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THE EFFECT OF UV LIGHT ON THE YIELD AND CHARACTERISTICS OF BIODIESEL FROM CANDLENUT OIL USING A TiO_2-K_2O/NATURAL ZEOLITE COMPOSITE

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Abstract

This study examines the effect of UV irradiation on the yield and physical characteristics of biodiesel from candlenut oil using a TiO_2-K_2O/natural zeolite composite. Natural zeolite was activated with KOH and impregnated with TiO_2. The formed composite was analyzed with an X-ray diffractometer. Biodiesel was synthesized with candlenut oil to methanol molar ratio and catalyst loading (w/w oil) 1:4, 1:6, 1:8, and 2, 4, and 6%, respectively. The XRD analysis shows peak patterns of anatase and rutile TiO_2, K_2O, and zeolite. UV light can increase biodiesel yield, with the highest yield at 82.08% at oil to methanol molar ratio of 1:8 and a catalyst loading of 2%. The physical properties of biodiesel are in accordance with national standard SNI 7182:2015. GCMS results shows that the main components of fatty acid methyl ester from biodiesel are methyl oleate, methyl palmitate, and methyl linoleate.

Keywords: Biodiesel; Candlenut oil; Yield; Ultraviolet (UV) light; TiO_2-K_2O/natural zeolite

1. INTRODUCTION

Indonesia's biodiesel consumption is increasing every year. According to the national news daily, Indonesia's total installed biodiesel production capacity reached 16.6 million kiloliters in 2021 (Merdeka, 2022). One of the factors causing the high production of biodiesel in Indonesia is related to the B30 program launched by the government, where diesel fuel sold must be mixed with biodiesel as much as 30% and has the potential to increase in the future, so it is interesting to study.

Researchers have investigated non-consumable oils utilization as raw materials for biodiesel production to evade competition between oil for consumption and biodiesel raw material, including jatropha, neem, Karanja, rubber seed, and candlenut oil (Athar et al., 2022; AVSL et al., 2021; Kashyap et al., 2019; Noreen et al., 2021; Shaah et al., 2022). In this case, candlenut oil can be a raw material solution for making biodiesel.

Biodiesel production generally uses a homogeneous catalyst because it produces a high conversion but is difficult to separate. Heterogeneous catalysts can be used to overcome this problem. Many heterogeneous catalysts have been studied, starting from CaO, zeolite, ZnO, and ZnO/SiO_2 (Alismaeel et al., 2018; Degfie et al., 2019; Justine et al., 2021). To reduce production costs, the catalyst used must be economically feasible.

Bayah, a sub-district in Lebak, Banten province, Indonesia, is widely known as a producer of natural zeolite. Natural zeolite is one of the inexpensive materials that can be used as a catalyst for biodiesel synthesis. There have been many studies on zeolite. CaO/zeolite in lard waste produces yields of up to 90% (Lawan et al., 2020). Waste cooking oil catalyzed by barium-modified zeolite yields up to 93% (Yusuff et al., 2021). Biodiesel synthesis from rice bran oil using kno3-impregnated zeolite produces up to 83.2% yield (Hidayat et al., 2018). Zeolite, with its affordable price and high yield, is attractive for use as a catalyst for biodiesel production.

The performance of zeolite can be increased by adding TiO_2, which is known as a photocatalyst with high effectiveness. Combining these two catalysts is expected to provide a good yield and characteristics of biodiesel. The use of photocatalyst with light irradiation in biodiesel synthesis has been widely used (Corro et al., 2017; Guo et al., 2021). However, biodiesel produced with and without light irradiation is rarely compared and studied. Using a CaO/TiO_2 catalyst with the help of UV light can increase the yield compared to using only CaO alone (Mohamad et al., 2018). Another study found that CaO/TiO_2 with UV light had a higher yield than without UV light (Mohamad et al., 2017). This research aims to examine the effect of UV light on the yield and physical characteristics of biodiesel produced from candlenut oil with a K_2O-TiO_2/zeolite catalyst.

2. MATERIALS AND METHOD

TiO_2 P25 was received from Evonik. Natural zeolite was received from a local miner in Bayah, Banten Province, Indonesia. Aquadest and technical-grade methanol (purity >99%) were purchased from a local chemical shop. ACS reagent grade of HCl (37%) and KOH (>90%) EMSURE for analysis received from Merck. Candlenut oil (*Aleurites moluccana*) with 1,65% FFA content was received from the local market.

2.1 Preparation Of Natural Zeolite

Bayah natural zeolite, as much as 200 grams, was soaked in distilled water for 24 hours. The zeolite was then separated from the distilled water and dried at 110°C for 24 hours to remove the remaining water. The zeolite was soaked in 6 M HCl for 4 hours. After that, it was washed using distilled water until the pH was neutral and dried at 110°C for 24 hours. The zeolite was then crushed and filtered through a 200-mesh filter.

2.2 Activation Of Natural Zeolite

The 200-mesh zeolite was impregnated with K_2O. First, while stirring at room temperature, zeolite was added to 100 ml of 20% KOH solution. The catalyst was then dried in an oven at 110°C for 24 hours. The dry catalyst was then calcined at 500°C for 3 hours to increase the contact surface area of the catalyst by removing organic impurities and KOH will be converted to K_2O during the calcination process (Fitriana et al., 2018).

2.3 Synthesis Of TiO_2-K_2O/Natural Zeolite Composite

Activated zeolite and TiO_2 were added to distilled water (catalyst to distilled water weight ratio 1:1) with a TiO_2:zeolite ratio of 1:9 (w/w) while stirring for 2 hours. The mixture was put into a hydrothermal bottle and heated at 90°C for 16 hours in the oven. After cooling, it is filtered and dried in an oven at 110°C for 2 hours. The composite was then calcined at 400°C for 2 hours.

2.4 XRD Analysis Of The TiO_2-K_2O/Natural Zeolite Composite

The composite was characterized with an X-ray diffractometer PANalytical Aeris to identify its crystal structure. The radiation of the Cu-Kα monochromator was 1.5406 Å, with a diffraction angle of 10-90° at 40 kV and 30 mA.

2.5 Biodiesel Synthesis

Biodiesel synthesis is done through a transesterification reaction under UV light irradiation at the photocatalyst reactor. The reactor was a 70×48×42 cm plastic box covered in aluminum foil with six 10-watt UV lamps installed, 3 each on the left and right sides of the box. Candlenut oil and methanol with a molar ratio of 1:8 was put in the reactor. 2% catalyst (w/w oil) was then added. The reaction took place at 60°C for 1 hour. The catalyst loading was varied at 2, 4, and 6% (w/w oil). The candlenut oil to methanol molar ratio was varied at 1:4, 1:6, and 1:8. The procedure was repeated without UV light irradiation.

2.6 Biodiesel Purification

The transesterification product was put into a separatory funnel and allowed to stand for 24 hours. The glycerol part is then separated from the biodiesel part. The biodiesel was washed using 250 ml of warm distilled water while stirring and then allowed to stand for 15 minutes. The biodiesel part is then separated from the distilled water. Washing was done several times to neutralize the pH and purify the biodiesel. After that, the biodiesel is dried by heating at 120°C for 15 minutes to remove any remaining water.

2.7 Biodiesel Yield

Biodiesel yield was calculated using eq. 1:

$$\%yield = \frac{biodiesel\ mass\ (gram)}{candlenut\ oil\ mass\ (gram)} \times 100\% \quad (1)$$

2.8 Biodiesel Characterization

2.8.1 Density analysis

The pycnometer was rinsed with distilled water until clean, then rinsed with ethanol and dried. The dry pycnometer is weighed as W_1. The pycnometer is then filled with biodiesel and weighed as W_2. The density of biodiesel is calculated using the eq. 2:

$$\rho = \frac{W_2 - W_1}{V} \quad (2)$$

where ρ is the density of biodiesel, kg/m^3; W_1 is the mass of the empty pycnometer, kg; W_2 is the mass of the pycnometer + biodiesel, kg; V is the volume of the pycnometer, m^3.

2.8.2 Viscosity analysis

A viscosity analysis was carried out using an Oswald viscosimeter. The eq. 3 used is as follows:

$$\eta = \eta_0 . \frac{t.\rho}{t_0.\rho_0} \quad (3)$$

where η is the biodiesel viscosity, cSt; η_0 is the viscosity of water, cSt; t is the biodiesel flow time, s; t_0 is the water flow time, s; ρ is the density of biodiesel, kg/m^3; and ρ_0 is the density of water, kg/m^3.

2.8.3 Fatty acid methyl ester composition analysis

Gas chromatography - mass spectroscopy Shimadzu QP 2010 SE was used to analyze the biodiesel's fatty acid methyl ester composition. The biodiesel sample with the best yield under UV light irradiation was chosen for the analysis. As a comparison, a biodiesel sample with the same variation of feed mole ratio and catalyst loading without UV light irradiation was also analyzed.

3. RESULTS AND DISCUSSION

3.1 XRD Analysis Result

Figure 1 shows the XRD pattern of the synthesized TiO_2-K_2O/natural zeolite composite. Typical peaks of anatase and rutile TiO_2 were detected at a diffraction angle of 25.24°; 38.35°; 47.93° according to JCPDS No. 21-1272 for the anatase phase, and 27.55°; 44.62° according to JCPDS No: 21-1276 for the rutile phase. The diffraction peak detected at 13.74°; 21.83°; 26.53°; 29.73°; 34.70°; 48.41°; 65.03° was corresponded to the zeolite peak according to JCPD No. 21-1272. The diffraction peaks at 23.46 and 26.16 indicate the presence of K_2O compounds according to JCPDS File No. 47-1701; 77-2176 (Mutreja et al., 2014). The narrow curve indicates the material has good crystallinity (Adiwibowo et al., 2018, 2019). It is well-known that the higher the crystallinity, the better the photocatalyst performance.

3.2 Effect Of UV Light Irradiation On Biodiesel Yield

Figure 2 (oil to methanol ratio of 1:8) and Figure 3 (catalyst loading of 2%w/w oil) show that UV light irradiation can increase biodiesel yield at all variables. The highest biodiesel yields using UV light and without UV light irradiation were 82.08 and 74.81%, respectively. In this biodiesel synthesis process, the TiO_2-K_2O/natural zeolite composite has two roles: as a catalyst and photocatalyst. The photocatalyst mechanism that occurs is as follows:

$$TiO_2 + hv \rightarrow TiO_2\ (e^- + h^+) \quad (4)$$

$$CH_3OH + h^+ \rightarrow CH_3O\bullet + H^+ \quad (5)$$

$$RCOOH + e^- \rightarrow RCO\bullet OH \quad (6)$$

$$RCO\bullet OH + CH_3O\bullet + H^+ \rightarrow RCOOCH_3 + H_2O \quad (7)$$

Electrons in TiO_2 are excited when exposed to UV light to form positive holes (h^+) and excited electrons (e^-) (eq. 4). The adsorbed methanol on the surface of the catalyst then interacts with holes (h^+) to form $CH_3O\bullet$ radicals and hydrogen ions (H^+) (eq. 5). Fatty acids and triglycerides react with excited electrons (e^-) to form radical compounds (eq. 6). The radical compounds react with each other to produce biodiesel and OH• which subsequently react with hydrogen ions (H^+) to form water (eq.7). The same thing was also found in other studies where the use of UV light in biodiesel synthesis using photocatalysts or photocatalyst composites increased biodiesel yields (Abdala et al., 2020; Mohamad et al., 2017).

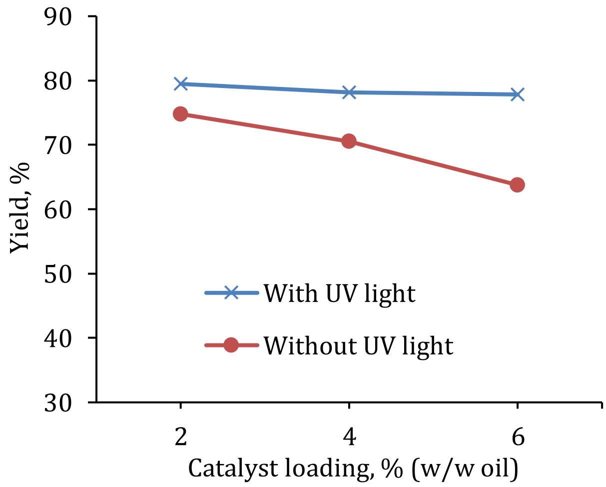

Figure 2. Effect of UV light irradiation on biodiesel yield at various catalyst loading

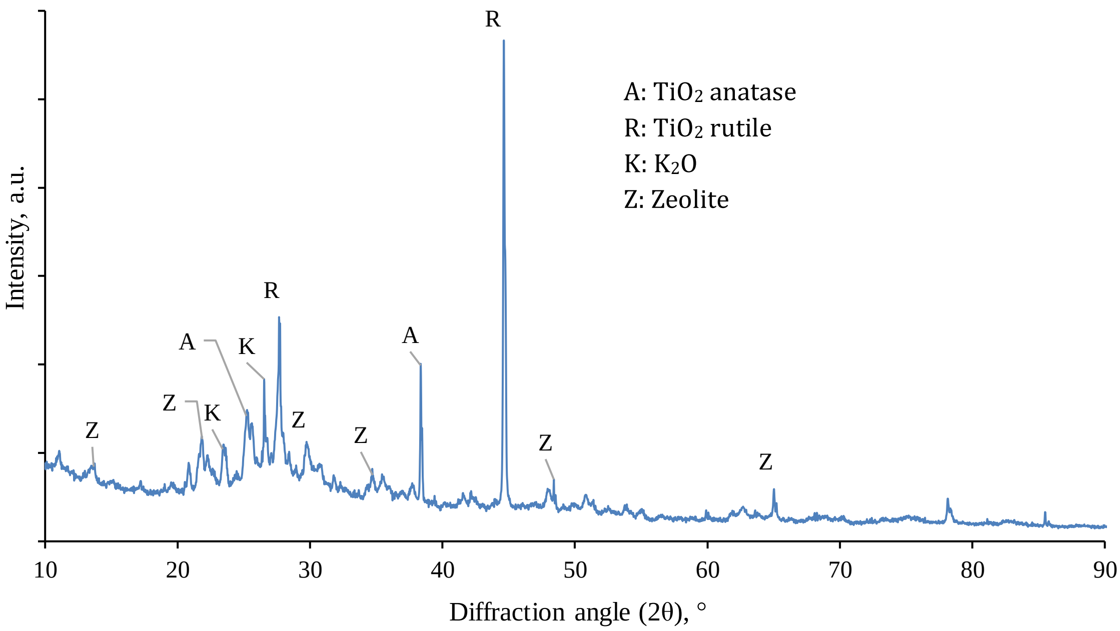

Figure 1. XRD pattern of the natural zeolite-TiO_2/K_2O

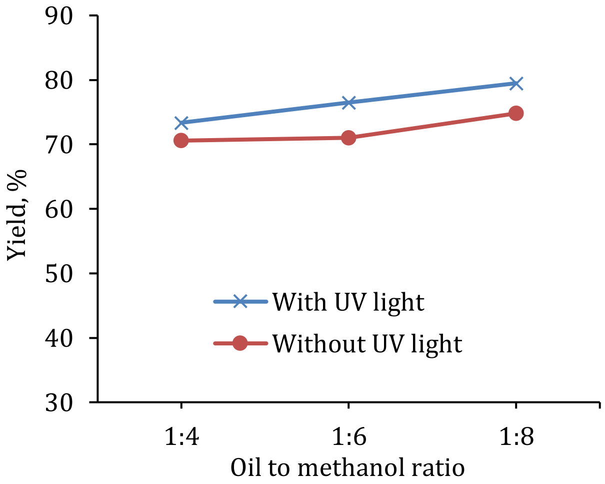

Figure 3. Effect of UV light irradiation on biodiesel yield at various oil to methanol ratio

3.3 Effect Of UV Light Irradiation On Biodiesel Density And Viscosity

Based on Table 1, the density and viscosity for the synthesis of biodiesel assisted with and without UV light irradiation produce properties that follow the national standard SNI 7182: 2015, where the density is in the range of 850-890 kg/m^3 (40°C) and a viscosity of 2.3-6.0 (40°C).

Table 1. The physical properties of biodiesel

Properties	SNI 7182: 2015	Biodiesel (room temperature 26°C)	
		UV light	Without
Density, kg/m^3	850-890 (40°C)	858-888	839-853
Viscosity, cSt	2.3-6.0 (40°C)	3.03-3.63	2.52-3.54

3.4 Determination Of Fatty Acid Methyl Ester In Biodiesel

Table 2 shows the biodiesel composition of the best sample with maximum yield at the methyl ester from the GCMS analysis. The methyl ester compounds that make up the main biodiesel produced from the most to the least are methyl oleate, methyl palmitate, methyl linoleate, methyl linolenate, methyl myristate, arachidic acid methyl ester, methyl palmitoleate, methyl elaidate, methyl laurate, methyl lignocerate, and methyl behenate. The two compounds with the largest areas obtained were similar to those obtained by Mohamad et al., (2017). There is no significant difference between the content of biodiesel produced with the help of UV light and without UV light. This result shows that TiO_2 photocatalyst activity can increase biodiesel yield without changing the biodiesel composition. Further analysis needs to be done to validate this claim.

Table 2. Methyl ester component from GCMS analysis

Compound	Area, %*	
	With UV light	Without UV light
Methyl oleate	45,65	45,27
Methyl palmitate	36,60	36,94
Methyl linoleate	14,73	14,62
Methyl linolenate	1,04	1,03
Methyl myristate	0,72	0,88
Arachidic acid methyl ester	0,43	0,37
Methyl palmitoleate	0,25	0,24
Methyl elaidate	0,18	0,18
Methyl laurate	0,11	0,16
Methyl lignocerate	0,09	0,14
Methyl behenate	0,07	0,00

*Compounds with %area less than 0,07% are not shown in the table

4. CONCLUSION

UV light irradiation in biodiesel synthesis using the TiO_2-K_2O/natural zeolite composite can increase the yield at all tested variables. The best conditions were obtained at a feed ratio of 1:8 and 2% catalyst loading under UV light irradiation, yielding 82.08%. The physical properties of the biodiesel produced are in accordance with SNI 7182: 2015 standards.

5. REFERENCES

Abdala, E., Nur, O., & Mustafa, M. A. (2020). Efficient biodiesel production from algae oil using Ca-doped ZnO nanocatalyst. Industrial & Engineering Chemistry Research, 59(43), 19235–19243.

Adiwibowo, M. T., Ibadurrohman, M., & Slamet. (2018). Synthesis of Zno Nanoparticles and their nanofluid stability in the presence of a Palm Oil-Based Primary Alkyl Sulphate surfactant for detergent application. International Journal of Technology, 9(2), 307–316.

Adiwibowo, M. T., Ibadurrohman, M., & Slamet. (2019). Synthesis and performance test of nanofluidic detergents from palm oil-based primary alkyl sulfates surfactant and zinc oxide. AIP Conference Proceedings, 2085(1), 20049.

Alismaeel, Z. T., Abbas, A. S., Albayati, T. M., & Doyle, A. M. (2018). Biodiesel from batch and continuous oleic acid esterification using zeolite catalysts. Fuel, 234, 170–176.

Athar, M., Imdad, S., Zaidi, S., Yusuf, M., Kamyab, H., Klemeš, J. J., & Chelliapan, S. (2022). Biodiesel production by single-step acid-catalysed transesterification of Jatropha oil under microwave heating with modelling and optimisation using response surface methodology. Fuel, 322, 124205.

AVSL, S. B., Subramaniapillai, N., Mohamed, M. S. B. K., & Narayanan, A. (2021). Effect of rubber seed oil biodiesel on engine performance and emission analysis. Fuel, 296, 120708.

Corro, G., Sánchez, N., Pal, U., Cebada, S., & Fierro, J. L. G. (2017). Solar-irradiation driven biodiesel production using Cr/SiO2 photocatalyst exploiting cooperative interaction between Cr^{6+} and Cr^{3+} moieties. Applied Catalysis B: Environmental, 203, 43–52.

Degfie, T. A., Mamo, T. T., & Mekonnen, Y. S. (2019). Optimized biodiesel production from waste cooking oil (WCO) using calcium oxide (CaO) nano-catalyst. Scientific Reports, 9(1), 18982.

Fitriana, N., Husin, H., Yanti, D., Pontas, K., Alam, P. N., & Ridho, M. (2018). Synthesis of K_2O/Zeolite catalysts by KOH impregnation for biodiesel production from waste frying oil. IOP Conference Series: Materials Science and Engineering, 334(1), 012011.

Guo, M., Jiang, W., Chen, C., Qu, S., Lu, J., Yi, W., & Ding, J. (2021). Process optimization of biodiesel production from waste cooking oil by esterification of free fatty acids using La^{3+}/ZnO-TiO_2 photocatalyst. Energy Conversion and Management, 229, 113745.

Hidayat, A., Mukti, N. I. F., Handoko, B., & Sutrisno, B. (2018). Biodiesel production from rice bran oil over modified natural zeolite catalyst. International Journal of Technology, 9(2), 400–411.

Justine, M., Prabu, H. J., Johnson, I., Raj, D. M. A., Sundaram, S. J., & Kaviyarasu, K. (2021). Synthesis and characterizations studies of ZnO and ZnO-SiO_2 nanocomposite for biodiesel applications. Materials Today: Proceedings, 36, 440–446.

Kashyap, S. S., Gogate, P. R., & Joshi, S. M. (2019). Ultrasound assisted intensified production of biodiesel from sustainable source as karanja oil using interesterification based on heterogeneous catalyst (γ-alumina). Chemical Engineering and Processing-Process Intensification, 136, 11–16.

Lawan, I., Garba, Z. N., Zhou, W., Zhang, M., & Yuan, Z. (2020). Synergies between the microwave reactor and CaO/zeolite catalyst in waste lard biodiesel production. Renewable Energy, 145, 2550–2560.

Merdeka. (2022). Konsumsi Biodiesel Terus Meningkat, Diprediksi Capai 10,1 Juta Kiloliter di 2022. Merdeka.

Mohamad, M., Ngadi, N., Wong, S. L., Jusoh, M., & Yahya, N. Y. (2017). Prediction of biodiesel yield during transesterification process using response surface methodology. Fuel, 190, 104–112.

Mohamad, M., Ngadi, N., Wong, S., Yahya, N. Y., Inuwa, I. M., & Lani, N. S. (2018). Synthesis and characterization of CaO-TiO_2 for transesterification of vegetable palm oil. International Journal of Engineering, 31(8), 1326–1333.

Mutreja, V., Singh, S., & Ali, A. (2014). Potassium impregnated nanocrystalline mixed oxides of La and Mg as heterogeneous catalysts for transesterification. Renewable Energy, 62, 226–233.

Noreen, S., Khalid, K., Iqbal, M., Baghdadi, H. B., Nisar, N., Siddiqua, U. H., Nisar, J., Slimani, Y., Khan, M. I., & Nazir, A. (2021). Eco-benign approach to produce biodiesel from neem oil using heterogeneous nano-catalysts and process optimization. Environmental Technology & Innovation, 22, 101430.

Shaah, M. A., Hossain, M. S., Allafi, F., Ab Kadir, M. O., & Ahmad, M. I. (2022). Biodiesel production from candlenut oil using a non-catalytic supercritical methanol transesterification process: optimization, kinetics, and thermodynamic studies. RSC Advances, 12(16), 9845–9861.

Yusuff, A. S., Bhonsle, A. K., Bangwal, D. P., & Atray, N. (2021). Development of a barium-modified zeolite catalyst for biodiesel production from waste frying oil: Process optimization by design of experiment. Renewable Energy, 177, 1253–1264.