- Dewajani, H., Zamrud, W., Saroso, H., Paramarta, S., Mulya, W. 2019. Conversion of Crude Glycerol from by-Product Biodiesel Into Bio-additive of Fuel through Acetylation Reaction based on Modified Zeolite Catalyst. *Alchemy*. 7(2): 46.
- Ferreira, P., Fonseca, I. M., Ramos, A. M., Vital, J., Castanheiro, J. E. 2009. Glycerol Acetylation Over Dodecatungstophosphoric Acid Immobilized Into a Silica Matrix as Catalyst. *Applied Catalysis B: Environmental*. 91(1–2): 416–422.
- Gholami, Z., Abdullah, A. Z., Lee, K. T. 2014. Dealing With the Surplus of Glycerol Production From Biodiesel Industry Through Catalytic Upgrading to Polyglycerols and Other Value-added Products. *Renewable and Sustainable Energy Reviews*. 39: 327–341.
- Gonçalves, V. L. C., Pinto, B. P., Silva, J. C., Mota, C. J. A. 2008. Acetylation of Glycerol Catalyzed By Different Solid Acids. *Catalysis Today*. 133–135(1–4): 673–677.
- Gryglewicz, S. 1999. Rapeseed Oil Methyl Esters Preparation Using Heterogeneous Catalysts. *Bioresource Technology*. 70(3): 249–253.
- Kale, S., Umbarkar, S. B., Dongare, M. K., Eckelt, R., Armbruster, U., Martin, A. 2015. Selective Formation of Triacetin by Glycerol Acetylation Using Acidic Ion-exchange Resins as Catalyst and Toluene as an Entrainer. *Applied Catalysis A: General*. 490: 10–16.
- Manurung, R., Dedi Anggreawan, M., Gery Siregar, A. 2020. Triacetin Production Using SiO<sub>2</sub>-H<sub>3</sub>PO<sub>4</sub> Catalysts Derived From Bamboo Leaf Biomass Waste For Esterification Reactions of Glycerol and Acetic Acid. *IOP Conference Series: Materials Science and Engineering*. 801(1): 01252.
- Meireles, B. A., Pereira, V. L. P. 2013. Synthesis of Bio-additives: Transesterification of Ethyl Acetate With Glycerol Using Homogeneous or Heterogeneous Acid Catalysts. *Journal of the Brazilian Chemical Society*. 24(1): 17–25.
- Mou, R., Wang, X., Wang, Z., Zhang, D., Yin, Z., Lv, Y., Wei, Z. 2021. Synthesis of Fuel Bioadditive By Esterification of Glycerol With Acetic Acid Over Hydrophobic Polymer-based Solid Acid. *Fuel*. 302(March): 121175.
- Murdijanto, D.N., Setiabudi, A., Eko, R. 2010. Sintesis, Karakterisasi Dan Uji Aktivitas Katalis Ni/Al<sub>2</sub>O<sub>3</sub> Pada Reaksi Hydrocracking Minyak Nabati. *Jurnal Sains dan Teknologi Kimia*. 1.
- Mufrodi, Z., Budiman, A. Purwono, S. 2018. Operation Conditions In Synthesize of Bioadditive From Glycerol as By-product Biodiesel: A Review. *Energy Procedia*. 145: 434–439.
- Mufrodi, Z., Rochmadi, R., Sutijan, S., Budiman, A. 2013. Continuous Process of Reactive Distillation to Produce Bio-additive Triacetin From Glycerol. *Modern Applied Science*. 7(10): 70–78.
- Mufrodi, Z., Rochmadi, Sutijan, Budiman, A. 2014. Synthesis Acetylation of Glycerol Using Batch Reactor and Continuous Reactive Distillation Column. *Engineering Journal*. 18(2): 29–39.
- Okamoto, Y. 1998. A Study on the Preparation of Supported Metal Oxide Catalysts Using JRC-reference Catalysts. I. Preparation of a Molybdena–Alumina Catalyst. Part 1. Surface Area of Alumina. *Applied Catalysis A: General*. 170(2): 315–328.
- Okoye, P. U., Hameed, B. H. (2016). Review on Recent Progress in Catalytic Carboxylation and Acetylation of Glycerol As a Byproduct of Biodiesel Production. *Renewable and Sustainable Energy Reviews*. 53: 558–574.
- Quispe, C. A. G., Coronado, C. J. R., Carvalho, J. A. 2013. Glycerol: Production, Consumption, Prices, Characterization



- and New Trends in Combustion. Renewable and Sustainable Energy Reviews. 27: 475–493.
- Reinoso, D. M., Boldrini, D. E. 2020. Kinetic Study of Fuel Bio-additive Synthesis From Glycerol Esterification With Acetic Acid Over Acid Polymeric Resin as Catalyst. Fuel. 264(December 2019): 116879.
- Savitri, S., Nugraha, A. S., Aziz, I. 2016. Pembuatan Katalis Asam (Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) dan Katalis Basa (Mg/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) untuk Aplikasi Pembuatan Biodiesel dari Bahan Baku Minyak Jelantah. Jurnal Kimia VALENSI. 2(1): 1–10.
- Silva, L. N., Gonçalves, V. L. C., Mota, C. J. A. 2010. Catalytic Acetylation of Glycerol With Acetic Anhydride. Catalysis Communications. 11(12): 1036–1039.
- Sun, J., Tong, X., Yu, L., Wan, J. 2016. An Efficient and Sustainable Production of Triacetin From the Acetylation of Glycerol Using Magnetic Solid Acid Catalysts Under Mild Conditions. Catalysis Today. 264: 115–122.
- Zhou, L., Nguyen, T. H., Adesina, A. A. 2012. The Acetylation of Glycerol Over Amberlyst-15: Kinetic and Product Distribution. Fuel Processing Technology. 104: 310–318.