Biodiesel characteristics of tuna fish bio-oil waste in the transesterification process with variation of reaction time and stirring speed

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Abstract. Waste from fishery production from canned fish production in Indonesia is very abundant, this waste can be used as raw material for making biodiesel. In this research, the production of biodiesel from tuna oil waste is carried out through the transesterification process. The purpose of this study was to determine levels of Free Fatty Acid, the effect of reaction time and stirring speed on the transesterification process on the characteristics of biodiesel. Fixed variables used consisted of methanol plus bio-oil in a ratio (6:1), methanol at a concentration of 98%, reaction temperature of 60 °C, KOH catalyst weighing 3.5 grams, while the independent variable consisted of the time of transesterification reaction and stirring speed. The variation of transesterification reaction time used is 1, 2, and 3 hours while the variation of the speed of stirring the transesterification reaction is 160, 245, and 360 rpm. The optimal conditions obtained were 2 hours reaction time and 360 rpm stirring speed with biodiesel characteristics, namely a density of 849 kg/m³, viscosity of 3.53 cSt, water content of 0.6%, calorific value of 9,390 cal/g, flash point 84 °C, and acid number 3.6343 mg KOH/g.

1. Introduction
Indonesia is the second largest capture fisheries producer in the world after China (12.24 million tons) with a production volume reaching 6.10 million tons. Followed by the United States (4.89 million tons), Russia (4.46 million tons), and Peru (3.7 million tons) [1]. One type of fish that is widely produced is tuna, in 2016 tuna production in Indonesia amounted to 1,129,375 tons [2].

A large amount of production surely has an impact on the residual waste of the production process which is also large and often causes environmental problems. Waste generated from fisheries activities is around 20-30% of annual fish production, fishery waste products can be in the form of solids, liquids or gases. Fish oil as one of the fisheries processing waste is a material that has the potential for making biodiesel (environmentally friendly fuel) because it has a high fat content [3].

Research on making biodiesel from baung fish waste with solid clay catalyst with variable levels of catalyst and methanol from fish oil. The results of this study were obtained Biodiesel can be directly used on diesel engines because physical and chemical properties have met the characteristics of biodiesel or Standar Nasional Indonesia (SNI) [4].
Research on the amount of reaction and reaction time on biodiesel production from pangasius waste, the hypothesis with variables is the reaction time and the amount of catalyst. The results of this study are, The longer the reaction time, the less the yield and conversion of biodiesel produced due to the reversible nature of the transesterification reaction [5].

This research has a high urgency, the need for this Biofuel is very large and demands fast action steps in accordance with the Minister of Energy and Mineral Resources Regulation No.12 / 2015, which is about the Government's efforts to encourage the use of Biofuel to reduce the consumption of fossil fuels derived from fossil fuels. The government is targeting biofuel to be 30% biodiesel and 20% bioethanol from the total needs of diesel oil and gasoline by 2025. The aim of this research is to determine the effect of reaction time and speed of stirring in the characteristics of biodiesel fuels resulting from the transesterification process.

2. Methodology

2.1 Fuel Preparation and Properties

Based on 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 diesel engines. The use of biodiesel in Europe is done by mixing biodiesel fuel with conventional diesel with a certain ratio which is more due to maintaining the technical factors in the engine for new products and maintaining the quality of the biodiesel cetane number which must be the same or greater [6].

Biodiesel can be used as a diesel mixture because it can be mixed with High Speed Diesel in any composition and can be applied without engine modification. The following is a comparison of the characteristics of biodiesel with diesel oil. There are several standards in the world that regulate the quality of biodiesel for example ASTM (American Society for Testing Material), EN (European Commite for Standadization), and SNI (Standar Nasional Indonesia). The applicable standard for the quality standard of biodiesel in Indonesia is SNI presented in table 1.

| Properties                      | Standard     | Test Methods          |
|--------------------------------|--------------|-----------------------|
| Density [kg/m³] at 40 oC        | 850-890      | ASTM D 1298 or D 4052 |
| Kinematic Viscosity [cSt] at 40°C and 1 Atm | 2,3 - 6,0   | ASTM D 445            |
| Cetane number, min              | 51           | ASTM D 613 atau D 6890|
| Flash Point °C, min             | 100          | ASTM D 93             |
| Acid Number mg-KOH/g, max       | 0,5          | ASTM D 664            |
| Water Content % Vol, Max        | 0,05         | ASTM D 2709           |
| Higher heating value [kJ/kg]    | 46,10        | ASTM D 5865           |

Source: ASTM International

2.2 Biodiesel Process

Basically the process of making biodiesel is very simple. Biodiesel is produced through a process called free fatty acid esterification reaction or triglyceride transesterification reaction with alcohol with the help of a catalyst and from this reaction methyl esters / ethyl esters of fatty acids and glycerol are
produced. The process of esterification with an acid catalyst is required if the oil contains an FFA above 5%, if the oil that has a FFA content of more than 5% is transfetified directly with a basic catalyst [7].

Esterification reaction is a reaction between fatty acids with alcohol to produce esters and water with the help of an acid catalyst. The esterification reaction is also a reaction that is reversible (reversible). The purpose of the esterification reaction is to reduce the content of free fatty acids in the ingredients [5].

\[
\text{RCOOH} + \text{CH}_2\text{OH} \rightleftharpoons \text{RCOOCH}_3 + \text{H}_2\text{O}
\]

Figure 1. Esterification reaction

Transesterification reaction is a reversible reaction, so if the reaction has reached equilibrium, the reaction can shift back toward the reactants. Transesterification is the conversion stage of triglycerides (vegetable / animal oils) to alkyl esters, through reaction with alcohol, and produces a by-product, glycerol. Triglycerides through the transesterification reaction with glycerol are converted into monoglycerides and diglycerides with the help of catalysts such as sodium methoxide and other Lewis bases [5].

Figure 2. Transesterification reaction

Factors that influence biodiesel production include reaction time, ratio of alcohol to oil, catalyst type, temperature, stirring, settling time, water content, methanol, biodiesel quality standard.

2.3 Properties Biodiesel Testing
2.3.1 Free Fatty Acid Testing

The raw material is first analyzed its free fatty acid levels, if the raw material used contains high free fatty acid levels (FFA) which is more than 5%, then the esterification process is necessary to reduce the levels of free fatty acids to less than 5%. The test is carried out by titration using KOH 0.1 N. The first stage is to put as much as 10 ml of sample into the erlenmeyer. Next we add 10 ml of 95% alcohol and heat it to a temperature of 50°C while stirring. After heating, drops with a solution of phenolphthalein indicator as much as 2-3 drops, shake the mixture. Final titration with 0.1N KOH until the color of the sample turns pink which does not disappear for 10 seconds indicates the end point of the titration. Calculate the levels of FFA contained in raw materials using the following formula:

\[
\text{FFA (\%)} = \frac{V \times M \times M_m}{m} \times 100\%
\]

2.3.2 Density Testing
Density testing was carried out at the Basic Chemistry Laboratory, Department of Chemical Engineering, Faculty of Engineering, Sultan Ageng Tirtayasa University. The first stage of the 100 ml erlenmeyer is weighed empty. Then the sample is put into 25 ml erlenmeyer, then the sample is weighed. The result of density testing is the scale of the sample divided by 25 ml.

2.3.3 Viscosity Testing

Viscosity testing is carried out using a viscometer. The obtained viscosity value is the value of dynamic viscosity, it is necessary to convert to kinematic viscosity with the following equation:

$$\nu = \frac{\mu}{\rho} \quad (2)$$

where $\nu$ is kinematic viscosity (cSt), $\mu$ is dynamic viscosity (poise) and $\rho$ is density (g/cm$^3$)

2.3.4 Water Content Testing

Water Content testing is carried out using the toluene distillation method. The first stage is by weighing a sample of 25 ml, then the sample is inserted into the distillation flask. Then 75 ml of toluene solution is added, then put the distillation flask in a special distillation device with a reservoir of evaporating water. The next stage is to set the distillation heating temperature to 80 °C. The distillation process is carried out for 1 hour, the water will drip and be collected by a measuring cup.

2.3.5 Caloric Value Testing

Analysis of the heating value of a fuel is intended to obtain data about the heat energy that can be released by a fuel by the reaction or combustion process. The amount of heat is measured in calories and is produced when a briquette is oxidized completely in a bomb calorimeter. The size of the sample does not exceed 1.5 mg, testing is done by measuring the temperature of the initial and final conditions of the sample on the test equipment.

2.3.6 Flash Point Testing

Flash point testing is performed using the SYD-261 PMCC Flash Point Tester. Where the principle of analysis is a number of samples heated with a certain heating speed while stirring in a closed cup. The ignition test starts at every 3 °C temperature rise by bringing the igniter closer to the sample surface, until the flash point is detected.

3. Results and discussion

3.1. FFA Content

| No | V (ml) | N  | M   | M (gr) |
|----|--------|----|-----|--------|
| 1  | 29     | 0,1| 28,2| 2,5    |
| 2  | 31     | 0,1| 28,2| 2,5    |
| 3  | 30     | 0,1| 28,2| 2,5    |

From the table 2, using equation 2.3.1, the FFA value is 33.84%. High levels of FFA are caused by spoilage that occurs in the raw material, so the esterification process is needed to reduce the free fatty acid levels.

The esterification process was carried out by adding a 98% mixture of methanol as much as 30% by volume of bio-oil and HCL 32% by 1% by weight of bio-oil into 1400 ml bio-oil. The esterification
reaction time is 60 minutes with a stirring speed of 245 rpm at 60 °C. The results of FFA levels of raw materials after esterification process are as follows:

Table 3. Free fatty acid (FFA) after esterification

| No | V (ml) | N | M | M (gr) |
|----|--------|---|---|-------|
| 1  | 4.60   | 0.1| 28.2  | 2.5   |
| 2  | 4.60   | 0.1| 28.2  | 2.5   |
| 3  | 4.59   | 0.1| 28.2  | 2.5   |

Using equation sub bab 2.3.1, the FFA value is 5.18%. The esterified bio-oil is then transesterified.

3.2 Biodiesel Production Results (Transesterification)

The biodiesel process is carried out with a composition of 250 ml bio-fish oil and 98% methanol mixture of 1500 ml and KOH weighing 3.5 grams. Transesterification reaction carried out with fixed variables is the reaction temperature of 60 °C with the independent variables being the reaction time and stirring speed. The reaction time used is 1, 2 and 3 hours, the stirring speed used is 160, 245 and 360 RPM. There are 9 samples where each sample has a different treatment, the results of biodiesel and byproducts can be seen on the table as follows:

Table 4. Experimental data transesterification production.

| Sample | Time (hours) | RPM | Biodiesel (ml) | Glycerol (ml) | Visual Appearance |
|--------|--------------|-----|----------------|--------------|------------------|
| 1      | 1            | 160 | 800            | 50           | Turbid-light     |
| 2      | 1            | 245 | 800            | 75           | Turbid-light     |
| 3      | 1            | 360 | 650            | 100          | Dark-Turbid     |
| 4      | 2            | 160 | 430            | 120          | Turbid-light     |
| 5      | 2            | 245 | 450            | 130          | Light           |
| 6      | 2            | 360 | 380            | 150          | Light           |
| 7      | 3            | 160 | 330            | 130          | Light           |
| 8      | 3            | 245 | 350            | 150          | Turbid-light     |
| 9      | 3            | 360 | 320            | 170          | Dark-Turbid     |

From the visual appearance in table 4, with a stirring time of 2 hours showed a lighter appearance close to SNI standard biodiesel and considered the most ideal time for stirring. The longer the stirring time of biodiesel produced is reduced and the glycerol production increases.

3.3 Biodiesel Characteristics

3.3.1 Density Analysis
Based on these figure 3, it can be seen that the reaction time fluctuates with the density of biodiesel produced because it is caused by the nature of the transesterification reaction which when it reaches an equilibrium point then the reaction can reverse. While the stirring speed affects the resulting density increases. Increasing the stirring speed will accelerate the movement of molecules and increase the chance of collisions between molecules so that the reaction speed increases. The biodiesel density that is closest to the requirements of biodiesel SNI 7182: 2015 (850-890 kg / m³) is sample 6 with a variation of 2 hours, 360 RPM.

3.3.2 Viscosity Analysis

| Sample | Dynamic Viscosity (mPa.s) | Kinematic Viscosity (cSt) |
|--------|--------------------------|--------------------------|
| 1      | 2                        | 2,54                     |
| 2      | 2                        | 2,52                     |
| 3      | 2                        | 2,51                     |
| 4      | 3,5                      | 4,19                     |
| 5      | 3                        | 3,59                     |
| 6      | 3                        | 3,53                     |
| 7      | 3                        | 3,69                     |
| 8      | 2,8                      | 3,44                     |
| 9      | 3                        | 3,54                     |

Based on the table 5 The effect of reaction time on the viscosity of biodiesel produced fluctuates to form an up and down pattern caused by the nature of the reversible transesterification reaction. While the effect of stirring speed on the viscosity of biodiesel is likely not to affect the viscosity produced because the density of biodiesel produced is not too much different. The viscosity value of the biodiesel produced meets the SNI 7182: 2015 biodiesel standard (2.3 - 6.0 cSt).
3.3.3 Water Content Analysis

Reaction time affects the water content in biodiesel, the longer the reaction time the smaller the water content contained in biodiesel. Presented in figure 5, while the stirring speed does not significantly affect the biodiesel produced. The biodiesel water content is more influenced by the water content in the raw material, the accuracy of the washing process in the separating funnel, and the process of removing the water content in the biodiesel purification process. Based on measurements of water content of samples 7.8, and 9 have met the SNI 7182: 2015 biodiesel standard (max 0.05). However, samples 1,2,3,4,5, and 6 have not met.

3.3.4 Caloric Value Analysis

The difference in the heating value of each biodiesel treatment but not too significant. The heating value is influenced by the density and composition of the fatty acid constituents. The heating value for Samples 4,5,6, and 9 has fulfilled the SNI 7182: 2015 biodiesel standard (8,880 cal / gr),
3.3.5 Flash Point Analysis

Based on figure 7, it can be seen that the reaction time fluctuates to the flash point of biodiesel produced due to transesterification reactions that can be reversed when the reaction experiences equilibrium. While the stirring speed influences the flash point of the biodiesel produced. The flash point value produced by the biodiesel does not meet the standards of biodiesel SNI 7182: 2015 (min 100 °C).

3.3.6 Acid Number Analysis
Figure 8. Time reaction and RPM effect to flash point

Based on the figure 8, it can be seen that the reaction time fluctuates with the number of biodiesel acids produced because the transesterification reaction can be reversed when the reaction is in equilibrium. While the stirring speed has no effect on the number of biodiesel acids produced. Acid numbers are influenced by the composition of fatty acid constituents of raw materials. The value of acid numbers produced by biodiesel does not meet biodiesel standards SNI 7182:2015 (max 0.5).

4. Conclusion

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

1. The level of Free Fatty Acid (FFA) contained in the bio-oil raw material from Tuna fish waste is quite high at 33.84%.
2. Biodiesel from Tuna fish bio-oil cannot be used in diesel engines because the acid level of the raw material does not meet the SNI 7182:2015 biodiesel standard and Pertamina's diesel standard which can damage the engine. Utilization of Bio-oil as a mixture of making biodiesel fuels can improve the quality characteristics of methanol as fuel.
3. The optimum treatment in this study was 2 hours, 360 RPM.

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References

[1] Food And Agriculture Organization Of The United Nations 2018 The state of world fisheries and aquaculture ISBN 978-92-5-109185-2.
[2] Batungbacal, Ephraim Dan Mitchell, James 2018 From sea to can 2018 southeast asia canned tuna ranking GREENPEACE
[3] Tri Nugroho 2010 Pemanfaatan minyak ikan untuk produksi biodiesel squalen
[4] Hernanda, Sukiman, Dkk 2014 Pembuatan biodiesel dari limbah ikan baung dengan katalis padat lempu Jurnal Online Mahasiswa (JOM) Bidang Teknik Dan Sains
[5] Moeksin, Rosdiana, Dkk. 2016. “Pengaruh Jumlah Katalis Dan Waktu Reaksi Terhadap Produksi Biodiesel Dari Limbah Pangasius Hypothalamus”.

[6] Arpiwi, Ni Luh 2015 Diktat kuliah bioenergi: biodiesel dan Bioetanol Prodi Biologi Fakultas Matematika Dan Ilmu Pengetahuan Alam Universitas Udayana

[7] Hikmah, M.N., Zuliyana 2010 Pembuatan metal ester (biodiesel) dari minyak dedak dan metanol dengan proses esterifikasi dan transesterifikasi Skripsi Semarang Universitas Diponegoro.