Development of Utilization of Tuna Bone Waste as a Catalyst for Biodiesel Production Using Padina sp. Seaweed and Palm Oil

I W Sutapa*, A Bandjar, J Latupeirissa, M M A F Toesik

Department of Chemistry, Faculty Mathematics and Natural Science, University of Pattimura Jl. Ir. Putuhena Poka 97233, Ambon-Maluku- Indonesia

*E-mail: wayansutapa@fmipa.unpatti.ac.id

Abstract. The development research of heterogeneous catalyst applications from tuna bone waste for biodiesel production with palm oil and Padina sp seaweed oil as a source of oil has conducted. Synthesis of heterogeneous catalysts from tuna bone waste performed through calcination process at 1000 °C for 2 hours. The result of the catalyst conversion from tuna bone waste 49.69%. The use of catalysts in biodiesel production is carried out through the transesterification process using Padina sp. and palm oil. The yield of Padina sp. seaweed oil biodiesel was obtained 0.001%, while biodiesel sourced from palm oil obtained a yield of 66.03%. The biodiesel results obtained were tested physically and chemically according to the minimum requirements as biodiesel.

1. Introduction

Biodiesel is an alternative energy source that can be used to help deal with the fuel crisis that predicted to experience global scarcity. This scarcity is due to the increasing energy needs of human activities such as increased industrial production, transportation, electricity generation. In addition, biodiesel is non-toxic and biodegradable; it can be used on diesel engines to reduce the use of fossil fuels [1–5]. Biodiesel is a mixture of monoalkyl (mostly methyl or ethyl) fatty acid esters obtained from renewable resources such as plant oils and animal fats [1,6,7]. The development of biodiesel up to now continues to be done to obtain alternative fuels that are economical and environmentally friendly so that a biodiesel standard is carried out. Development is carried out from raw materials, production processes (time, temperature), and catalyst [4,5,8].

In biodiesel production, generally following the transesterification method need oil, methanol, and catalyst assistance. The catalyst serves to accelerate the reaction by lowering the activation energy possessed by the reaction system, the amount and types. To date, the transesterification reaction used homogeneous catalysts and enzymes [9–11]. However, the use of these catalysts has not been efficient because the cost of biodiesel production is still quite high. The development of heterogeneous catalysts needs to be done because it can reduce the cost of biodiesel production because heterogeneous catalysts do not cause saponification process, thereby reducing the costs for the biodiesel refining process [12–14]. The development of essential materials of heterogeneous base catalysts now can direct the use of waste such as fish scales and tuna bones [15,16].
Tuna bones can apply as a catalyst raw material. It supported by the hydroxyapatite carbonate content found in the bones. At high-temperature conditions, hydroxyapatite carbonate can converted into calcium phosphate which can be used as a catalyst [16,17]. Tuna bone is one of the wastes from the tuna processing can be used as a catalyst raw material because it can be obtained in bulk. Tuna waste produced is high because the tuna fish processing continues. Research on the utilization of tuna bones as a catalyst raw material has conducted previously. It can produce from the process of changing hydroxyapatite to Ca$_3$(PO)$_2$. Biodiesel produced using this catalyst has a yield of 58.75% [18,19].

The literature studies show that there has never been a test of the catalysis ability of tuna fish bones for biodiesel production from Padina sp and palm oil. Based on this fact, a biodiesel production study was carried out using a catalyst from tuna bones using Padina sp., and palm as a source of oil.

2. Experimental

2.1 Materials
The tools used include glassware, a set of pyrex reflux equipment, Cimarec electric heaters, magnetic stirrers (Science Ware), Ohaus analytical scales, mortars, ovens (Sheldon), furnaces, thermometer, sieve, Buchi evaporator, Ostwal viscometer, pycnometer, Scanning Electron Microscopy (SEM). Materials used are seaweed Padina sp., palm oil, tuna bone waste, n-hexane (technical), methanol (Merck), H$_2$SO$_4$ 1 M (Merck), KOH, HCl, H$_3$PO$_4$ 20%, ethanol 95%, Na$_2$SO$_4$ anhydrous (Merck), indicator, Whatman filter paper No. 41, distilled water.

2.2 Preparation and characterization of heterogeneous catalysts from tuna bone waste
The tuna bone waste cleaned the remnants of meat and washed with hot water several times until it is free of meat and fats. Furthermore, the material is dried in the oven at 100°C for 6 hours. The dried tuna bone waste mashed until smooth. The powder inserted into the calcination device. The calcination process is carried out by heating the solid at a temperature of 1000°C for 2 hours. The catalyst obtained was characterized by using Scanning Electron Microscopy (SEM).

2.3. Seaweed oil preparation
The seaweed obtained is cleaned of dirt and washed thoroughly. Furthermore, the sample is dried a constant weight achieved. The seaweed has dried then crushed by grinding. Additionally, the sample 15 grams put into soxhlet and extracted oil contained in it using n-hexane. The oil obtained separated from the solution by using an evaporator.

2.4. Degumming process
The degumming process is done by adding 20% phosphoric acid by 0.5% (w/w) of oil, heated at 80°C for 15 minutes, the oil separated from the phosphatide compound, then the oil is washed with warm distilled water to clear, and the oil dried with a vacuum dryer.

2.5 Analysis of free fatty acid levels
A sample of 5 g was put into an Erlenmeyer flask 250 ml, of 50 mL ethanol 95% added. Furthermore, the sample heated in a water bath at a temperature of 70°C for 10 minutes. Then it cooled and added a few drops of the indicator phenolphthalein. Then, the titration conducted by using KOH 0.1 N until the pink color achieved.

2.6 Esterification and transesterification reactions
The esterification process is carried out by mixing oil with methanol and using an acid catalyst. In this process, oil: methanol ratio is 1: 3 with a sulfuric acid catalyst (H$_2$SO$_4$) of 1.25%. The esterification process is carried out at 60-65°C for 2 hours. The esterification reaction results obtained in two layers, the upper layer is methanol, and methyl ester, while at the lower layer is triglyceride. Triglycerides
separated from the mixture. The transesterification process carried out using a heterogeneous catalyst from tuna bone waste with a weight presentation of 1.01%. The oil/methanol ratio 1:6.27 carried out at a temperature of 70-75 °C, 60-65 °C, and 50-55 °C with the reaction times of 3, 5, 7 and 9 hours. Transesterification results will be obtained in 3 layers, successively from top to bottom of methyl ester (biodiesel), glycerol, and catalyst. The methyl ester (biodiesel) separated from the glycerol and catalyst. The methyl ester is washed with warm distilled water to remove the remaining glycerol. The evaporation process is carried out to remove the residual solvent. The obtained methyl ester is then added anhydrous Na$_2$SO$_4$ and filtered to obtain methyl ester (biodiesel). The last step is determining chemical and physical parameters.

3. Results and Discussion

3.1 Preparation of heterogeneous catalysts from a tuna bone

The catalyst preparation of tuna bone waste in this study done by cleaning tuna bones from the remnants of meat attached to the bones of tuna fish (Fig. 1). In the cleaning process, using hot water repeatedly until the meat breaks easily. Next, clean tuna bones are dried in an oven at 100 °C for 6 hours to remove moisture after washing. The tuna bones crushed and sieved using a 200 mesh sieve to obtain a relatively small catalyst particle size. The purpose of sifting is not only to get a small catalyst size but also to increase the catalyst surface area.

![Figure 1. Tuna fishbone](image)

3.2 Synthesis of catalysts from tuna bone waste

The results of the catalysts from tuna waste characterized by a change in catalyst color from golden yellow to white. The change indicates the loss of organic components such as collagen, lipids, and keratin sulfate [15,19] and water contained in tuna waste. The XRD results from Tuna fish waste obtained other studies show that the calcination process at 1000 °C causes a change in hydroxyapatite (HAP) to Ca$_3$(PO$_4$)$_2$ due to CO$_2$ loss [20–22]. The results of the conversion of catalysts from tuna bone waste obtained 49.69%. Calcination results from tuna bones being a catalyst shown in Fig. 2.

![Figure 2. The catalyst from tuna bone waste](image)

(a) Catalyst before calcination; (b) Catalyst after calcination
3.2 Catalyst characterization of tuna bone waste
In this study, the characterization of heterogeneous catalysts from tuna bone waste by using the Scanning Electron Microscope (SEM) instrument. The results of the heterogeneous catalyst characterization of tuna waste showed differences in the catalyst surface before and after the calcination process was carried out at 1000 °C. The surface shape of the catalyst before calcination looks solid, while the catalyst after calcination shows the cavities on the surface. The results of heterogeneous catalyst characterization of tuna bone waste with a Scanning Electron Microscope (SEM) instrument with a magnification of 30,000x shown in Fig. 3.

![Catalyst morphology of tuna waste](image)

(a) (b)

**Figure 3.** Catalyst morphology of tuna waste (a) before calcination (b) after calcination

3.3 Oil preparation from Padina sp. Seaweed
The process of making seaweed oil is carried out using the soxhlet extraction method. *Padina sp.* seaweed is cleaned of impurities and dried until the weight of *Padina sp.* seaweed becomes constant. The purpose of drying to remove the water content contained in *Padina sp.* The water content will affect and disrupt the extraction process. The next process is to crush the dried seaweed *Padina sp.* to facilitate the solvent extracting the oil contained optimally. The seaweed powder is shown in Fig. 4.

![Seaweed after being crushed](image)

**Figure 4.** Seaweed after being crushed

The oil contents of the seaweed have extracted by using the solvent extraction method. The solvent extraction was chosen due to the solvent extraction have the advantage could be obtained and reused. N-hexane used as a solvent because it has good extraction ability. The seaweed extraction is carried out for ± 6 hours. The final step of seaweed extraction obtained in the form of fat at room temperature (Fig. 5). The result of seaweed oil extraction produced is 11.91% of the dry weight.
3.3 Biodiesel production from seaweed

The seaweed oil esterification process was carried out with a 1.25% catalyst presentation and an oil: methanol ratio of 1:3 at 60-65 °C for 2 hours. Seaweed oil used ±2 grams. The esterification process begins by heating the fat at 60 °C, which aims to convert the solid phase (fat) into the liquid phase (oil). The esterification process aims to convert free fatty acids into esters. The overall reaction is the replacement of the -OH group from acid with -OR group from alcohol. The result of the esterification process is methanol and methyl esters (top layer) and triglycerides (bottom layer). The triglyceride layer separated for use in the transesterification process.

The transesterification process was carried out using a tuna bone waste catalyst with a percentage of 1.01% catalyst weight. The percentage of catalyst 1.01% used because the results of research conducted by other researchers showed the results of the conversion of biodiesel with soybean oil as a raw material is very good with oil/methanol ratio of 1:6.27 [19]. The transesterification process in this process is carried out at 60-65 °C for 9 hours and at 70-75 °C for 5 and 7 hours. The final output of biodiesel production from seaweed oil through the transesterification process is 0.001%. The small product probably caused by the content of free fatty acids in oil or seaweed fat content is very high, creating the ability of heterogeneous catalysts from tuna waste to convert triglycerides into minimal alkyl esters.

3.3 Biodiesel production from palm oil

Palm oil is used as an oil source because it quickly obtained, free fatty acid levels are relatively low and currently used in bio-solar blends. The process of biodiesel production of palm oil also goes through the esterification process due to the free fatty acid content of palm oil is 2.8. The esterification process of palm oil using an acid catalyst (H₂SO₄), the percentage of the weight of the catalyst used is 1.25%, and oil/methanol ratio 1:3 for 2 hours. Esterification results obtained are methanol (top) and triglycerides (bottom), then triglycerides are separated from methanol for transesterification process.

The transesterification process is carried out by mixing triglycerides, methanol, and catalysts. This process was carried out using a heterogeneous catalyst of 1.01%. The oil/methanol ratio is 1:6.27 for 3, 5, 7, and 9 hours at 50-55, 60-65, and 70-75 °C. The process of transesterification produces three layers, namely methyl esters (top), glycerol (middle), and catalyst (bottom). The catalyst separated from the mixture by decantation step, the glycerol separated from methyl esters by using a separating funnel. The methyl ester washed by distilled water to remove the remaining glycerol. The methyl ester evaporated for 2 hours at 60-65 °C to remove the solvent. The resulting methyl ester added anhydrous to remove the remaining water. The final step is then filtered methyl ester to separate the anhydrous with a funnel and filter paper.

The transesterification results show the triglyceride conversion, and the perfect reaction results at a temperature of 60-65 °C with a reaction time of 9 hours with a yield of 65.87%. At a temperature of 70-75 °C with reaction times 3, 5, 7, and 9 hours with the result of the conversion of alkyl esters 47.30; 70.42; 71.20; and 66.04%. This result supported by the physical form of the biodiesel color produced,
which is yellowish-white and the presence of a spark or flame after a fuel test. The biodiesel yield from palm oil shown in Fig. 6.

![Biodiesel production results](image)

**Figure 6.** Biodiesel production results (a) temperature 60-65 °C (b) temperature 70-75 °C

3.4. **Chemical properties parameter test**

The chemical properties tested on the results of biodiesel in this study are saponification rates and acid numbers. The saponification number obtained from the test results was 152.44 mg KOH, while the acid number 66 mg KOH/g. The comparison of the results of the test parameters of the chemical biodiesel with ASTM (American Standard Test of Materials) and SNI (Indonesian Nasional Standard) of biodiesel shown in Table 1.

| Characteristics     | ASTM    | SNI    | Test Results |
|---------------------|---------|--------|--------------|
| Acid number         | Max 0.5 | Max 0.8 | 0.66         |
| Saponification number | 261.26  | 261.26 | 152.44       |

**Table 1.** Comparison of chemical parameter test results

b. **Physical Parameter Test**

The biodiesel physics parameter test compared to the biodiesel standards by ASTM and SNI are shown in Table 2.

| Characteristics       | ASTM    | SNI    | Test Results  |
|-----------------------|---------|--------|---------------|
| Density (g/mL)        | 0.86-0.90 | 0.85-0.89 | 1.06 g/cm³    |
| Viscosity (Cst)       | 1.9-6.0  | 2.3-6.0 | 7.36 s/cm²   |

**Table 2.** Comparison of physical parameter test results

![Biodiesel flame test](image)

**Figure 7.** Biodiesel flame test
Table 3. The results of the flame test

| Times | Test result | Transesterification Temperature |
|-------|-------------|---------------------------------|
| 9 hour| Light       | 60-65 °C                        |
| 3 hour| Light       | 70-75 °C                        |
| 5 hour| Light       | 70-75 °C                        |
| 7 hour| Light       | 70-75 °C                        |
| 9 hour| Light       | 70-75 °C                        |

The test results obtained a flame that ignited quickly in a short time ± 30-40 seconds, shown in Fig. 7. The results of flame tests on biodiesel products produced with temperature differences and time variations shown in Table 3.

4. Conclusions
The biodiesel conversion by using tuna bone catalysts with *Padina* sp seaweed oil source obtained 0.001%. Whereas palm oil as an oil source at a temperature of 60-65 °C with a reaction time of 9 hours got conversion results of 65.87%. At a temperature of 70-75 °C with a reaction time of 3, 5, 7, and 9 hours have got the conversion results 47.30; 70.42; 71.21; and 66.03%, respectively.

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