

Characterization and Production of Environmentally Friendly Biodiesel from Patin Fish

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ABSTRACT

Energy consumption in Indonesia increases annually but fossil fuel reserves are limited. Biodiesel is an environmentally friendly fuel that has physical and chemical properties similar to that of diesel. Biodiesel can be made from animal oil, one of which is oil derived from the waste of patin fish. This research aims to determine the effect of reaction time on the biodiesel characteristics produced to comply with SNI 7182-2015. Patin fish oil was obtained by steaming, pressing, and boiling and then oil obtained was purified by a solution of 2.5% v/v NaCl. Biodiesel was made using the transesterification process with the mole ratio of Patin fish oil:Methanol at 1:4, the temperature of 55°C, and the KOH catalyst of 0.5% w/w patin fish oil. The biodiesel production process was done with three variations of reaction time, i.e. 1 hour, 2 hours, and 3 hours. Determining the value of oxidation stability was done by the Rancimat method with a temperature of 110°C. Biodiesel produced was tested its characteristics of density, viscosity, moisture content, acid number, and oxidation stability. The parameter that already meets the standard is viscosity. The best reaction time of biodiesel production in this study is 3 hours, producing density, viscosity, acid number, and moisture content of 942.62 kg/m³, 4.173 cSt, 0.5534 mgKOH/g, and 5.79%, respectively. However, the best oxidation stability of 7 minutes was obtained from the reaction time of 2 hours.

Keywords: Biodiesel; patin fish waste; transesterification; reaction time

1. INTRODUCTION

Energy consumption in Indonesia increases every year but fossil fuel reserves are limited. Increasing energy consumption will increase imports and subsidies to meet domestic energy needs [1]. Based on Government Regulation no. 79 year 2014, regarding the National Energy Policy, the need for petroleum, new and renewable energy (EBT), coal and gas will cumulatively increase almost 5 times over the 2015-2050 period. An increase in energy use will result in an increase in air pollution. Therefore, it is necessary to conduct research on renewable fuels that are environmentally friendly, one of which is biodiesel.

Biodiesel in Indonesia is generally made from crude palm oil (CPO) which comes from palm oil. The increase in the

use of biodiesel results in an increase in the need for CPO as the basic material for its manufacture. In addition, the need for CPO also competes with the need for food as a raw material for making consumption oil. As a result, there will be an increase in carbon emissions due to meeting the need for CPO as a raw material for making biodiesel [2].

A waste that can replace CPO as a raw material for making biodiesel is patin fish waste. Patin fish waste can produce oil that contains triglycerides, where the oil can be reacted with alcohol compounds to form biodiesel. The patin fish waste was chosen as the raw material for biodiesel production in this research because of the large amount of patin fish production, resulting in waste that can pollute the environment. Based on data from the Ministry of Marine Affairs and Fisheries [3], patin fish

production in 2016 increased by 22.4% or 98,042 tons compared to production in 2015, while in 2018 patin fish production became 604,587 tons. Therefore, this study was conducted to determine the best time and characteristics of biodiesel produced from fish oil of patin fish waste, as a base material through a transesterification reaction. The biodiesel produced was compared with the requirements of SNI 7182-2015.

2. THEORY

2.1 Biodiesel

Biodiesel is an alternative fuel as a substitute for diesel fuel which is made from vegetable oil or animal fat. Chemically, biodiesel is a lipid derivative of the monoalkyl ester group with a carbon chain length of 12-20 [4].

Biodiesel has physical properties close to diesel so that it can be used as an alternative fuel for diesel engines [5]. In addition, biodiesel has advantages over fossil fuels, namely the raw material for making biodiesel can be renewed (renewable), use more efficient energy, and reduce toxic air emissions. [6].

2.2 Patin Fish Waste

One of the main materials for producing biodiesel is fish oil. In this study, oil derived from patin fish waste. Fish oil is an oil produced from fresh fish or fish waste such as fish offal, heads, bones and even fishtails through heating and pressing processes. Patin fish oil contains the highest saturated fatty acids, namely palmitic acid by 30.6% and the highest unsaturated fatty acids, namely oleic acid by 51.57% [7].

2.3 Transesterification Reaction

The process of making biodiesel can be done through an esterification or transesterification reaction. Oil containing high free fatty acids can be made into biodiesel through an esterification reaction followed by a transesterification reaction to convert the remaining triglycerides [8]. If the oil has a free fatty acid content of < 2%, biodiesel production can be done directly through a transesterification reaction [9]. Patin fish oil has a low free fatty acid content of 0.55% so that biodiesel made from patin fish waste can be made directly through a transesterification reaction. [10].

The transesterification reaction is a reaction between triglycerides and alcohol with the help of an alkaline or acid catalyst to produce glycerol and esters. In the transesterification reaction, there is a change in the position of fatty acids to produce new esters. The transesterification

process usually uses an alkaline catalyst such as KOH or NaOH, because the reaction is very fast, perfect, and can be carried out at low temperatures, namely 55-60°C. The transesterification reaction stages are shown in Figure 1 [11].

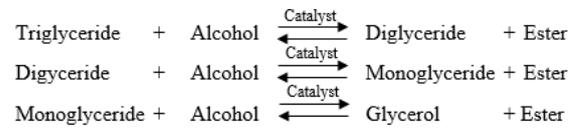


Figure 1 Transesterification Reaction Stages [11]

2.4 Biodiesel Quality Standards Based on SNI 7182 – 2015 and EN 14214

The requirements for the quality of biodiesel in Indonesia are contained in SNI 7182-2015 [12]. Another standard that is commonly used to check the quality of biodiesel is the European EN 14214-2012 [13]. The standard values of various important parameters in the biodiesel quality standard to be analyzed in this study can be seen in Table 1 and Table 2.

Table 1 Biodiesel Quality Standards Based on SNI 7182-2015

Parameters	SNI-7182-2015
Density at 40°C (kg/m ³)	850-890
Kinematic Viscosity at 40°C (cSt)	2.3–6.0
Water and Sediment (% volume)	Max 0.05
Acid Number (mgKOH/g)	Max 0.5
Oxidation Stability (minutes)	480

Table 2 Biodiesel Quality Standards Based on EN 14214-2012

Parameters	EN 14214-2012
Density at 15°C (kg/m ³)	860-900
Kinematic Viscosity at 40°C (cSt)	3.5-5.0
Water Content (mg/Kg)	Max 500
Acid Number (mgKOH/g)	Max 0.5
Oxidation Stability (minutes)	360

3. METHOD

3.1 Preparation of Patin Fish Waste

Patin fish waste (*Pangasius sp.*), namely fish heads, was obtained from the ITC market, Kebon Kalapa, Bandung, Indonesia. After cleaning the fish waste, it is ready to be steamed and pressed.

3.2 *Steaming, Pressing, and Boiling*

The waste of the patin fish head is steamed using a steamer for 1 hour. The pressing process after steaming is carried out to remove the fat/oil and water in the fish waste. The pressed fish still contains oil, so it is boiled for 15-30 minutes to extract the oil.

3.3 *Separation and Purification*

The separation process is carried out for 24 hours to separate 2 layers, namely the upper part which is fish oil and the bottom part which is impurity. The upper part in the form of fish oil was purified with a 2.5% v/v NaCl solution [14] to remove oil-soluble impurities.

3.4 *Analysis of Physical Properties of Patin Fish Oil*

Analysis of the physical properties of patin fish oil is to determine the level of FFA. The determination of free fatty acid (FFA) is conducted by the titration method using standard 0.1 N KOH solution and phenolphthalein (PP) indicator.

3.5 *Homogenisation of Catalysts and Methanol*

The transesterification reaction will not take place well if the mixture is not homogenized, especially during the early stages of the process [15]. The homogenization process is a process of mixing 0.5% w/w KOH catalyst and methanol, using a magnetic stirrer [16].

3.6 *Transesterification by Stirring and Heating*

The transesterification process is carried out after the KOH homogenization process with methanol has been conducted. This transesterification process uses a stirring motor in a three-neck flask with varied reaction times of 1 hour, 2 hours and 3 hours. This process is carried out at a temperature of 55°C using an anchor stirrer. During the process, cooling water flows to the condenser [7] [16].

3.7 *Separation and Purification*

Biodiesel separation is carried out in a separating funnel. To prevent oxidation, the entire surface of the separating funnel is covered using aluminum foil. The reaction mixture forms two insoluble layers, namely the top layer is biodiesel while the bottom layer is glycerol. The reaction mixture is left for

± 24 hours at room temperature and pressure and then separated. Biodiesel is washed using distilled water (60-80°C) with a ratio of 1: 1, the pH of the washed distilled water must be the same as the pH of the original distilled water. After washing, anhydrous salt is added to allow the drying process to occur.

3.8 *Induction Period (IP) Determination using the Rancimat Method*

The IP values are determined using the Rancimat method, namely by injecting a certain amount of heat and oxygen. In this determination process, the air is flowed and brought into contact with the biodiesel sample which is placed in a closed vessel and conditioned at a temperature of 110°C.

4. RESULTS AND DISCUSSION

4.1 *Patin Fish Oil as Raw Material for Biodiesel Production*

The yield of patin fish oil from the pressing process was 9.14 ml from every kg of patin fish head. From the boiling process, it was obtained patin fish oil of 20.3 - 37.6 ml from every kg of patin fish head. The total amount of patin fish oil produced was 1,207 ml from 46 kg of patin fish heads.

4.2 *Patin Fish Oil Characteristics Determination*

Before making biodiesel, it is necessary to measure the density, viscosity and free fatty acids of patin fish oil. The results of these measurements are presented in Table 3.

Table 3 Physical Properties of Patin Fish Oil

Parameters	Results
Density at 40°C (kg/m ³)	984.60
Kinematic Viscosity at 40°C (cSt)	30.4072
Free fatty acid (FFA, %)	0.987

Based on Table 3, it is shown that patin fish oil has a low free fatty acid (FFA) content of 0.987%. Therefore, the process of making biodiesel can be done by means of the transesterification process.

4.3 Biodiesel Production

The process of biodiesel production was carried out by means of the transesterification process. The molar ratio of patin fish oil to methanol used for this study was 1:4. The addition of the KOH catalyst was 0.5% w/w of patin fish oil. The KOH catalyst was mixed with methanol to accelerate the reaction to form methyl esters. The catalyst will bind water.

4.4 Determination of Biodiesel Characteristics

The biodiesel obtained was tested for the density value at 40°C, viscosity at 40°C, acid number, moisture content, and the values of oxidative stability. The test results were compared with SNI Biodiesel 7182-2015 and EN 14124-2012, which are described as follows:

4.4.1 Biodiesel Conversion

The transesterification reaction of biodiesel production affects the reaction time. The graph of biodiesel conversion to reaction time variations is presented in Figure 2.

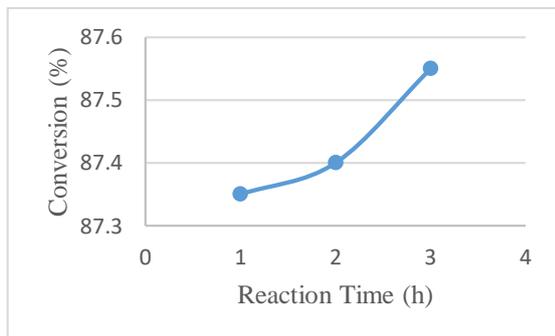


Figure 2 Reaction Times versus Biodiesel Conversion

Based on Figure 2, the transesterification reaction time affects the yield of biodiesel conversion. The largest conversion was obtained at the reaction time for 3 hours, namely 87.55%. This is because the longer the reaction time, the more reactant particles will collide with each other [17]. Based on the research results, the longer the reaction time, the higher the biodiesel conversion produced. This is in accordance with Le Chatelier's principle, namely that the shift in equilibrium is influenced by changes in volume, temperature, partial pressure and concentration, while the reaction time only represents the time when equilibrium is reached. [18].

4.4.2 Density of Biodiesel

Figure 3 shows that the resulting biodiesel density at 40°C does not show a significant difference to the variations in reaction time. The density of biodiesel after 3 hours of reaction is greater than the requirements of SNI 7182-2015 and EN 14214-2012.

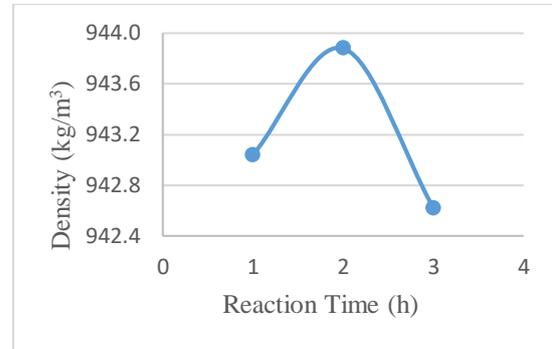


Figure 3 Reaction Times versus Biodiesel Density

Based on biodiesel density standards, 942.62 kg/m³, the biodiesel produced in this study did not meet the standards [19]. Biodiesel which has a density exceeding the provisions will increase wear on the engine, and it will also produce high emissions. The high-density values obtained in this study are probably caused by incomplete washing and purification processes. The presence of glycerol in biodiesel affects biodiesel density because glycerol has a high density of 1.26 g/cm³ [20], so that if the glycerol is not properly separated from biodiesel, the biodiesel density will increase.

4.4.3 Kinematic Viscosity of Biodiesel at 40°C

The graph of the viscosity of biodiesel against the variations in reaction time is presented in Figure 4.

The kinematic viscosity of the resulting biodiesel decreases with the increase in the variations of the transesterification reaction time.

In Figure 4, it can be seen that the reaction time is inversely related to the kinematic viscosity of the biodiesel produced. Research by [21] found that the viscosity of biodiesel decreased with the length of reaction time and the increase of reaction temperature. The decrease in the viscosity of biodiesel in this study occurs because with the increase in reaction time, more triglyceride molecules react to become biodiesel.

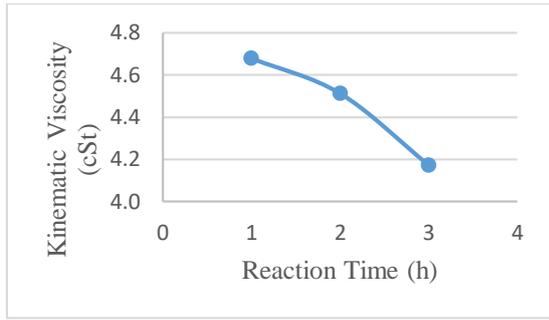


Figure 4 Reaction Times versus Kinematic Viscosity of Biodiesel

Triglycerides with a higher molecular weight than biodiesel have a higher viscosity. With increasing reaction time, the triglycerides are reduced and more biodiesel is produced so that the viscosity decreases with increasing reaction time. The difference in viscosity between 2 hours and 3 hours of reaction time is 33.90%. In this study, 3 hours reaction time is 33.90%. In this study, 3 hours produced the best viscosity of biodiesel. The kinematic viscosity values of biodiesel in this study were 4.678, 4.512, and 4.173 cSt, respectively, so that they meet SNI 7182-2015 and EN 14214-2012.

4.4.4 Acid Number of Biodiesel

The acid number can be defined as the mass of potassium hydroxide (KOH) in milligrams needed to neutralize free fatty acids (FFA) in one gram of sample [7]. The acid values of biodiesel obtained in this study decrease with increasing reaction times (Figure 5).

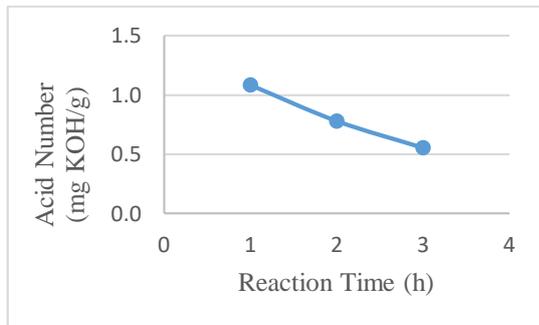


Figure 5 Reaction Times versus Acid Number of Biodiesel

Figure 5 shows that the reaction time is inversely proportional to the acid number of biodiesel produced. The longer the reaction time results in the lower acid number of biodiesel produced. The acid numbers in biodiesel produced in this study were 1.085, 0.5534, and 0.7804 mgKOH/g, at 1 hour, 2 hours, and 3 hours of reaction time, respectively. The resulting biodiesel acid value is still higher than the standard, which is a maximum of 0.5 mg KOH/g. This shows that the biodiesel produced still has a high acid content so that it cannot be used as a mixture of diesel oil. The high acid number in biodiesel obtained in this study is probably caused by the use of technical grade methanol

(30% water content) as a reagent. As a result, the reaction is less than perfect. [22].

4.4.5 Water Content and Sediment of Biodiesel

Water content affects the quality of the biodiesel produced. The graph of biodiesel moisture content against variations in transesterification reaction time is presented in Figure 6.

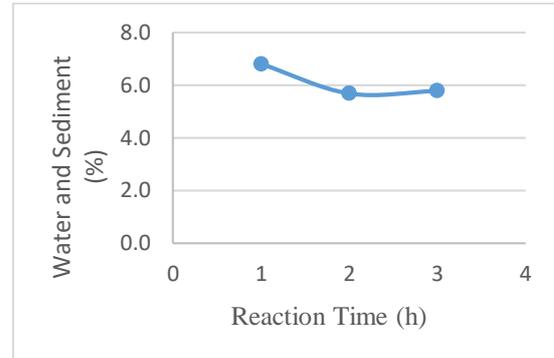


Figure 6 Reaction Times versus Water Content of Biodiesel

In this study, it was found that the moisture and sediment contents were 5.69%, 5.79%, and 6.82%, respectively (Figure 6). They did not meet the biodiesel standards. The high moisture content obtained in biodiesel might be caused by incomplete separation and drying processes. In addition, the moisture content of biodiesel is more influenced by the physical characteristics of the initial fish oil as a raw material for making biodiesel. The high moisture content of biodiesel can cause microbes to easily grow, pollute biodiesel, increase the acid number and cause corrosion in the engine. [20].

4.4.6 Oxidation Stability of Biodiesel

The standard value of oxidation stability for biodiesel according to SNI 7182-2015 is at least 480 minutes. In this study, the value of oxidative stability at the time variations of 1 hour, 2 hours, and 3 hours were 5 minutes, 7 minutes and 5 minutes, respectively. It means that these values did not meet the standard. This is in line with research [23]. In their research, biodiesel made from oil from fish canning industry waste has a low oxidation value of around 1.05-2.22 hours. The low induction period (IP) value of biodiesel made from fats/oils because animal fats or oils do not have natural antioxidants such as plant oils so they are easily oxidized [24]. In addition, the presence of Polyunsaturated Fatty Acid (PUFA) in fish oil causes the biodiesel produced to be susceptible to oxidation. [21].

5. CONCLUSION

The reaction time affects the quality of the biodiesel produced. The highest conversion yield of biodiesel produced occurs when the reaction time is 3 hours, with a conversion value of 87.55%. Parameters of kinematic viscosity, density, acid number, moisture content and biodiesel sediment produced at a reaction time of 3 hours are 4.173 cSt, 942.62 kg/m³, 0.5534 mgKOH/g, and 5.79%, respectively.

Biodiesel derived from patin fish waste has very low oxidative stability, which is only 7 minutes for a reaction time of 2 hours. For this reason, it is necessary to add antioxidants to meet the biodiesel requirements according to the standard. Another characteristic test that needs to be done is the cetane number and flashpoint. The results of the analysis of biodiesel that meet the SNI 7182-2015 and EN 14214-2012 standards based on the results of this study are the viscosity.

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