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Characteristic Study of Biodiesel from Waste Cooking Oil using Nipah Skin Ash as a Heterogeneous Catalyst

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Abstract

One type of renewable alternative energy that has great potential to be developed is biodiesel. Biodiesel is a fuel consisting of a mixture of mono-alkyl esters of long-chain fatty acids made from renewable sources such as vegetable oils or animal fats. Such as vegetable oils or animal fats. One of the vegetable oil products that can be used as feedstock for biodiesel production is waste cooking oil. Waste cooking oil is used oil. The purpose of this research is to study the characteristics of the effect of catalyst mass, the ratio of waste cooking oil mole to methanol mole, and the effect of adding THF 1:1 co-solvent on the purity of biodiesel using heterogeneous catalyst ash derived from Nipah fruit skin calcined at 500 °C for 4 hours. The process variables were transesterification reaction time 60, 90, 120, and 150 minutes, a mole ratio of methanol to oil 1:19, 1:21, and 1:23 with the addition of THF: methanol v/v 1:1 co-solvent. Biodiesel properties such as yield (%), density (kg/cm^3), viscosity (mm^2/s), biodiesel compound composition analysis (GC-MS), and morphology and composition test of Nipah skin ash catalyst (SEM-EDX) were evaluated and compared with the Indonesian National Standard (SNI). The characteristics of biodiesel were obtained with a density of 860.2 kg/m^3 and a viscosity of 2.37 mm^2/s. They contained 44.14% Palmitic acid and 43.04% Octadecenoic acid (oleic), following the Indonesian National Standard (SNI) number 7182:2015. The maximum yield obtained was 93.3598% using a mole ratio of oil: methanol 1:23 at 60°C for 120 minutes, TFT 1:1, and 3% catalyst mass. The results obtained in this study indicate that heterogeneous catalysts made from kapok skin can be used to produce biodiesel. Adding TFT co-solvent can increase biodiesel production and methyl ester yield so that high purity is obtained.

Keywords: Biodiesel, Catalyst, Methyl Ester, Nipah skin ash, Transesterification

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INTRODUCTION

Indonesia's industrial development will increase fuel consumption and domestic oil production. The demand for fuel oil will increase Indonesia's dependence on imported materials. From 2011-2030, domestic oil demand is expected to double from 327 million barrels to 578 million barrels by 2030, but this is not the case with oil production. During the same period, oil production decreased from 329 to 124 million barrels [1].

An alternative liquid fuel that can be used as a substitute for petroleum is vegetable oil because it is abundant and renewable. Vegetable oil that is widely used in Indonesia comes from palm oil which is rich in palmitic acid (saturated fatty acid) and oleic acid (unsaturated fatty acid). Biodiesel can be produced from vegetable oils, animal fats, waste oils, and so on [2].

According to the American Society for Testing Materials (ASTM D6751), biodiesel is defined as long-chain mono-alkyl esters of fatty acids derived from renewable sources used in diesel engines. Biodiesel is a renewable, biodegradable, non-toxic, and environmentally friendly fuel. Waste cooking oil is one of the raw materials that can be used to produce biodiesel because it still contains free fatty acids [3].

Biodiesel is made from vegetable oil by converting triglycerides into fatty acid methyl esters. The transesterification reaction is the reaction of triglycerides and methanol to form methyl esters and glycerol. Two types of catalysts can be used to produce biodiesel: homogeneous and heterogeneous

catalysts. The use of homogeneous catalysts has several disadvantages, namely that it takes a long time to separate from the mixture and cannot be reused [4]. One way to reduce the pollution of biodiesel products and improve the efficiency of the manufacturing process is to use heterogeneous solid catalysts in the transesterification process [5].

Because homogeneous base catalysts are relatively expensive in the market, it is tried to use catalysts from natural materials. Various studies have used heterogeneous catalysts in biodiesel production, such as banana stem ash, palm empty fruit bunch ash, and eggshell ash, as heterogeneous catalysts in biodiesel production. In this research, the author would like to improve by using Nipah skin ash as a catalyst in the production of biodiesel made from waste cooking oil. Nipah fruit leather chemically contains inorganic elements such as Na, K, Cl, Mg, Ca, Si, P, S, and Al so that it can be applied as a heterogen base catalyst in biodiesel [6-7].

MATERIALS AND METHODS

Materials

Nipah skin samples were taken from Gereugok, Bireuen, Aceh, while waste cooking oil was taken from fried chicken sellers around the city of Lhokseumawe, Aceh. Chemicals and reagents for methyl ester synthesis including Methanol, KOH, Phenolphthalein, and Tertrahydrofuran (TFT) were purchased from Merck. Distilled water was used to make reagents.

Synthesis of Methyl Ester

The biodiesel production process consists of preparing Nipah skin ash, preparing waste cooking oil, transesterification reaction, and purification. The variables in this research are a variation of the mole ratio of methanol and oil 1:19; 1:21; 1:23, and reaction times 60, 90, 120, and 150 minutes. The analyses conducted were yield (%), density (kg/cm^3), viscosity (mm^2/s), biodiesel compound composition analysis (GC-MS), and morphology and composition test of Nipah skin ash catalyst (SEM-EDX).

In the catalyst preparation process, Nipah skin was put into a furnace with a temperature of 500 ºC for 4 hours. Furthermore, the preparation was carried out to determine the initial ALB content in used cooking oil before continuing the transesterification reaction process [8].

The transesterification process was carried out in a batch reactor by mixing 50 of waste cooking oil and methanol following the variation of oil to methanol ratio determined using Nipah skin ash catalyst 3% of the oil weight. The oil was heated to a temperature of 60 °C and stirred using a magnetic stirrer. Then methanol and Nipah skin ash catalyst were added and stirred until homogeneous with a temperature of 60 °C with a predetermined time variation. After the temperature and reaction time were reached, filter the solution mixture from the heterogeneous catalyst. Then, separate the mixture into a separating funnel and let it stand for 24 hours. Two layers will be formed, the top layer is methyl ester, and the bottom layer is glycerol [9].

The methyl ester was distilled at 60 °C to remove methanol. The purified methyl ester is stored in a sample bottle.

RESULTS AND DISCUSSION

Effect of Mole Ratio and Reaction Time on Yield (%)

The effect of the methanol mole ratio and reaction time on the yield of biodiesel produced can be seen in **Figure** 1.

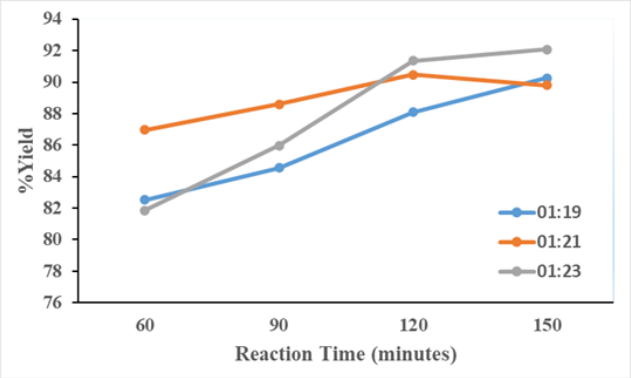


Figure 1. Graph of Effect of Mole Ratio and Reaction Time on Yield (%)

Based on theory, the longer the reaction time, the greater the contact between substances so that it will produce a large conversion [5]. In the research that has been done, the data obtained that during the time of 60 to 150 minutes with a mole ratio of 1:19, 1:21, and 1:23, the yield conversion results continue to increase. This proves that the longer the reaction time, the yield produced will continue to increase. Figure 1 shows that at a mole ratio of 1:21 with a reaction time of 150 minutes, the yield produced increased to 39.8094%, while at a mole ratio of 1:23 with the same reaction time, the yield decreased to 22.0714%.

At the ratio of 1:21, the reaction has reached the equilibrium point. In the ratio of 1:23, the yield obtained decreased because the higher the ratio of alcohol used, the higher the glycerol level produced. According to Yunnowati *et al*., high glycerol in the methyl ester solution will encourage the reaction to turn left to form monoglycerides so that the biodiesel yield will decrease [10].

Effect of Mole Ratio and Reaction Time on Density

The effect of the mole ratio and reaction time on density can be seen in **Figure** 2.

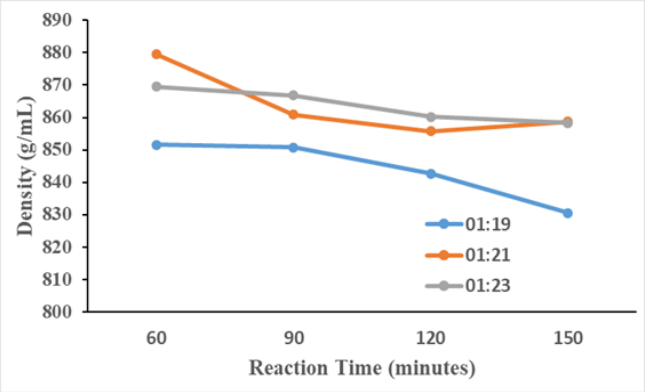


Figure 2. Graph of Effect of Mole Ratio and Reaction Time on Density (g/mL)

The amount of methanol does not affect the density produced, but the amount states that the density of biodiesel produced meets the SNI or does not meet the SNI. The density results obtained at a methanol mole ratio of 1:19, 1:21, and 1:23 at transesterification reaction times of 60, 90, 120, and 150 minutes can be seen in **Figure** 2.

Based on the density test results, it can be seen that the reaction time affects the density of biodiesel, namely the density value increases and decreases. This can be caused by the lack of perfection in the distillation process so that there is still methanol content or impurities in the sample. According to Affandi *et al.*, a poor purification stage can affect and cause the density of biodiesel to vary [11].

According to SNI number 7182:2015, the density of biodiesel is between the range of 850-890 Kg/m^3, but from the results obtained, not all biodiesel produced is by the SNI. According to Hadrah *et al*., the density value of biodiesel that is by the quality standard (SNI) then its use can produce perfect combustion, while biodiesel with a density that does not meet the SNI standard will cause incomplete combustion reactions that can increase emissions and engine wear [12].

Effect of Mole Ratio and Reaction Time on Viscosity

The effect of the mole ratio and reaction time on viscosity can be seen in **Figure** 3. The viscosity results obtained at a methanol mole ratio of 1:19, 1:21, and 1:23 at transesterification reaction times of 60, 90, 120, and 150 minutes can be seen in **Figure** 3. Viscosity has an inversely correlative relationship with the length of reaction time. The longer the reaction time, the lower the viscosity of the biodiesel. Saputra *et al*. have conducted biodiesel research using snail shells, and the longer the reaction time, the viscosity of biodiesel also decreases. Viscosity is closely related to density; the higher the density, the higher the viscosity value.

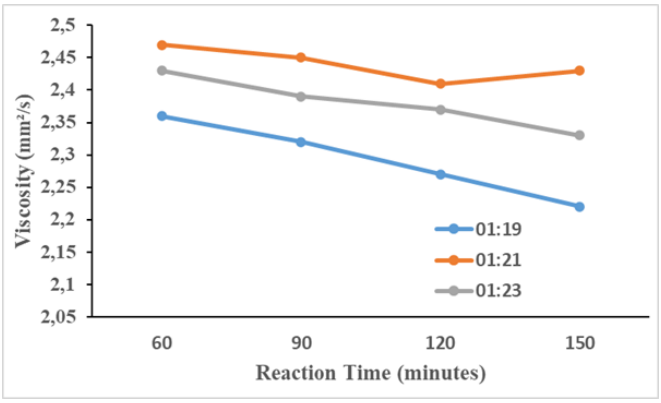


Figure 3. Graph of the Effect of Mole Ratio and Reaction Time on Viscosity

The expected viscosity is the viscosity by the SNI. The results of the study found that the viscosity value was not constant and tended to fluctuate. The expected viscosity is viscosity by SNI standards. If the fuel is too viscous it can make it difficult to flow, pump, and ignite. If the fuel is too watery it is difficult to spread the fuel, making it difficult to burn and will cause leaks in the injection pipe [13].

Composition Analysis of Biodiesel

Qualitative and quantitative analysis is an analysis that can be used to determine the type of fatty acid content in biodiesel and its quantity. Methyl ester biodiesel analyzed by GC-MS showed four dominant peaks, as shown in **Table** 1 and **Figure** 4. The results of Table 1 and Figure 4 show that thermal based on the results of GC analysis, the main fatty acid component in the waste cooking oil sample is at peak 1, namely palmitic acid at 44.14%. At peak 2, namely saturated fatty acid octadecadienoic acid (linoleic acid) at 10.52%, at peak 3, unsaturated fatty acid in the form of octadecenoic acid (oleic) at 43.04%, and the last peak of the results of the analysis with GCMS, namely saturated fatty acid in the form of stearic acid at 2.30% which is the minor fatty acid. Based on the results of the GC-MS test analysis, it can be stated that the data are actual biodiesel compounds, namely methyl esters. This shows that waste cooking oil can produce biodiesel from methyl esters [14].

Table 1. Peak Report TIC

Peak	R.Time	Area	Area, %	Name
1	20.117	3102846	44.14	Methyl Ester, ester, Hexadecenoic Acid
2	23.993	739269	10.52	9,12-Octadecadienoic acid, ME
3	24.227	3024915	43.04	9-Octadecenoic acid (Z), ME
4	24.944	161901	2.30	Octadecenoic acid, ME Methyl stearate,
	Total	7028931	100.00	

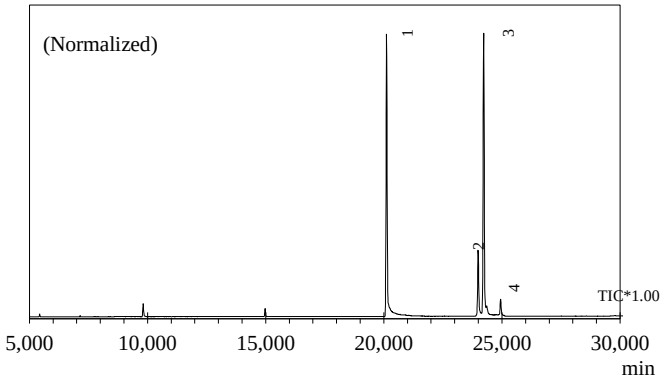
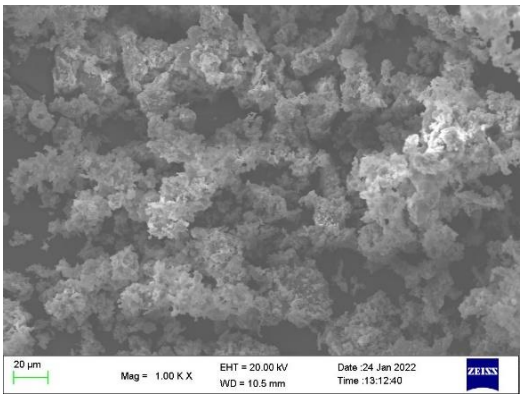


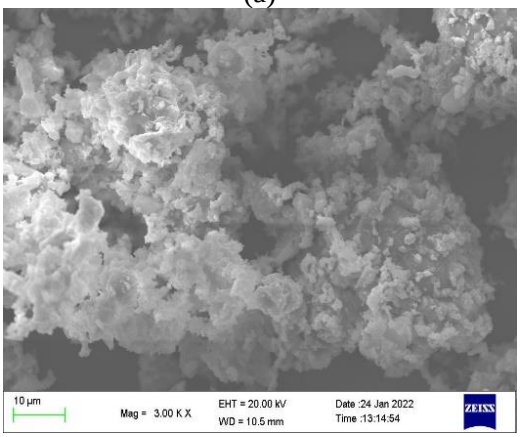
Figure 4. Results of GC-MS Analysis

SEM Analysis of Morphology and Elemental Composition of Catalysts

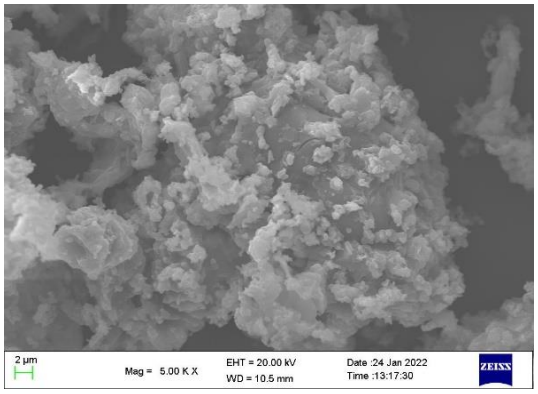
SEM-EDS analysis displays the components in an elemental form, as shown in **Figure** 5.



(a)



(b)



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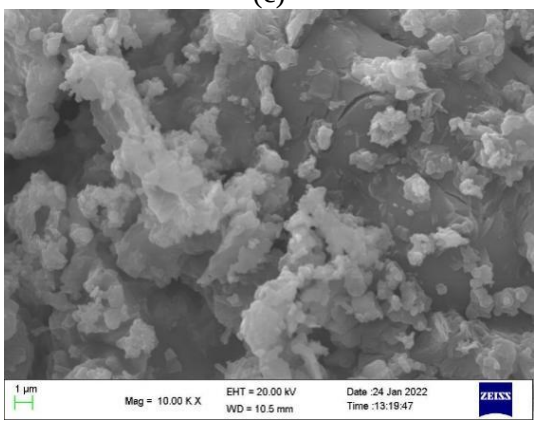

(d)

Figure 5. Photographs of SEM Test Results of Nipah Skin Ash with Magnification (a) 1000× (b) 3000× (c) 5000× (d) 10.000×

The purpose of SEM analysis of Nipah skin ash is to determine the morphological structure of Nipah skin ash. The picture above shows the morphological structure of Nipah skin ash from the SEM analysis. **Figure** 5(a) clearly shows the structure of Nipah skin ash, with a magnification of 1000x and a particle size of 20 µm. Figure 5(b) shows the result of SEM analysis of Nipah skin ash with 3000x magnification with a particle size of 5 µm. **Figure** 5(c) shows the effect of Nipah skin ash with an embellishment of 5000x, with a particle size of 2 µm. Figure 5(d) shows the result of Nipah skin ash with 10000x magnification, Nipah skin ash with a particle size of 1 µm with a slightly concave surface that blends. The catalysts from the experiment tended to be irregularly round in structure.

The results of **Table** 2 and **Figure** 6 show that there are twelve prominent components in this catalyst sample, namely Oxygen, Sodium, Magnesium, Aluminium, Silicon, Phosphorus, Sulphur, Chlorine, Potassium, Manganese and Iron. These components are the components found in Nipah skin ash. This identifies the presence of potassium content, so that Nipah skin ash can be used as a catalyst in the transesterification process to make biodiesel from waste cooking oil, also proven by the formation of methyl ester from waste cooking oil. Preparation of potassium catalyst calcined at 500°C for 4 hours on Nipah skin catalyst can open the pores of the catalyst so that the surface area is getting bigger [15].

Table 2. Elemental Composition of Nipah Skin Ash Catalysts

Element	Unn. C [wt. %]	Norm. C [wt. %]	Atom. C [at. %]
Carbon	1.93	2.14	3.86
Oxygen	39.94	44.28	60.01
Sodium	5.75	6.38	6.01
Magnesium	4.61	5.11	4.56
Aluminium	1.30	1.44	1.16
Silicon	8.29	9.18	7.09
Phosphorus	0.76	0.84	0.59
Sulfur	0.97	1.07	0.72
Chlorine	1.21	1.34	0.82
Potassium	7.05	18.90	10.48
Calcium	6.33	7.02	3.80
Manganese	0.99	1.10	0.43
Iron	1.09	1.21	0.47
Total	90.21	100.00	100.00

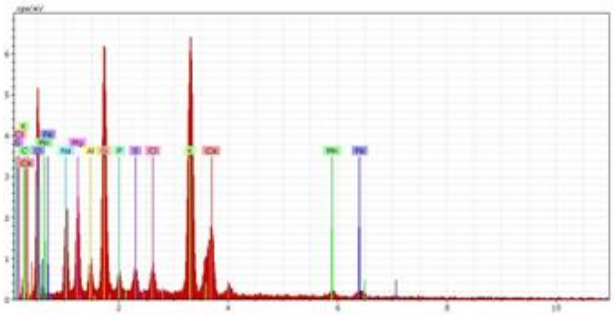

Figure 6. Substance Composition Photograph of Nipah Skin Ash SEM Test Results

CONCLUSION

Nipah skin waste can be used as a heterogeneous catalyst in making biodiesel from waste cooking oil with the highest yield of 93.3598% at a mole ratio of 1:21 with a transesterification reaction time of 150 minutes. The GC-MS test proved that the yield obtained was methyl ester. The primary fatty acids contained in the waste cooking oil raw material were palmitic acid at 44.14% and Octadecenoic acid (oleic) at 43.04%. The characteristics of the biodiesel produced were obtained density and viscosity of 858.7 Kg/m^3.

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REFERENCES

[1] X. Fan, R. Burton, and G. Austic, "Preparation and characterization of biodiesel produced from recycled canola oil", *The Open Fuels and Energy Science Journal*, vol. 2, pp. 113–118, 2019, doi: 10.1007/s10553-010-0225-4.

[2] I. Ibrahim, A. M. Syam, M. Muhammad, and Z Ginting, "Biodiesel production from a mixture of rubber seed oil and waste oil through the alcoholysis process with catalysts based on vegetable waste", *Int. J. Eng. Res. Technol*., vol. 1, no. 4, 2021, doi: 10.52088/ijesty.v1i4.182.

[3] I. M. W. Putra, "Production of biodiesel from waste cooking oil by transesterification process using heterogeneous catalyst". *Nigerian Journal of Environmental Sciences and Technology*, vol. 5, no. 2, pp. 501–510, 2021, doi: 10.36263/nijest.2021.02.0308.

[4] L.C. Meher, V.S.S. Dharmagadda, and S.N. Naik, "Optimization of alkali-catalyzed transesterification of pongamia pinnata oil for production of biodiesel", *Bioresour. Technol.*, vol. 97, pp. 1392–1397, 2016, doi: 10.1016/j.biortech.2005.07.003.

[5] R. D. N. Affandy, T. R. Aruan, Taslim, and Iriany, "Biodiesel production from beef fat by transesterification process with NaOH Base Catalyst, *USU Journal of Chemical Engineering*, vol. 2, no.1, pp. 173-181. 2013. doi: 10.1007/4-540-11394-7_26.

[6] I.S. Dalimunthe, F. Restuhadi, and R. Efendi, "Synthesis of biodiesel from used cooking oil using heterogenous catalyst based on chicken egg shells", *J. Agric. Sci.*, vol. 3, no.2, pp. 1–6, 2016, doi: 10.1016/j.asj.2016.07.135.

[7] J. Jalaluddin, Z. Ginting, and S. Maliki, "Biodiesel production from crude palm oil using kapok skin KOH (Ceiba Pentandra) catalyst as solid green catalyst", *Ecol. Eng.*, vol. 23, no. 5, pp. 286–292, 2022. doi: 10.12911/22998993/147404.

[8] J. Jitputti, B. Kitiyanan, P. Rangsunvigit, K. Bunyakiat, L. Attanatho, and P. Jenvanitpanjakul, "Transesterification of crude palm kernel oil and crude coconut oil by different solid catalysts", *Chem. Eng. J.*, vol. 116, pp. 61–66, 2016, doi: 10.1016/j.cej.2005.09.025.

[9] Y. Liu, Q. Tu, G. Knothe, and M. Lu, "Direct transesterification of spent coffee grounds for biodiesel production". *Fuel*, vol. 199, pp. 157–161, 2017, doi : 10.1016/j.fuel.2017.02.094.

[10] T. E. Agustina, E. Heraldy, and F. Hadiah, "Biodiesel production of palm oil mill effluent by using hydrotalcite catalyst", *J. Ecol. Eng*. vol. 23, no. 6, pp. 172–181, 2022, doi: 10.12911/22998993/148153.

[11] M. Pathak, N. Kalita, D. Baruah, and R. Bhowmik, "Production of biodiesel from waste cooking oil", 5th International Conference on Science Technology Engineering and Mathematics, ICONSTEM, vol. 5, pp. 270–274, 2019, doi: 10.1109/ICONSTEM.2019.8918857.

[12] S. Wahyuni, and R. Mahrizal, "The effect of process temperature and deposition time on the quality of biodiesel from used cooking oil", *Pillar of Physics*, vol. 6, no. 10, pp. 33–40, 2019, doi: 10.16582/11523653/163553.

[13] A. Jumina, Y. Yasodhara, S. Triono, Y.S. Kurniawan, Y. Priastomo, H.M. Chawla, and N. Kumar, "Preparation and evaluation of alpha-cellulose sulfate based new heterogeneous catalyst for production of biodiesel", *J. Appl. Polym. Sci.*, vol. 138, pp. 49658, 2021, doi: 10.1002/app.49658.

[14] S.A. Mantovani, "The effect of catalyst mass and reaction time on the conversion of biodiesel from used cooking oil with CaO catalyst from eggshells", *J. Ind. Eng*., vol. 19, no. 2, pp. 212–222, 2020, doi: 10.13621/22997381/147923.

[15] A. Prihanto, and T.A.B. Irawan, "The effect of temperature, catalyst concentration, and methanol-oil ratio on biodiesel yield from used cooking oil through neutralization-transesterification process". *Methane Journal*, vol. 13, no. 1, pp. 30–36, 2017, doi: 10.1007/4-540-11394-7_26.