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Research Article

Lampung Natural Zeolite Dopped with of $ZnO-TiO_2$ Metal Oxide as Catalyst for Biodiesel Production

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Abstract

Research has been carried out on making biodiesel from palm oil using natural zeolite catalysts impregnated with metal oxides such as zinc oxide and titanium oxide. This research aims to produce biodiesel using natural zeolite and $ZnO-TiO_2/NZ$ catalysts. The catalysts were analyzed using X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF), Scanning Electron Microscope (SEM), and Brunauer-Emmet-Teller (BET). The catalyst was tested in the transesterification reaction to produce biodiesel. The oil and methanol mole ratio varied from 1:15, 1:18, and 1:20. In addition, the biodiesel product was analyzed using Gas Chromatography-Mass Spectroscopy (GC-MS). The results showed the optimum condition for converting triglycerides to 1:18 variation of oil:methanol mole ratio was 60.53% using a $ZnO-TiO_2/NZ$ catalyst. The $ZnO-TiO_2/NZ$ catalyst is very promising for use as a catalyst for converting palm oils into biodiesel.

Keywords: Natural zeolite; $ZnO-TiO_2/NZ$ catalyst; transesterification reaction; biodiesel

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1. Introduction

Fossil fuels are natural resources used in everyday life as energy sources. Most energy used today comes from petroleum, natural gas, and coal. In addition, population growth and increasing economic development cause higher energy needs. Therefore, rising energy consumption will result in the depletion of these fuel reserves, which are non-renewable natural resources. As a result, the stock of crude oil derived from fossils tends to decrease while demand increases yearly. Besides that, the continuous use of fossil fuels will negatively impact the environment, especially air pollution due to CO_2 emissions from burning fossil fuels [1].

Therefore, looking for alternative fuels, especially renewable materials, is necessary. One alternative renewable source is biodiesel. Biodiesel is a fuel derived from biomass of vegetable oil or animal fat, and its manufacture is relatively fast [2]. The advantages of biodiesel are lower viscosity than vegetable oils or animal fats; it can be used as an environmentally friendly

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engine fuel because it has a high cetane number, does not contain sulfur, and produces little CO [3]. Catalysts commonly used in the transesterification reaction process for biodiesel consist of two production catalysts: homogeneous and heterogeneous. The homogeneous catalysts commonly used consist of acid and base catalysts, namely H_2SO_4 and HCl and KOH and NaOH, respectively [4–6]. While heterogeneous catalysts such as natural zeolite, HZSM-5, alumina, silica, hydrotalcite, etc. Natural zeolite was used as a heterogeneous catalyst because it has a different facade and does not mix with the reactants and products. The advantage of this catalyst is that it is easier to compare with homogeneous, non-toxic, and easy-to-separate catalysts [1]. Natural zeolite also has a porous material with acidity. The use of zeolite as a support provides acidity for the catalyst. In the previous study by Kardawati *et al.* [7], natural zeolite has various advantages, including high ion exchange capacity, relatively low price, ease of obtain because of its abundant supply, the function as a molecular sieve, the fact that its structure is stable even in acidic environments, can neutralize acidic solutions through the exchange of H^+ ions in the solution and the fact that its structure is porous so that it can provide a high surface area.

In a previous study, silica was synthesized with ZnO metal as a composite for the transesterification reaction of used cooking oil and methanol to produce biodiesel. The optimum results obtained in this study were using a ZnO catalyst with a yield of 81.57% [8]. Another study reported that using alumina assisted with ZnO as the active site to produce biodiesel from kesambi (*Schleichera Oleosa L.*) oil (SOO). The optimum result obtained in this study was a yield of 92.29% with a mole ratio of oil to methanol of 1:12 [9]. Liu *et al.* [10] reported a reaction between soybean oil and methanol. The amount of catalyst used is 0.5% - 4% by weight of soybean oil. The optimal result obtained is the amount of catalyst 4% with the percentage of methyl ester reaching 98%. Taufiq *et al.* [11] conducted a study that reacted palm oil with methanol using an Al_2O_3 catalyst. The difference in the number of catalysts in this study was 1 to 5%, with an additional range of 1%. The optimum result obtained in this study is to use the amount of 3% catalyst, which produces a 99% methyl ester yield. Palm oil was initially chosen due to its easy availability. Previous studies by Zhu *et al.* [12] and Shi *et al.* [13] found that vegetable oils have comparable compositions, each with different compounds. However, this similarity can be the basis for the performance of the catalyst we tested on palm oil, for example. This similarity comes from the dominant C=O group as well as the length of the carbon chain.

This study investigates the effect of natural zeolite catalysts with impregnated metal oxides zinc oxide and titanium oxide on biodiesel production. The advantages of using bimetallic oxide in the previous study show that bimetallic oxide is known to have high thermal stability. This is based on X-ray diffraction (XRD), which shows that the crystalline phase present in the mixed oxide catalyst can be maintained and the pure oxide even up to a temperature of 900 ^{o}C. In addition, the bimetallic oxide system significantly improves heterogeneous catalytic stability [14]. Generally, ZnO/TiO_2 oxides are used as photocatalysts, environmentally friendly degradation agents, and adsorbents. The presence of metal oxides such as ZnO and TiO_2 on natural zeolite supports catalysts in biodiesel production by transesterification, which is still rare and needs further exploration. The properties of the catalysts were characterized by X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF), Scanning Electron Microscope (SEM), and Brunauer-Emmet-Teller (BET). The product was analyzed using Gas Chromatography-Mass Spectroscopy (GC-MS).

2. Materials and Methods

2.1 Materials

In this study, natural zeolite was obtained from Lampung. Palm oil to produce biodiesel was from a local market in Lampung. Zinc oxide powder (purity 99.9%), titanium oxide powder (purity 99.9%), and methanol (purity 99.9%) were purchased from Merck.

2.2 Preparation of Catalyst

The catalyst preparation method was followed by Al Muttaqii *et al.* [15,16]. First, the natural zeolite was dried in the oven to remove the water in the pores at 110 °C for 8 h. Then, 150 g of natural zeolite was chemically activated using 1 M HCl solution and stirred for 1 h at a temperature of 60 °C. The mixture was washed with distilled water to pH = 5 and dried in the oven for 12 h at a temperature of 110 °C. After that, the 30 g solid of natural zeolite was dissolved in a 0.5 M NaOH solution. The mixture was washed with distilled water to pH neutral and dried in the oven for 12 h at a temperature of 110 °C. Metal oxide loading on natural zeolite was 10% with a metal ratio of 2:1. First, 1.26 g of zinc oxide solution and 0.42 g of titanium oxide solution were dissolved into 13.5 g of natural zeolite. Then, it was stirred for 15 min and aged for 12 h. Then, it was dried for 8 h at 110 °C. Lastly, the solid catalyst was calcined using a furnace for 7 h at 500 °C. The catalyst was obtained and ready for use in the transesterification process.

2.3 Characterization of Catalyst

X-ray diffraction (XRD) was performed using XRD PANalytical X'Pert 3 Powder. The metal contents in catalyst were analyzed by XRF portable analyzer type Olympus Innov X DS-6000-C. The specific surface area, total pore volume, and pore size of catalysts were measured using BET type Micromeritics TriStar II 3020. The morphology of catalyst was analyzed by The Thermo Scientific™ Quattro ESEM.

2.4 Production of Biodiesel

This research produced biodiesel from a transesterification reaction between palm oil and methanol. First, 3 g of catalyst and 50 mL of palm oil were added into three neck-rounded flasks mounted on a reflux device. The oil and methanol mole ratio varied from 1:15, 1:18, and 1:20. Then, it was mixed for 5 h at a temperature of 65 ^oC. The product was collected and analyzed using Gas Chromatography-Mass Spectroscopy (GC-MS, Merk Agilent, Type 19091S-433:9392873 HP-5MS 5% Phenyl Methyl Silox) to determine the chemical composition of biodiesel.

3. Results and Discussion

3.1 Characterizations of Catalyst

The XRD diffractograms of natural zeolite and ZnO-TiO_2/NZ catalyst are represented in Figure 1. Based on the results of XRD analysis, natural zeolite has a characteristic diffraction peak at 2θ of 11.12, 22:35, 25.98, and 28.03°. These results indicate that natural zeolite Lampung is included in the clinoptilolite type according to JCPDS No. 25-1349 [17]. After impregnating zinc oxide and titanium oxide, the ZnO-TiO_2/natural zeolite catalyst showed almost the same diffractogram as natural zeolite. The TiO_2 peak is seen at 2θ of 25.08, 37.64, 47.69, and 53.76, indicating the anatase phase (JCPDS TiO_2 No. 21-1272). The peak of ZnO was seen at 2θ of 31.64, 34.18, 47.69, 56.40, 62.62, and 67.55 (JCPDS ZnO No. 00–36-1451) [18,19]. The diffraction peaks of ZnO and TiO_2 metal oxides become sharper in proportion to the amount of metal oxides contained in the natural zeolite. The higher and sharper the metal oxide diffraction peak indicates, the greater the crystallinity of the catalyst [20]. In addition, the conformity of the diffractogram pattern showed that adding metal oxides ZnO and TiO_2 did not change the crystal structure of clinoptilolite natural zeolite but instead indicated the presence of metal oxides on the surface of natural zeolite [21,22].

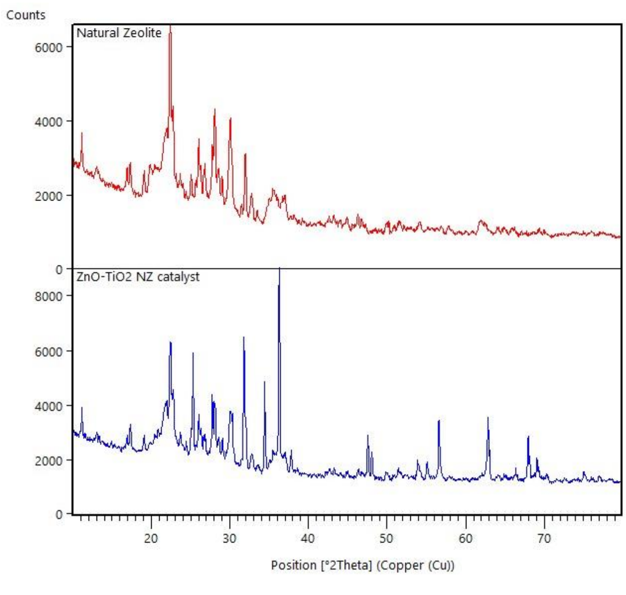


Figure 1. Diffractogram of Lampung natural zeolite and ZnO-TiO_2/NZ catalyst.

Figure 2 shows the SEM of Lampung natural zeolite and ZnO-TiO_2/NZ catalyst loading 10% with a magnification of 5000x. Figure 2(a) shows the surface morphology of natural zeolite in the form of lumps, which tend to agglomerate and not have a regular size. After impregnation, the morphology of the ZnO-TiO_2/NZ catalyst was in the form of lumps with small flakes or white dots on the surface. The flakes or white dots indicated that the metal oxide was successfully dispersed in

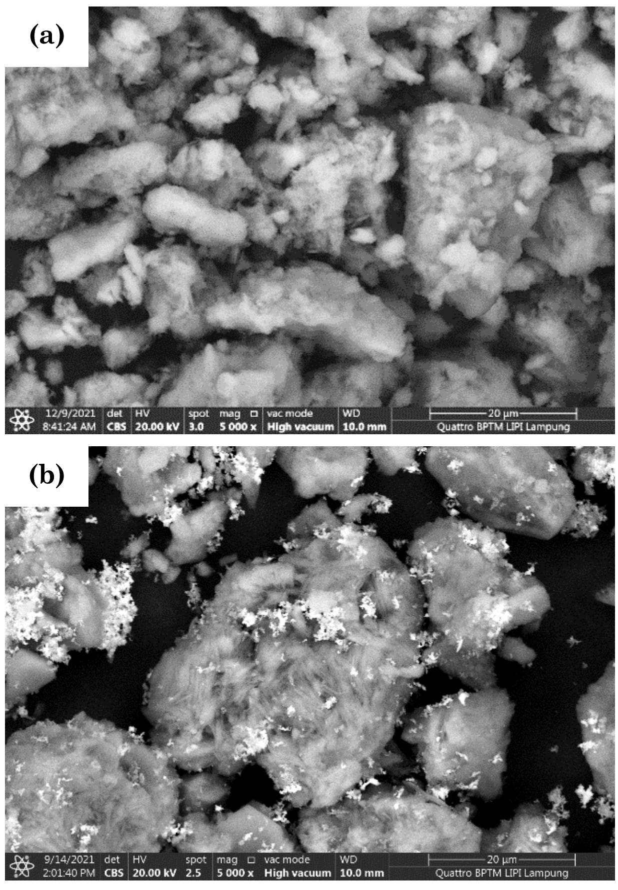


Figure 2. SEM of Lampung natural zeolite and ZnO-TiO_2/NZ catalyst loading 10%.

the natural zeolite. The white color in the SEM results is due to the atomic numbers of Zn and Ti metals being higher than the atomic numbers of Al and Si metals, resulting in lighter colors [23]. Zilfaalso reported that metal oxides impregnated on natural zeolites produced lighter colors on SEM analysis [24].

Table 1 shows the properties of natural zeolite and ZnO-TiO_2/NZ catalysts. Natural zeolite has the highest surface area of 97.7747 m^2/g. After metal addition, the surface area of the zeolite decreased due to the presence of ZnO and TiO_2 particles [25,26]. This happens because the more metal oxides are impregnated, the more natural zeolite pores are penetrated by metal oxides, so the surface area decreases due to being covered with metal oxides [21]. As a result, the pore diameter on the catalyst is larger than the pore diameter of natural zeolite because the increased metal oxide levels in the catalyst will increase the pore diameter [27]. It can be seen in Table 1 that a catalyst with a higher percentage of metal oxide produces a catalyst with a larger pore diameter. Table 1 shows the results of the XRF analysis of Lampung natural zeolite and catalyst with 10% metal loading. These results indicate that the metals ZnO and TiO_2 do not match the desired loading on the catalyst. This is due to the uneven impregnation process, so the metal charge in the sample is not homogeneous. In addition, impregnation, which has a value smaller than its charge, occurs due to imperfect stirring so that the metal does not enter the pores ideally [28,29].

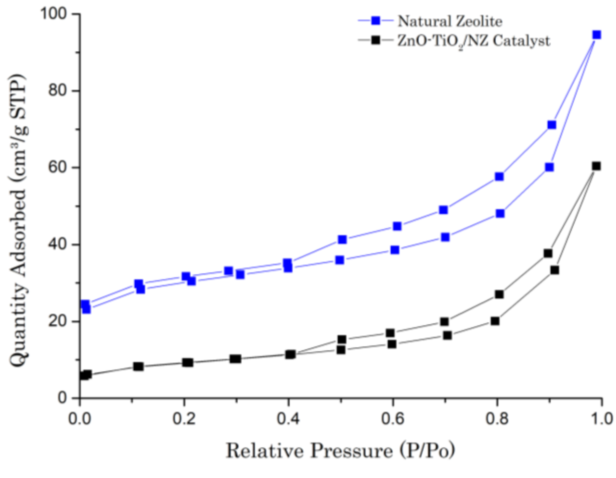


Figure 3. Nitrogen adsorption-desorption isotherms of Lampung natural zeolite and ZnO-TiO_2/NZ catalyst.

Figure 3 shows analysis using N_2 adsorption-desorption showed the presence of microporous and mesoporous structures on the synthesized natural zeolite and ZnO-TiO_2/NZ catalyst. Furthermore, the synthesized catalyst showed the same type of isotherm, a combination of type I and IV isotherms. Natural zeolites' desilication and dealumination processes increase surface area and pore volume [30]. So, the emergence of mesopores in the synthesized natural zeolite catalyst.

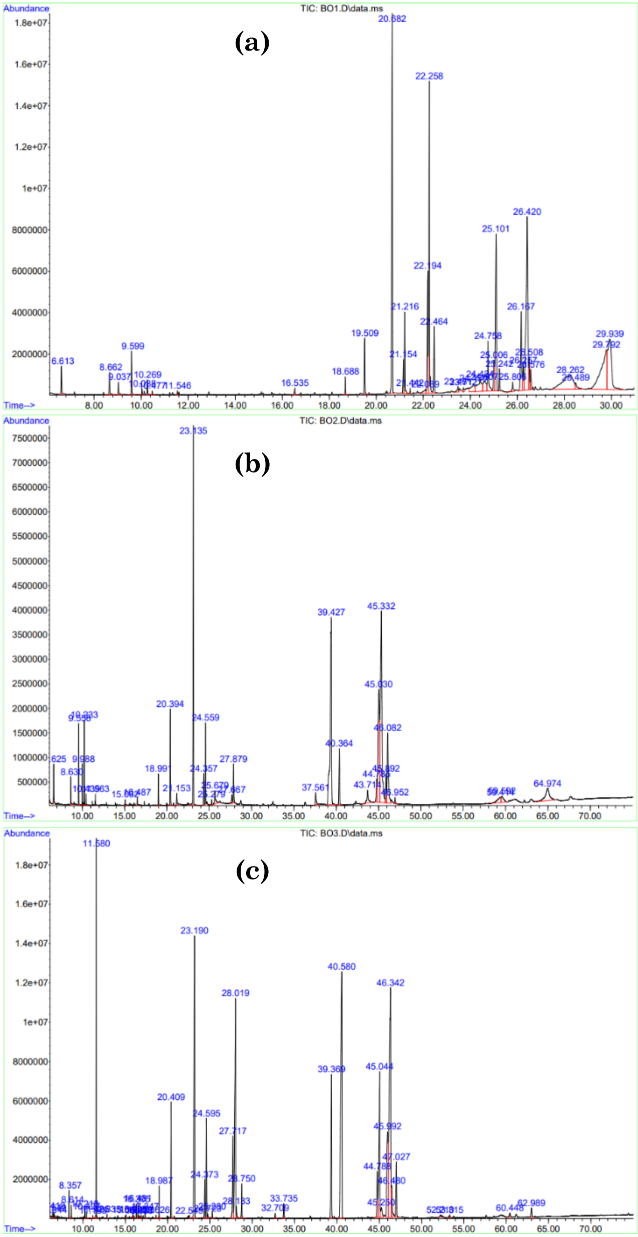


Figure 4. The chromatogram of biodiesel with oil to methanol mole ratio varied from (a) 1:15, (b) 1:18, and (c) 1:20 using natural zeolite catalyst.

Table 1. The Properties of natural zeolite and ZnO-TiO_2/NZ catalyst.

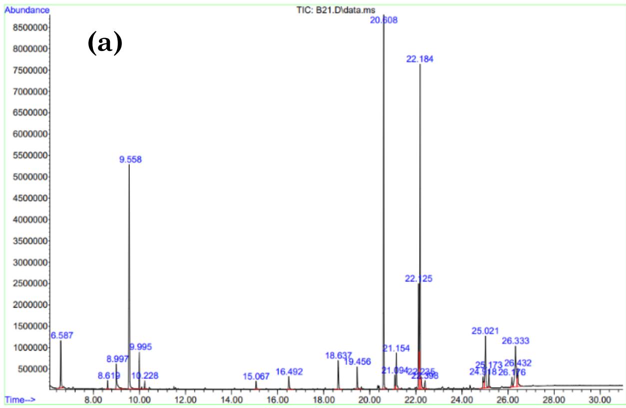
Catalyst	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)	Metal contents (%wt)	
				Zn	Ti
Natural Zeolite	97.7747	0.146	5.9851	-	-
ZnO-TiO_2/NZ	31.3689	0.093	11.9177	3.449	1.402

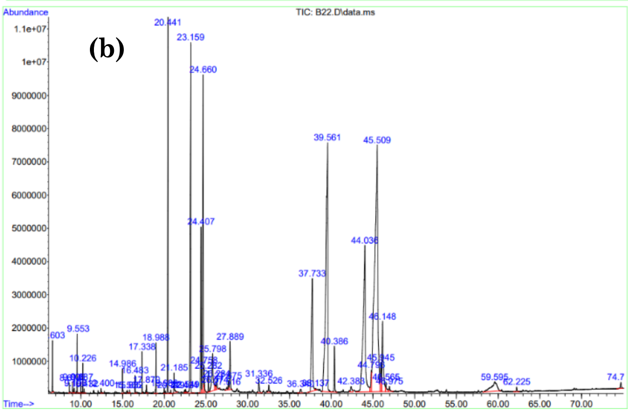
However, there is a distinction in the mesoporous volume between the natural zeolite catalyst and the ZnO-TiO_2/NZ catalyst. The natural zeolite catalyst has a greater mesoporous volume than the ZnO-TiO_2/NZ catalyst, and this distinction is reflected in the hysteresis loop being smaller after impregnation. This difference can be attributed to the clogging of some pores of the natural zeolite catalyst after impregnation of metal ions (ZnO and TiO_2) and the formation of an amorphous phase in the zeolite structure during the calcination process [31].

3.2 Production of Biodiesel

The results of the catalytic test obtained from the transesterification reaction were analyzed using GC-MS which aims to identify the components of the compounds in the product. Furthermore, the product was identified using MS based on library data from the library the Wiley275 and NIST02 to determine the type of compound component. Figure 4 shows the chromatogram of biodiesel with oil to methanol mole ratio varied from (a) 1:15, (b) 1:18, and (c) 1:20 using natural zeolite catalyst. The chromatogram shows the effect of variations in oil and methanol ratio. Figure 5 shows the chromatogram of biodiesel with oil to methanol mole ratio varied from (a) 1:15, (b) 1:18, and (c) 1:20 using ZnO-TiO_2/NZ catalyst. The palm oil transesterification reaction product contained 9 compounds, as indicated by many peaks from GCMS analysis. The compound with the highest intensity appears at a retention time (RT) between 20-45. Methyl ester 9-octadecenoic acid (z)-oxiranyl was the main compound in the product.

Figure 6 shows the yield of biodiesel with oil and methanol mole ratio varied from 1:15, 1:18, and 1:20 using natural zeolite and ZnO-TiO_2/NZ catalyst. The optimum yield FAME was obtained at the variation of oil and methanol 1:18 by 29.17% using natural zeolite catayst. While the variation of 1:15 and 1:20 mole ratios obtained yield FAME of 22.93% and 6.26%, respectively. This indicates a decrease in FAME after the addition of 1:20





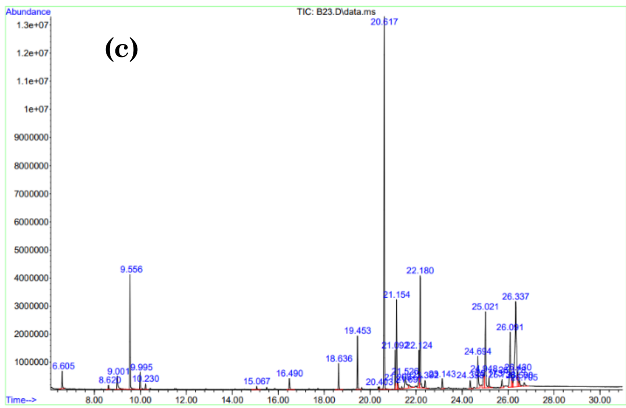


Figure 5. The chromatogram of biodiesel with oil and methanol mole ratio varied from (a) 1:15, (b) 1:18, and (c) 1:20 using ZnO-TiO_2/NZ catalyst.

Table 2. Chemical composition of biodiesel produced by transesterification process over natural zeolite catalyst.

Compound name	Chemical Formula	Mole ratio of oil:methanol		
		1:15	1:18	1:20
Methyl tetradecanoate	$C_{15}H_{30}O_2$	-	-	0.12
Methyl Palmitate	$C_{17}H_{34}O_2$	1.63	2.35	2.21
Linoleic Acid, methyl ester	$C_{19}H_{34}O_2$	0.82	0.92	0.99
Methyl Trans Oleate	$C_{19}H_{36}O_2$	2.15	2.66	2.77
Methyl stearate	$C_{19}H_{38}O_2$	0.13	0.17	0.17
Benzene, (3-methyl-2-butenyl)-	$C_{11}H_{44}$	1.7	-	-
Hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl)ethyl ester	$C_{19}H_{38}O_4$	-	0.86	-
9-Octadecenoic acid (Z)-, 2,3-dihydroxypropyl ester	$C_{21}H_{40}O_4$	3.56	1.27	-
9-octadecenoic acid (z)- oxiranyl, methyl ester	$C_{21}H_{38}O_3$	12.94	20.94	-

methanol. The increasing content of methanol causes it, so the mole ratio of the amount of catalyst to reactants (oil and methanol) decreases. In addition, the separation of glycerol becomes more difficult when the amount of methanol is more than 1:15, which causes a decrease in biodiesel yield [11]. The results are tabulated in Table 2.

Based on the chromatogram, the optimum yield FAME results at 1:18 variation of oil:methanol mole ratio was 60.53% using ZnO-TiO_2/NZ catalyst. While the variation of oil:methanol mole ratio of 1:15, and 1:20 obtained yield FAME of 5.27% and 19.52%, respectively. The effect variation of oil:methanol mole ratio on biodiesel products showed different results when using a ZnO-TiO_2/NZ catalyst than natural zeolite catalysts. The ZnO-TiO_2/NZ catalyst showed the same optimum conditions, with oil:methanol mole ratio variations of 1:18. Excess methanol was favorable for converting triglycerides to FAMEs. Fawas et al. reported that the FAME yield decreased as the molar ratio of methanol to oil was increased to 25:1 [32]. This trend is due to the negligible recombination of FAME and glycerol to produce monoglycerides. The increase in yield produced is due to the addition of metal loading on the catalyst support by 10%. The lowest yield results were obtained when there was no addition

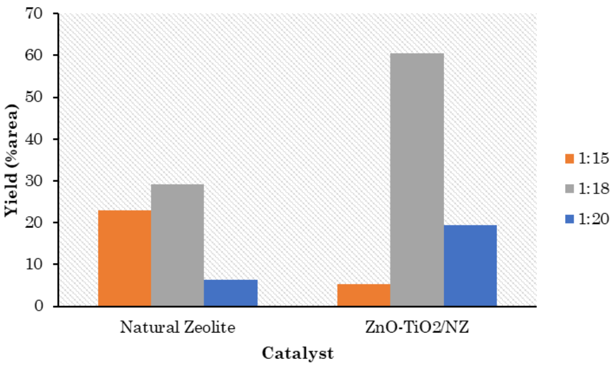


Figure 6. The yield of biodiesel with oil and methanol ratio varied from 1:15, 1:18, and 1:20 using natural zeolite and ZnO-TiO_2/NZ catalyst.

of ZnO and TiO_2 metal oxides. When ZnO and TiO_2 metal oxides (based on Table 1, the metal contents were 3.339 and 1.402, respectively) are added to natural zeolite supports, the catalyst's active sites tend to increase. In addition, the macroporous structure of the catalyst provides an appropriate outer surface that acts as an active site for rapid mass transfer in the process. The additional active centers of metal particles introduced into the catalyst surface and the corresponding metal precursors can also explain these results. Metal particles introduced onto the surface of the zeolite become active centers of the reaction studied because of the activation process. It can improve the production of fatty acid methyl ester (FAME) from the transesterification reaction to achieve higher oil conversion. The catalyst drives the transesterification reaction by accelerating the reaction rate to produce high levels of biodiesel without being consumed in the reaction [33–38]. The results are tabulated in Table 3.

4. Conclusions

This work presents the catalytic activity of natural zeolite and ZnO-TiO_2/NZ catalyst in the transesterification process. The influence of the catalyst was also investigated in this work. The results showed that the impregnation of metal oxide on natural zeolite influence on the catalytic activity in biodiesel production. The transesterification process of palm oil was carried out in three neck-rounded flasks mounted on a reflux device. The mole ratio of oil to methanol 1:18 showed the maximum conversion of biodiesel yield of 60.53%. using ZnO-TiO_2/NZ catalyst. It can be concluded that the ZnO-TiO_2/NZ catalyst has great potential for use as a catalyst for biodiesel production.

Acknowledgments

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Table 3. Chemical composition of biodiesel produced by transesterification process over ZnO-TiO_2/NZ catalyst.

Compound name	Chemical formula	Mole ratio of oil:methanol		
		1:15	1:18	1:20
Methyl tetradecanoate	$C_{15}H_{30}O_2$	-	0.34	-
Methyl Palmitoleate, methyl ester	$C_{17}H_{32}O_2$	-	0.07	-
Methyl Palmitate, methyl ester	$C_{15}H_{30}O_2$	1.68	6.04	3.24
Oleic acid, methyl ester	$C_{19}H_{34}O_2$	0.89	3.08	2.23
Methyl Trans Oleate	$C_{19}H_{36}O_2$	2.7	8.25	5.94
Methyl stearate	$C_{19}H_{38}O_2$	-	0.33	
Hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl)ethyl ester	$C_{19}H_{38}O_2$	-	4.56	2.58
9-Octadecenoic acid (Z)-, 2,3-dihydroxypropyl ester	$C_{21}H_{40}O_4$	-	11.01	5.53
9-Octadecenoic acid (Z)-, oxiranylmethyl ester	$C_{21}H_{38}O_3$	-	26.85	-

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CRediT Author Statement

Author Contributions: *M. Al-Muttaqii*: Conceptualization, Methodology, Investigation, Resources, Data Curation, Writing, Review and Editing, Supervision; *M.P. Marbun* and *S. Priyanto*: Draft Preparation, Methodology, Investigation; *A. Sibuea*, *W. Simanjuntak*, *F. Syafaat A.M.*, *H.S. Huttur S.R.*, *R. Alviany*: Investigation, Resources, Writing; *T. Maryani, T. Sulistyaningsih*: Data Curation, Writting Draft Preparation; *E. Prasetyo, Sudibyo, Indriyati*: Validation, Writing, Review and Editing. All authors have read and agreed to the published version of the manuscript.

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