TRANSESTERIFICATION OF PALM OIL USING THE TiO₂/nano-MONMORILLORITE (nano-MMT) COMPOSITE CATALYST FROM ACEH TAMIANG BENTONITE IN THE PRODUCTION OF BIODIESEL

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ABSTRACT

Transesterification of palm oil using a TiO₂/nano-Monmorillorite (nano-MMT) composite catalyst from Aceh Tamiang bentonite in Biodiesel production has been carried out. Biodiesel is bioenergy obtained from vegetable oils, animal fats, microorganisms, and plants. This is alternative energy to replace fossil fuels, especially diesel oil. Biodiesel is proven to be more environmentally friendly in reducing hydrocarbon and sulfur emissions. In this study, TiO₂ will be composited with nano-MMT using the solid-state method and analyzed using XRD. Both of these materials are used as catalysts for biodiesel production. The transesterification process will be used in the production of biodiesel, where the molar ratio of palm oil to methanol is 1:12. TiO₂/nano-MMT composite catalyst will be varied (2 and 4 grams). Biodiesel samples will be analyzed using GC-MS. The results obtained show that the TiO₂/nano-MMT composite catalyst from Aceh Tamiang bentonite can convert Fatty Acid Methyl Ester (FAME) from palm oil. The 2 grams of the composite catalyst produced biodiesel of 89.38% and 4 grams of 64.88%.

Keywords: Palm oil; TiO2; nano-Monmorillorite; Transesterification

Introduction

Oil reserves are decreasing from year to year, so there is a need for alternative energy. Fossil fuels, especially diesel, can be reduced in use with biodiesel which is proven to be more environmentally friendly, reducing hydrocarbon and sulfur emissions.¹ Biodiesel can be produced from animal fats and microorganisms.² Sivaprakash produces nanocomposite zinc-based iron oxide as a catalyst for the production of biodiesel from extracted Entermorpha intestinalis.³ Akabude uses CaO nanocatalysts for the production of biodiesel from microalgae.⁴ Also, it is produced from vegetable oils, such as palm oil fruit. Oil palm plants are very abundant in Indonesia because they can be grown in tropical areas.⁵ The transesterification process is one of the methods used in biodiesel production, as has been done by Mohammed Danish to produce biodiesel from flaxseed oil using KOH as a catalyst.⁶ Ana Farias, to get biodiesel from soybean oil, performs the ethanol transesterification process using CuO, ZnO, and CeO₂ which are supported on bentonite.⁷ The results showed that there was a conversion of 88% biodiesel using ZnO on bentonite. In addition, Istadi also produces biodiesel from soybean oil using an active solid acid catalyst from zinc oxide sulfate $(SO_4^2 - ZnO)$ and $SO_4^2 - /ZnO)$ which is characterized.⁸ Aceh Tamiang has natural bentonite which has been synthesized into nano-Monmorillorite (nano-MMT) by Tisna Harmawan for purifying patchouli oil.⁹ ZnO is a metal oxide which is a semiconductor and photocatalyst material. Apart from ZnO, TiO₂ is also a semiconductor and photocatalyst material.¹⁰ The TiO₂/nano-MMT composite catalyst from Aceh Tamiang, however, has not been studied in terms of the transesterification process for biodiesel production from palm oil.

*Corresponding author. E-Mail: andifadly@unsam.ac.id This article reports biodiesel production using a TiO₂/nano-MMT composite catalyst from Aceh Tamiang natural bentonite from palm oil. The percentage of biodiesel is generated from GC-MS (Chromatography-Mass Spectrometry) data from Shimadzu Brand, Type: QP2010 Plus. The study of biodiesel production from palm oil using a TiO₂/nano-MMT composite catalyst from Aceh Tamiang natural bentonite will broaden the prospect of the analysis.

Methods

TiO₂ analyzer (Emsure) is used in powder form as a catalyst. Nano-MMT powder from Aceh Tamiang natural bentonite obtained from previous research,⁹ solid as a heterogeneous catalyst. Synthesis of TiO₂/nano-MMT composites will be carried out using the solid-state method for 30 minutes¹¹ with a ratio of 25:75 wt%. The analysis will be carried out qualitatively from the results of the X-Ray Diffraction (XRD) Brand Shimadzu, Type: MAXima_X XRD-7000 in powder form. These results determine the peak crystals of TiO2 and nano-MMT and the absence of new crystal peaks in the composites. TiO₂/nano-MMT This determines the formation of the TiO2/nano-MMT composite.

Biodiesel production is carried out through a transesterification process using a threeneck flask equipped with a thermometer and condenser. The molar ratio of palm oil to methanol analyst (Emsure) to be used is $1:12.^{7}$ 2 grams of TiO₂/nano-MMT composite catalyst will be mixed with methanol and stirred for 5 minutes at a speed of 250 rpm. This was also done on a variation of the TiO₂/nano-MMT composite catalyst of 4 grams. Furthermore, the liquid catalyst and methanol will be mixed with palm oil. The three mixtures will be refluxed at a reaction temperature of 60 °C for 3 hours and stirred at a speed of 250 rpm. After the process is complete, the liquid will be allowed to stand in a separating funnel to form 2 layers. The bottom layer is glycerol and the top layer is biodiesel. The top layer of the liquid is separated and filtered using Whatman paper. Analysis of biodiesel from palm oil will be carried out by GC-MS testing with the concentration parameter (%) against the retention time (minutes) which describes the chromatogram.¹²

Result and Discussion

The diffraction patterns of TiO₂, nano-MMT, and TiO₂/nano-MMT composites from XRD results are shown in Figure 1.



Figure 1. XRD patterns for nano-MMT, TiO₂/nano-MMT composites, and TiO₂

Based on Figure 1, TiO₂ powder has an anatase phase identified (JCPDS number 96-

710-3589) and has a diffraction pattern with sharp crystal peaks from the XRD results. In

contrast to the nano-MMT powder which has a diffraction pattern with a low crystal peak, SiO₂ is identified as a quartz phase (JCPDS number 96-900-9667). The crystal peak is at 20, which is 20.86° and 26.62°. The MMT composition of XRF results from previous studies shows that SiO₂ has the most composition (Si = 25.04 wt%, O = 45.71 wt%) compared to Al, Fe, Ti, Ca, K, S..⁹ This shows the dominant SiO₂ crystal peak in nano-MMT and the shape of the diffraction pattern is MMT (JCPDS number 96-901-0958). The successful synthesis of $TiO_2/nano-MMT$ composites is shown by the crystalline peaks of TiO_2 and MMT which are separated and no new phase is formed.¹³

Intensity versus retention time (minutes) graph depicting the palm oil biodiesel chromatogram using GC-MS is shown in Figure 2. This confirms the formation of the methyl ester.



Figure 2. GC-MS analysis of biodiesel from palm oil using a TiO₂/nano-MMT composite catalyst with variations, (a) 2 grams and (b) 4 grams.

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The descriptions of the chromatograms obtained are shown in Tables 1 and 2. Based on Figure 1 (a) and Table 1, most of the biodiesel composition from palm oil is methyl tridecanoate (1.58%), methyl heptadecanoate (0.24%), methyl oleate (81.80%), and methyl dihydrochaumoograte (5.76%). The other composition is linoleic acid (2.58%) and 7.61% unknown. These results indicate the total concentration of Fatty Acid Methyl Ester (FAME) in biodiesel from palm oil is 89.38%. In addition, Figure 1 (b) and Table 2 illustrate the composition of biodiesel from palm oil, most of which are methyl palmitate (1.09 %)methyl oleate (63.79%). Another and composition is palmitic acid (15.54%), 1cyclododecene (5,63%), and carbonic acid-(1) (12.21%). These results indicate the total concentration of FAME in biodiesel, which is 64.88%. The use of $TiO_2/nano-MMT$ composite catalyst as much as 2 grams versus 4 grams, increases the production of biodiesel from palm oil. This is due to the formation of the slurry.³

TiO₂ as a metal oxide can increase catalyst activity in the transesterification reaction¹² and nano-MMT is contained in bentonite from Aceh Tamiang as an adsorbent that can absorb water and impurities in biodiesel production.¹⁴ Besides, the catalyst from natural bentonite as pure material no biodiesel conversion was obtained.⁷

Table 1. Results of GC-MS analysis on biodiesel from palm oil using 2 grams of TiO₂/nano-MMT composite catalyst.

No Peak	Compound	Structure	Retention Time (min)	Area%
1	Methyl Tridecanoate	$C_{14}H_{28}O_2$	19.767	1.58
2	Methyl Heptadecanoate	$C_{18}H_{36}O_2$	20.267	0.24
4	Methyl Oleate	$C_{19}H_{36}O_2$	24.189	20.85
5	Methyl Oleate	$C_{19}H_{36}O_2$	24.263	60.95
8	Methyl	$C_{19}H_{36}O_2$	25.050	5.76
	Dihydrochaumoograte			89.38
	Total Methyl Esters			10.60
	Other			

Table 2. Results of GC-MS analysis on biodiesel from palm oil using 4 grams of TiO₂/nano-MMT composite catalyst.

No Peak	Compound	Structure	Retention Time (min)	Area%
1	Methyl Palmitate	$C_{17}H_{34}O_2$	20.254	1.09
3	Methyl Oleate	$C_{19}H_{36}O_2$	24.229	24.11
4	Methyl Oleate	$C_{19}H_{36}O_2$	24.290	12.29
5	Methyl Oleate	$C_{19}H_{36}O_2$	24.365	26.72
	Total Methyl Esters			64.88
	Other			35.12

Conclusion

TiO₂/nano-MMT (25:75 wt%) composite from Aceh Tamiang bentonite as a catalyst can convert oil palm fatty acids into biodiesel. In addition, nano-MMT did not undergo acid activation. Comparison of the molar ratio of palm oil and methanol (1:12) and 2 grams of TiO₂/nano-MMT composite catalyst with an optimum reaction temperature of 65 °C for 3 hours to produce Fatty Acid Methyl Ester (FAME) on biodiesel which is 89.38%. In future studies, the catalyst composite TiO₂/nano-MMT should be tested with different raw material for biodiesel.

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