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The Effect of Zeolite Catalysis Size on Biodiesel Characteristics of Bio-Oil from Tuna Waste

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ABSTRACT

Indonesia is a country with the third largest tuna production in the world. Fish oil as a fishery product processing waste is a potential material for making biodiesel because it has a high fat content. In this research, biodiesel was made from bio-oil from tuna waste through esterification and transesterification processes at 60°C, stirring speed 360 rpm with a reaction time of 2 hours. The purpose of this study was to determine the levels of Free Fatty Acid (FFA) contained in bio-oil from tuna waste and to determine the effect of the size of the natural zeolite catalyst in the transesterification process on the characteristics of the biodiesel produced. The variables used were the size of the zeolite catalyst 10 - 20, 30 - 40, 50 - 60, 70 - 80, 100 - 120 mesh. From the research results, it can be concluded that the smaller the zeolite catalyst size, the resulting biodiesel is closer to the biodiesel standard and the size of 100-120 mesh which is very close to the SNI 7182: 2015 biodiesel standard with a density value of 849.6 kg/m^3, kinematic viscosity 3,413 cSt, moisture content. 0%, acid number 1.10 mg.KOH /gr, flash point 75 ° C, calorific value 8.240 Cal/gr.

Keywords: Tuna Fish, Catalyst, Biodiesel

INTRODUCTION

The growing need for oil is a challenge that needs to be anticipated by finding alternative sources of energy. Petroleum is a non-renewable energy source, it takes millions or even hundreds of millions of years to convert petroleum raw materials into petroleum, an increase in the amount of petroleum consumption causes the depletion of petroleum. Of the various petroleum refined products used as fuel, the most widely used is diesel fuel, because most transportation means, agricultural equipment, heavy equipment and propulsion of power generators use this fuel.

Indonesia is the world's third largest producer of tuna fisheries, with a contribution of 16 percent of the world's tuna fishery products [1]. Based on statistical data from the Ministry of Marine Affairs and Fisheries in 2011, in Indonesia there are around 114 fish canning companies. Total National Fishery Production is 23.26 million tons, of which captured fisheries are 6.04 million tons, aquaculture is 17.22 million tons. One type of fish that is widely produced is Tuna, in 2016 the production of tuna in Indonesia was 1,129,375 tons [2].

Fish oil as one of fishery product processing wastes is a potential material for making biodiesel (environmentally friendly fuel) because it has a high fat content. The advantage of fish oil when used as a raw material for biodiesel is that apart from having a higher variation of fatty acids compared to other oils or fats, it also has a higher amount of fatty acids. Fish oil carbon chain length reaches 22 and contains more types of unsaturated fatty acids. In principle, there are 3 types of fatty acids derived from fish, namely saturated, monounsaturated and plural unsaturated. Monounsaturated fatty acids contain one double bond and polyunsaturated fatty acids contain many (up to 6) double bonds per molecule [1].

Tuna is one of the most economically valuable fish in the world and also an important predatory species in marine ecosystems. The tuna industry provides thousands of jobs in the fishing, processing and trade sectors worldwide, including in many coastal developing countries, and generates significant income. In 2016, Indonesia was ranked first in the world in tuna production, namely 1,129,375 tonnes [2].

The abundant fish waste, which is around 20-30% can be used again, because it still has a high enough oil content, fish waste contains a lot of very long chain fatty acids with more than 20 carbon atoms, most of which have 5-6 double bonds [4].

Previous research [5] where the results of research on making biodiesel using bayah banten natural zeolite as a heterogeneous catalyst can produce biodiesel with results that meet SNI at an optimum temperature of 60^{o}C. Another research [6] that the biodiesel from baung fish waste can be directly used in diesel engines because the physical and chemical properties meet the characteristics of biodiesel or the Indonesian National Standard. (SNI).

Esterification reaction is a reaction between fatty acids and alcohols to produce esters and water with the help of an acid catalyst. The esterification reaction is a reaction that is reversible.

The transesterification reaction is also a reversible reaction, so that when the reaction has reached equilibrium, the reaction can shift back towards the reactants. In the transesterification reaction, it takes a long time and a high temperature of about 250°C without the help of a catalyst. Therefore the catalyst will help speed up the reaction rate in the transesterification reaction .

The esterification process with an acid catalyst is needed if the oil contains FFA above 5%, if the oil with an FFA content of more than 5% is transecetrified directly with an alkaline catalyst, the FFA will react with the catalyst and will form soap. Soap formed in large enough quantities can inhibit the separation of glycerol from biodiesel and result in the formation of emulsions during the washing process. So esterification is used as a preliminary process to convert FFA into methyl ester so as to reduce the FFA level in vegetable oil and then transesterification with an alkaline catalyst to convert triglycerides into methyl esters [6].

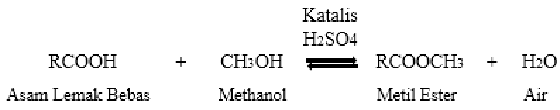

Figure 1. Esterification Reaction [7]

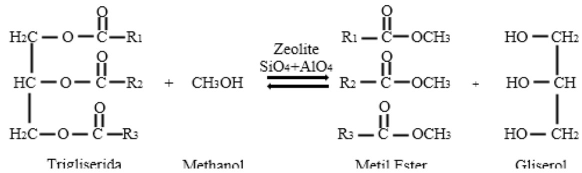

Figure 2. Transterification Reaction [7]

Zeolite is a good catalyst because it has large pores with a wide surface and also has an active side. The presence of an intracrystalline cavity, zeolite can be used as a catalyst. The catalytic reaction is influenced by the size of the mouth cavity and the flow system, because this reaction depends on the diffusion of the reagent and the reaction results [3].

The process of making biodiesel can be through an esterification-transesterification reaction or just a transesterification reaction. Based on the research that has been done, that biodiesel fuel has physical and chemical properties that are almost the same as conventional diesel fuel and also has an energy value that is almost equivalent without making modifications to the diesel engine [9].

Based on the background of the problems above, the following problems isthe level of Free Fatty Acid (FFA) contained in bio-oil from tuna waste. The second is the effect of size variations 10 - 20, 30 - 40, 50 - 60, 70 - 80, and 100 - 120 mesh of catalysts used on the characteristics of biodiesel from tuna fish waste oil .

The scope of this research consists of :

1. The raw material used is tuna fish oil waste. The catalyst used by Bayah's natural zeolite.
2. The transesterification reaction time used is 2 hours.
3. The temperature of the transesterification reaction used is 60 oC.
4. The speed of stirring the transesterification reaction used is 360 rpm.
5. Comparison of methanol versus bio-oil 6: 1.
6. The test is carried out to calculate the FFA content of the raw material and the characteristics tested are viscosity, density, moisture content, flash point, heating value, and acid level.

The objectives to be achieved from this research, first is knowing the levels of Free Fatty Acid (FFA) contained in bio-oil from tuna waste. The second is knowing the effect of variations in sizes 10 - 20, 30 - 40, 50 - 60, 70 - 80, and 100 - 120 mesh of catalysts used on the characteristics of biodiesel from tuna fish waste oil.

RESEARCH METHODS

This research was conducted at the Manufacturing Engineering Laboratory, Mechanical Engineering Department, and Basic Chemical Laboratory, Chemical Engineering Department, Engineering Faculty, Sultan Ageng Tirtayasa University, Cilegon, Banten. The research methodology used is literature study method and experimental method.

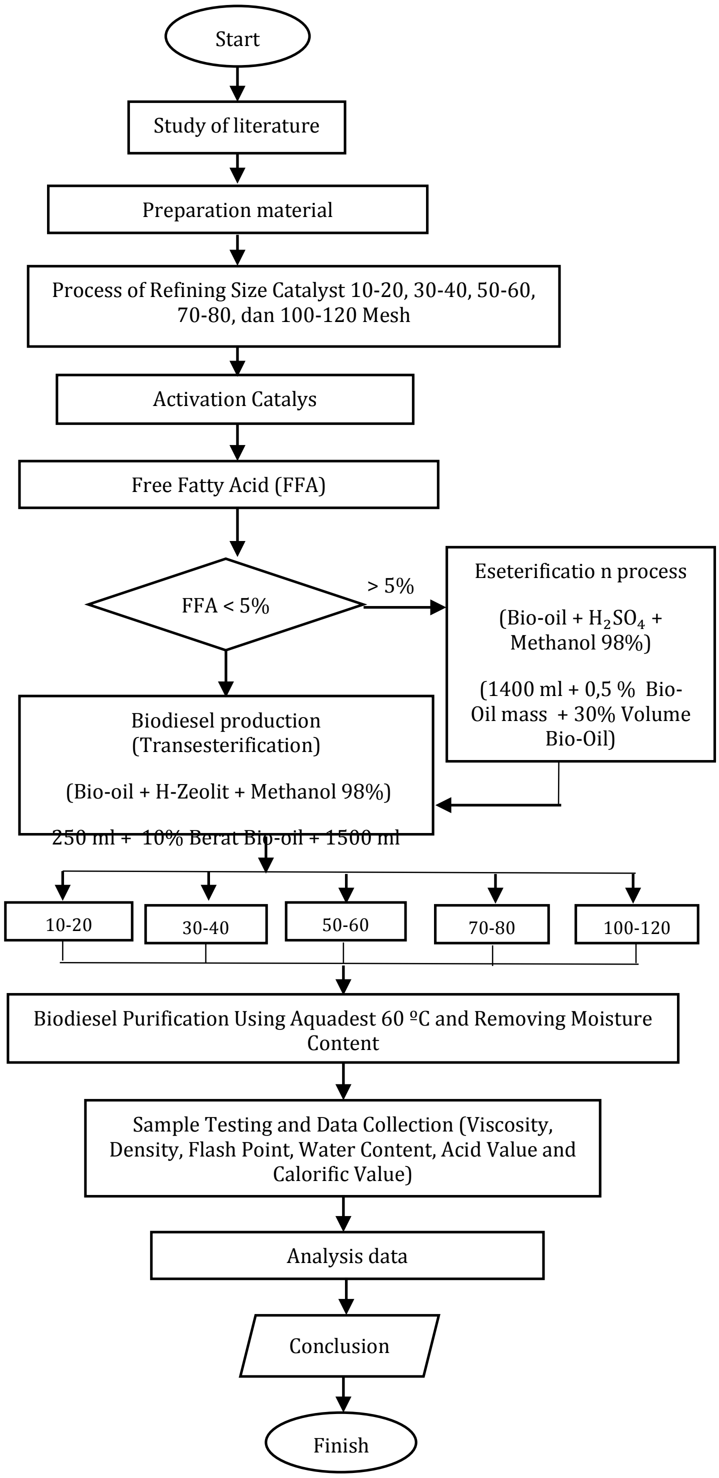

Figure 3. Research procedure

Research Procedure

1. Start Research.
2. Studying the literature on supporting research theories.
3. Prepare tools and raw materials for bio-oil from fishery waste processing in the Muara Angke area, North Jakarta.
4. Smoothing the catalyst by mashing the zeolite from the chunks into smaller sizes, then sieving it with a mesh sieve of 10 - 20, 30 - 40, 50 - 60, 70 - 80, and 100 - 120 mesh.
5. Activation of natural zeolite catalyst in each size of 10 grams is immersed in 100 ml of 1N H_2SO_4 solution and heated for 60 minutes at 120°C. Then washed several times, dry at 110°C for 2 hours.
6. Analysis of free fatty acid (FFA) levels is carried out by adding 50 ml of 98% ethanol to 2.5 grams of tuna fish waste bio-oil, then heating it to a boil while stirring for 10 minutes. Next, add 2-3 drops of the phenoftalein indicator solution and shake the mixture. Tritrate with the drops with 0.1N KOH until the color of the solution is constant pink for 10 seconds. After obtaining the required 0.1N KOH volume, calculate the FFA level.
7. The esterification process is carried out when the free fatty acid content in the raw material is more than 5%. This process aims to reduce levels of free fatty acids in raw materials, done by adding a mixture of Bio-oil 1400 ml + H_2SO_4 0.5% by weight of bio-oil + Methanol (98%) 30% by volume of bio-oil, then heating it to a temperature. 60°C and stirring speed of 245 rpm for 1 hour.
8. The transesterification process is carried out by mixing 250 ml of tuna fish waste bio-oil with 1500 ml methanol plus bayah natural zeolite which has been activated 10% of the bio-oil weight. Heated at 60°C while rotating at 360 rpm for 2 hours.
9. Washing the biodiesel product using distilled water with a temperature of 60°C and then removing the moisture content after the purification process.
10. Testing the characteristics of biodiesel which includes density, viscosity, moisture content, flash point, calorific value, and acid level at the Basic Chemistry Laboratory, Department of Chemical Engineering, Faculty of Engineering, Sultan Ageng Tirtayasa University.
11. Data collection was carried out after completing the characteristic testing of the Basic Chemistry Laboratory, Department of Chemical Engineering, Faculty of Engineering, Sultan Ageng Tirtayasa University.
12. Analyze the results obtained from the biodiesel characteristics test and then proceed to make the final report.
13. Conclude the results of the analysis of the research on the effect of the size of the natural zeolite catalyst.

RESULT AND DISCUSION

Analysis of Tuna Fish Waste Bio-oil Free Fatty Acid Levels

Calculating the levels of ALB contained in raw materials using the following formula [10]:

Percent ALB (%)

$$= \frac{V\,.\,N\,.\,M}{m \times 10} \times 100\ \%$$

$$= \frac{30\ ml\,.\,0,1\ N\,.\,282}{2,5\ gr \times 10} \times 100\%$$

$$= 33,84\ \%$$

Where :

V = volume of KOH required in the sample titration (ml)

N = Normality of KOH solution

M = molecular weight of dominant fatty acid (oleic acid is 282)

m = sample weight (gr)

The levels of Free Fatty Acids (FFA) contained in the Tuna waste bio-oil were 33.84%. The high level of FFA is due to the decay that occurs in the raw material, so the esterification process is needed to reduce the free fatty acid content. After esterification, the free fatty acid content is obtained with the formula :

$$\text{Persentage ALB (\%)} = \frac{V\,.\,N\,.\,M}{m \times 10} \times 100\ \%$$

$$= \frac{4,3\ ml\,.\,0,1\ N\,.\,282}{2,5\ gr \times 10} \times 100\ \%$$

$$= 4,85\ \%$$

The level of free fatty acids (FFA) contained in the tuna waste bio-oil after the esterification process is equal to 4,85 %.

Analysis of Biodiesel Yield Characteristics

1. Density Analysis

Ensity testing was carried out in the Basic Chemistry laboratory, Department of Chemical Engineering, Sultan Ageng Tirtayasa University, using an erlenmeyer tool and an analytical balance type Denver Instrument SI-234.

Based on the graph in Figure 4, it can be seen that the smaller the size of the zeolite catalyst, the density value obtained increases, but it does not meet the requirements of SNI 7182: 2015 [11] biodiesel because the triglycerides that have not been completely converted into methyl esters can be caused by poor biodiesel manufacturing processes.

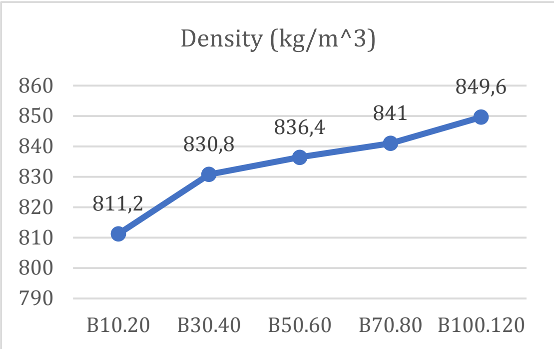

Figure 4. Effect of Catalyst Mesh Size (x) on Biodiesel Density Value (y)

The resulting biodiesel density value is relatively low because the ratio of methanol to bio-oil is more methanol (6: 1) so that the density is lower and is closer to the methanol density of 0.7918 kg/m^3. In Sample B70.80 (841.0 kg / m^3) and B100.120 (849.6 kg / m^3) it is close to SNI 7182: 2015 biodiesel requirements [11].

Viscosity Analysis

The tool used is the SYD-261 PMCC Flash Point Tester. Where the principle of analysis is a number of samples heated with a certain heating while stirring in a closed cup.

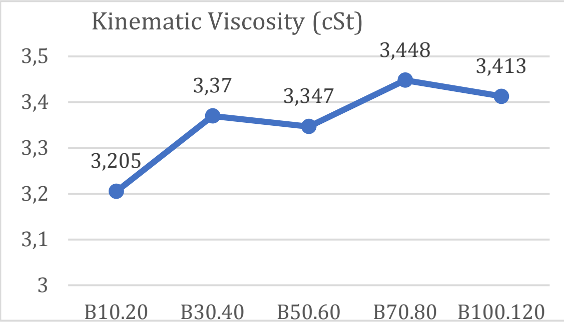

Figure 5. The Effect of Catalyst Mesh Size (x) on the Viscosity Value of Biodiesel (y)

Based on the graph in Figure 5, it can be seen that the effect of the size of the zeolite catalyst on the kinematic viscosity value of the resulting biodiesel forms a fluctuating pattern but tends to increase following the increase in the biodiesel density value.

The viscosity value produced by this biodiesel has met the SNI 7182: 2015 biodiesel standard. This is important, considering that viscosity is a parameter of fuel resistance to flow. A viscosity that is too high will complicate the flow of fuel and can result in incomplete combustion, whereas if it is low it allows leakage and does not have enough lubrication at the injection pump.

Water Content Analysis

Based on the graph above, it can be seen that the use of zeolite catalysts greatly affects the desired product yield target, one of which is the moisture content value which does not exist at all in the biodiesel yield. Due to the nature of activated zeolite, it is dehydrated when heated, which results in the zeolite's pores having no water content and is reversible or can re-tie water in the pores during the transesterification process.

In addition, the moisture content of biodiesel is more influenced by the moisture content in the raw material and the process of removing water content during the biodiesel refining process. Based on the measurement of moisture content, all samples have met the SNI 7182: 2015 biodiesel standard.

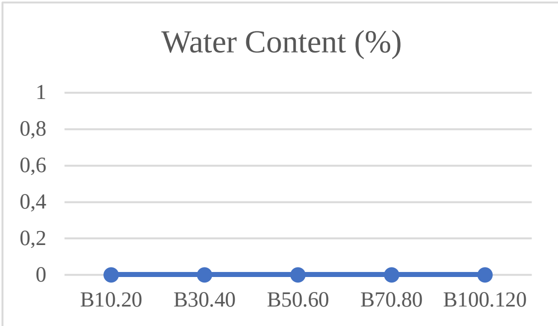

Figure 6. Effect of catalyst mesh size (x) on moisture content of biodiesel (y)

Analysis of Acid Numbers

Based on the graph in Figure 7, it can be seen that the size of the zeolite catalyst is getting smaller, expanding the surface of the zeolite, carrying out adsorption power to absorb a number of free fatty acids in biodiesel because of the ability of the silicate compounds present on the zeolite surface to play a role in the adsorption of water and organic compounds. This has an effect on reducing the acid number of biodiesel. The value of the acid number produced by biodiesel does not meet the SNI 7182: 2015 biodiesel standard. The acid number is influenced by the composition of the fatty acid constituents of the raw material, because the raw material from decaying waste has a high acid value.

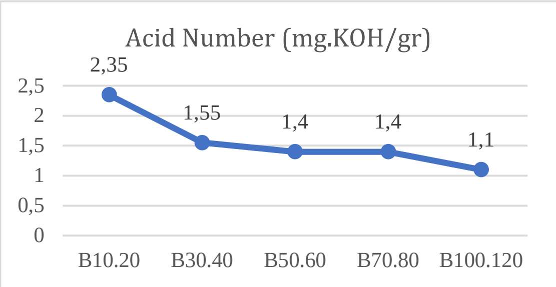

Figure 7. Effect of catalyst mesh size (x) on acid number of biodiesel (y)

Flash Point Analysis

Based on the graph in Figure 4.8, it can be seen that the effect of the smaller zeolite catalyst size on the flash point value forms an upward pattern but is not significant and the flash point value produced by the biodiesel does not meet the SNI 7182: 2015 biodiesel standard.

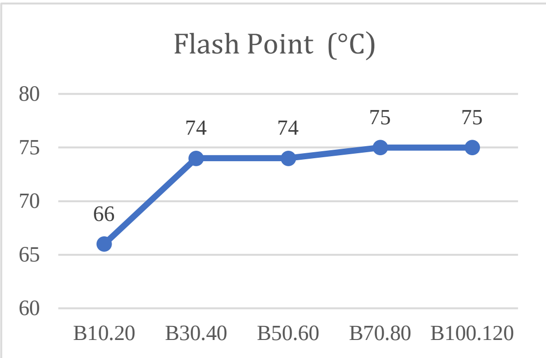

Figure 8. Effect of Catalyst Mesh Size (x) on Biodiesel Flash Point (y)

This is because the conversion of triglycerides into methyl esters is not perfect and the purity of the biodiesel produced is not good. The flash point value tends to be low, this can be because the ratio of methanol to bio-oil is too large for methanol (6: 1) which results in a lower flash point for biodiesel yields, because the flash point for methanol is low around 11-15.6 °C.

Caloric Value Analysis

Based on the graph in Figure 9, it can be seen that the effect of the smaller zeolite catalyst size on the heating value of biodiesel forms a fluctuating pattern but tends to increase.

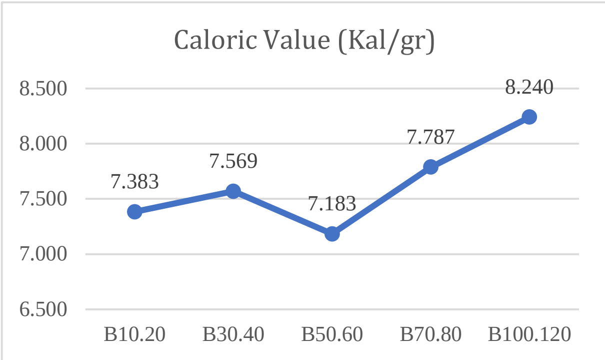

Figure 9 The Effect of Catalyst Mesh Size (x) on the Calorific Value of Biodiesel (y)

This is because the smaller the zeolite catalyst size will increase the surface area of the catalyst which causes the faster reaction rate and multiply the mass transfer rate of the reactants into products. The calorific value of the biodiesel has not met the SNI 7182: 2015 biodiesel standard because the conversion of triglycerides to methyl esters is not yet complete. The calorific value of the resulting biodiesel tends to be low, this can be due to the too large ratio of methanol to bio-oil (6: 1) which can affect the calorific value of biodiesel which tends to approach the calorific value of methanol 5827.83 Kal/gr.

CONCLUSION

Based on the research that has been done, conclusions can be drawn as follows :

1. The level of Free Fatty Acid (FFA) contained in the bio-oil raw material from tuna waste was quite high, namely 33.84%.
2. Density
   All samples have not met the SNI 7182: 2015 biodiesel standard, but the B70.80 (841.0 kg / m ^{3}) and B100.120 (849.6 kg / m ^{3}) samples are close to the SNI 7182: 2015 biodiesel standard. It can be concluded that the smaller the zeolite size, the closer the density value of SNI 7182: 2015.
3. Viscosity
   It can be concluded that all samples meet the SNI 7182: 2015 biodiesel standard, with the smallest value being sample B10.20 (3.205 cSt) and the largest sample being B70.80 (3,448 cSt).
4. Water content
   All samples met the SNI 7182: 2015 biodiesel standard, with a moisture content value of all samples of 0% or not containing water at all. It can be concluded that the use of zeolite catalyst has an effect on the value of the resulting moisture content.
5. Flash Point
   All samples have not met the SNI 7182: 2015 biodiesel standard, with the smallest value being 66°C and the greatest being 75°C. It can be concluded that the smaller the zeolite size, the greater the resulting flash point value.
6. Calorific Value
   All samples have not met the SNI 7182: 2015 biodiesel standard, but the sample B10.120 (8,240 cal / gr) is close to the SNI 7182: 2015 biodiesel standard. It can be concluded that the smaller the zeolite size, the greater the resulting calorific value.
7. The acid number is influenced by the composition of the fatty acid constituents of the raw material, because the raw material from decaying waste has a high acid value.
8. All samples have not met the SNI 7182: 2015 biodiesel standard, with the smallest value being 1.10 mg.KOH / g and the largest being 2.35 mg.KOH / g. It can be concluded that the smaller the zeolite size, the smaller the value of the resulting acid number. The acid number is influenced by the fatty acid composition of the raw material.

REFERENCES

[1]. R. Santos, A. Pabon, W. Silva, H. Silva, and M. Pinho, *Population structure and movement patterns of blackbelly rosefish in the NE Atlantic Ocean (Azores archipelago)*, vol. 29, no. 3. 2020.

[2]. Greenpeace international, “Greenpeace International Annual Report 2018,” no. July, pp. 5–11, 2019.

[3]. B. G. I. Samosir, F. Aulis, and L. Buchori,

"Pengaruh Katalis Asam (H2So4) Dan Suhu Reaksi Dalam Pembuatan Biodiesel Dari Limbah Minyak Ikan," *J. Teknol. Kim. dan Ind.*, vol. 1, no. 1, pp. 474–481, 2012, [Online]. Available: https://ejournal3.undip.ac.id/index.php/jtki/article/view/1091.

[4]. H. H. R.Hartono, Meliana R.S , Nurlaila, Rusdi, Anondho Wijanarko, "Proses Transesterifikasi Menggunakan Katalis Zeolit Alam Bayah," *Semin. Nas. Sains dan Teknol. 2017*, no. November, pp. 1–2, 2017.

[5]. H. Sukiman, Y. Yusnimar, and S. Bahri, "Pembuatan Biodiesel dari Limbah Ikan Baung Dengan Katalis Padat Lempung," *J. Online Mhs. Bid. Tek. dan Sains*, no. Vol 1, No 1 (2014): Wisuda Februari Tahun 2014, pp. 1–8, 2014, [Online]. Available: http://jom.unri.ac.id/index.php/JOMFTEKNIK/article/view/3650.

[6]. Maharani Nurul Hikmah dan Zuliyana, "ESTERIFIKASI DAN TRANSESTERIFIKASI," pp. 1–7, 2011.

[7]. M. N. Hikmah and D. Zuliyana, "Pembuatan Metil Ester (Biodiesel) Dari Minyak Dedak Dan Metanol Estrans," Diponegoro University, 2010.

[8]. B. Wahyudi, N. W. Triana, and E. Mulyadi, "Biodisel Dari Minyak Ikan," *J. Tek. Kim.*, vol. 11, no. 1, pp. 24–27, 2016.

[9]. N. L. Arpiwi, *Diktat Kuliah Bioenergi : Biodiesel Dan Bioetanol*. Prodi Biologi Fakultas Matematika dan Ilmu Pengetahuan Alam Universitas Udayana, 2015.

[10]. S. P. Handayani, "Pembuatan biodiesel dari minyak ikan dengan radiasi gelombang mikro," Universitas Sebelas Maret, 2010.

[11]. A. Wibowo, H. Febriansyah, and S. Suminto, "Pengembangan Standar Biodiesel B20 Mendukung Implementasi Diversifikasi Energi Nasional," *J. Stand.*, vol. 21, no. 1, p. 55, 2019, doi: 10.31153/js.v21i1.736.