

FISH WASTE OIL CONVERSION FOR BIODIESEL PRODUCTION USING TWO STAGES REACTION

Kusmiyati

Pusat Studi Energi Alternatif (PSEA), Department of Chemical Engineering,
Faculty of Engineering, Muhammadiyah University of Surakarta
email: kusmiyati@ums.ac.id and psea_ums2014@yahoo.com

Abstract

This study utilized the oil derived from fish waste as raw material. Biodiesel production from fish waste oil was carried out using a catalytic reaction with two stages processes: esterification and transesterification. The first step was the esterification process using an acid catalyst (H_2SO_4) to reduce the free acid content in waste fish oil. Then, it was followed by transesterification in the second step using alkaline catalyst (NaOH or KOH) to convert the oil into biodiesel. In the esterification reaction, waste fish oil was reacted with methanol at 60 °C and 2% H_2SO_4 catalyst in a three-neck flask apparatus for various times (2, 3, 4 hours) with various stirring speeds (500, 600, 700 rpm) and temperatures (50, 60, 70 °C). The results of esterification were used for transesterification. It was mixed with methanol (molar ratio 1: 6), 2% NaOH catalyst in a three-neck flask apparatus. The optimum conversion 66.09% was obtained at 60 °C for 4 hours. The effect of stirring speed shows that at the speed of 700 rpm for 4 hours, the maximum conversion 68.03% was obtained. The effect of alkaline catalyst types showed that optimum conversion was obtained using KOH (88.99%).

Keywords: *biodiesel; waste fish oil; esterification; transesterification*

1. INTRODUCTION

Alternative energy is the answer to the fuel crisis. The development of alternative energy needs to be conducted for some reasons: alternative energy sources available in nature and it will not be exhausted if it is managed properly. Alternative energy source include wind power, solar power, micro-hydro, geothermal, biomass and biofuels consisting biodiesel and bioethanol derived from plant materials. The development of alternative energy have been carried out recently, especially biodiesel. Biodiesel is one of the environmentally friendly alternative fuels because it has low emission that will not cause air pollution.

Currently, palm oil has been the major raw material used for biodiesel production (Demirbas, 2005). Other vegetable oils that can be used as raw material for the biodiesel production such as soybean oil, sunflower oil (Ramadhas et al., 2005), waste cooking oil (Zheng et al., 2006; Encinar et al., 2005;

Zhang et al., 2003), tallow oil derived from the processing of paper/pulp (Ma et al., 1999). Most of vegetable oils are edible oil such as palm oil, sunflower, soybean via and the oils are converted to biodiesel by transesterification process using sodium hydroxide as a catalyst (Widyan and Al-Shyoukh, 2002). The drawback of commercialization biodiesel production from those vegetable oils still are occurred due to high cost of the vegetable oil and the purification of biodiesel product (Kusmiyati et al, 2010). The high price of vegetable oil has been known affected to the production cost that have an impact on the high price of biodiesel. Therefore it is necessary to find out the cheap alternative raw material such as animal waste oils (Ma et al., 1998). Animal oils can also be used as raw material for biodiesel such as beef tallow oil derived from meat processing waste (Ma et al., 1998). In addition, fish oil derived from waste fish oil is a cheap raw material (Narasiman et al, 2012). Moreover, the availability of fish oil

is abundant in Indonesia that known as a maritime country with a large fish production. Currently, the byproduct of fish in Indonesia, the fish waste have been limited utilized. The abundant sources of waste fish have been used as animal feed with less utilized. Fish oil can be produced from fish waste in the form of fish liver, internal organs of fish, meat or fish (Astawan, 2004). Fish waste can produces fish oil that appears as potential materials for biodiesel in Indonesia. Nevertheless, only few studies have utilized fish waste for biodiesel production.

Biodiesel is produced from a chemical process called transesterification (transesterification) in which the reaction occurs between esters with alcohols with the addition of a catalyst. Biodiesel can be used as fuel oil and motor vehicle fuel. The use of biodiesel is applied in the form of 100% (B100) or blended with diesel. The ratio of biodiesel to diesel fuel mixture is 10% biodiesel : 90% diesel (B10) and 20% biodiesel : 80% diesel fuel (B20) (Loterio, 2005).

The production of biodiesel have been investigated previously using vegetable oils that have low free fatty acid (FFA) < 5% (Gerpen et al., 2005). The study obtained the yield biodiesel of 91.07% using palm oil raw material and KOH/Al₂O₃ and KOH/NaY catalysts for 3 h at 60 °C (Noiroj et al., 2009). Meanwhile, biodiesel from oil/animal fat was produced from beef tallow (beef fat) which resulted 90% yield using an alkaline catalyst (Ma et al., 1998). Usta et al. (2005) studied the biodiesel from oil containing high FFA (50%). The oil was reacted for an hour with methanol and sulfuric acid catalyst at 60 °C. After the acid esterification was completed, the NaOH was added and stirred at 60 °C. This process was used two kinds of catalysts to produce biodiesel with a yield of 97%. The high FFA content in the oil was more effective when 2-step process applied: acid esterification and alkali transesterification. In acid esterification, oil was pretreated to reduce FFA levels using an

acid catalyst. It was followed by alkaline transesterification with a base catalyst, which would change the oil (triglycerides) into methyl ester (Ramadhas, 2005). The purpose of this study was to produce biodiesel from fish waste oil as a raw material using esterification-transesterification process with two catalysts: acid and base catalysts. The effect of temperature and stirring speed in the esterification step on biodiesel product were studied. Also, the types of alkaline catalyst on biodiesel conversion were investigated. The variables was studied in order to find out the optimum conditions in the production of biodiesel from waste oil fish.

2. MATERIALS AND EXPERIMENTAL METHODE

A. Materials

Waste fish oil as a raw material for biodiesel was prepared from fish waste that collected from a traditional market in PasarGede Surakarta. The chemicals in analytical grade used were H₂SO₄, NaOH, KOH, and methanol (CH₃OH). A three-neck flask equipped with a condenser and string equipment was used for esterification-transesterification process.

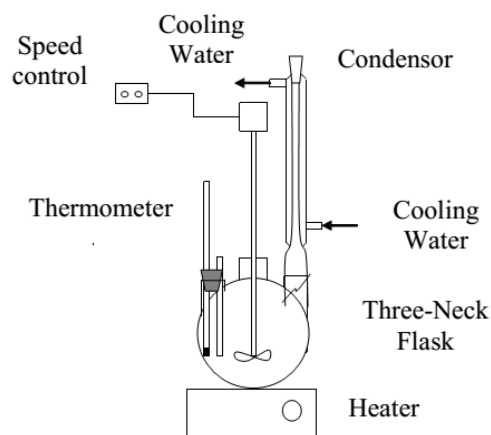


Figure 1. a three-neck flask equipment

B. Experimental Method

Preparation of fish oil. Fish waste in the form of a fish head, gills, heart and stomach of fish were washed. After that, the fish

waste was added with water as a solvent and it was boiled. Oil was then taken and put into separation funnel to separate it from the solvent. The oil could be used as raw material for biodiesel production or stored in sealed glass bottles.

Acid esterification process. The esterification process using H_2SO_4 acid catalyst was carried out in a three-neck flask. A 50 g fish waste oil was added with methanol at the oil-to-methanol molar ratio of 1:6 and 2% H_2SO_4 as acid catalysts. The mixture was esterified at constant temperature of 50, 60, or 70 °C. The esterification reaction was conducted at various time (2, 3, 4 h) with various stirring speed (500, 600, 700 rpm). The esterification process produced the product formation of two layers liquid. To take the oil in the top layer, the liquid was separated by a separating funnel.

Alkaline transesterification. The oil resulted from acid esterification was charged into the three-neck flask. Then 2% NaOH dissolved in methanol (molar ratio oil to methanol 1: 6) was added. The oil, NaOH and methanol mixtures were transesterified for 60 minutes at varying temperature and speed of stirring. After 60 minutes, alkaline

Analysis of raw materials. The oil prepared from waste fish was analyzed to determine the characteristics of fish oil. The Fish oil analysis was carried out using chromatograph GCMS-QP2010S (Shimadzu).

Analysis of FFA (free fatty acid). FFA analysis was conducted to determine the number of acid in fish oil. A 10 g of fish oil was put into Erlenmeyer and added with 25 mL of ethanol, and then heated for 5-10 minutes and with addition of pp indicator. Then it was titrated with 0.1 N-KOH solution until the samples color changed into pink. The analysis was repeated three times. From this titration would be recorded the volume of KOH titration.

Analysis of biodiesel. Biodiesel from fish oil was determine of its density, viscosity, ASTM analysis, and characteristic as a fuel in a diesel engine.

3. RESULTS AND DISCUSSION

A. Analysis of raw materials

The content of fish oil from the result of analysis using GCMS-QP2010S (Shimadzu), is shown in the table below:

Table 1. Composition in fish oil

No.	Component	Retention time	%
1.	$C_9H_{18}O_2$, <i>Octanoic acid</i>	17.783	6.48
2.	$C_{11}H_{22}O_2$, <i>Decanoic acid</i>	24.208	6.45
3.	$C_{13}H_{26}O_2$, <i>Dodecanoic acid</i>	29.825	34.6
4.	$C_{15}H_{30}O_2$, <i>Tetradecanoic acid</i>	34.825	19.7
5.	$C_{17}H_{34}O_2$, <i>Hexadecanoic acid</i>	39.308	11.5
6.	$C_{19}H_{38}O_2$, <i>9-Octadecanoic acid</i>	42.892	9.51
7.	$C_{20}H_{40}O_2$, <i>Nonadecanoic acid</i>	43.275	3.39

transesterification process was stopped. There were two layers of the reaction products, the top layer containing the methyl ester/biodiesel and the bottom layer containing glycerol. It was purified by washing with adding distilled water then shaking it for 5 minutes. The washing process was carried out in 3 times. After that, biodiesel was dried in an oven at 90 °C to remove the water content.

Table 1 shows the content of fish oil. The largest content was 34.6% dodecanoic acid, followed by 19.7% oftetradecanoic acid. Other contents are 6.48% octanoic acid, 6.45% decanoic acid, 11.5% hexadecanoic acid, 9.51% 9 octadecanoic acid and 3.39% nonadecanoic acid. The composition of fish waste oil was comparable from other oils such as beef tallow oil that had highest components consist of unsaturated oil such as

oleic and linoleic acids. The difference between vegetable oil and animal oil was found in the composition of saturated and unsaturated fatty acids; for vegetable oil contains 10-25% saturated fatty acids and 75-90% unsaturated fatty acids, while animal oil contains 40-50% saturated and 40-50% unsaturated fatty acids. The high saturated fatty acids has been found affected the characteristics of animal oil in gives higher cetane numbers and are less prone to oxidation than unsaturated compounds but they tend to crystallize at unacceptably high temperatures (Canakci, 2005). Some animal oils that can be used as biofuel raw materials include poultry fat contain 22.2% palmitic fatty acid, 42.3% oleic fatty acid and 19.3% linoleic acid; edible tallow contains 28.4% palmitic fatty acid, 44.6% oleic acid and 2.7% linoleic acid. Meanwhile, vegetables oil have been used as a biofuel raw materials include rapeseed oil containing 3.5% palmitic acid, 64.4% oleic acid and 22.3% linoleic acid; sunflower oil containing 6% palmitic acid, 18.7% oleic acid and 69.3% linoleic acid (Loter, 2005; Canakci, 2005). Saturation fatty acid methyl esters increase the cloud point, cetane number and improve stability whereas more polyunsaturates reduce the cloud point and cetane number and stability. The type and percentage of fatty acids contained in vegetable oil depends on the plant species and on the growth conditions of the plant. Though vegetable oils are of very low volatility in nature, it quickly produces volatile combustible compounds upon heating (Ramadhas, 2005).

The analysis on Free Fatty Acid (FFA) of oil was conducted prior to esterification process to determine the number of fatty acid in fish oil. From the analysis of FFA, it was found that the fish waste oil had FFA 12.468 mg KOH/g oil. The FFA content in fish oil was higher when compared with the standard FFA content of vegetable oil for biodiesel raw material (FFA less than 3%). The high FFA lead to requirement of pretreatment prior to transesterification process in order reduce the FFA content. It has been found that vegetable or animal oil which have high

FFA (> 4%) resultted low conversion (Ramadhas, 2005). An example of oil with high FFA content is rubber seed oil of 17% (acidity = 34), while the oil with low FFA is sunflower seed oil with acidity of 0.15; rapeseed oil of 1.14; cotton seed oil of 0.14; soybean oil of 0.2.

B. Effect of temperature in esterification step

Various temperatures (50 ° C, 60 ° C, and 70°C) and reaction times (2 , 3 , and 4 hours) were used in the esterification process. The experiment was conducted in constant molar ratio of reactants oil to methanol of 1: 6; H₂SO₄ catalyst and reaction time of 60 minutes in esterification step. A constant NaOHcatalyst and stirring speed of 600 rpm were used in transesterification. The effect of temperature in the acid esterification on the conversion of biodiesel can be seen in Figure 2.

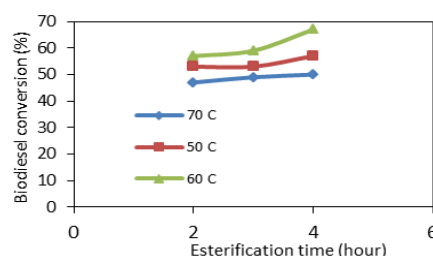


Figure 2. Effect of temperature and time in esterification on biodiesel conversion.

From Figure 2, it can be shown that biodiesel conversion was affected by temperature and time in transesterification process. An increased esterification time from 2,3, and 4 hours has resulted in increased biodiesel conversion. The maximum biodiesel conversion was obtained at 60°C. Lower conversion of 52.95%, 53.62%, and 56.85% at 2,3,4 h respectively was obtained at 50 ° C compared to 60°C . Conversion of 56.05%, 58.42 %, and 66.09% at 2, 3, 4 h respectively was observed at 60 ° C. Lower conversion of 47.06%, 49.65%, and 50.11% at 2, 3, 4 h respectively was obtained at 70 ° C than that of 60 ° C . The highest conversion was obtained at

esterification temperature of 60 °C. At 70 °C, biodiesel conversion was low due to an excess temperature that above methanol boiling point which resulted evaporation of methanol. Meanwhile, at the reaction temperature below the boiling point of methanol, resulted in low conversion due to the slow rate reaction.

C. Effect of stirring speed

This samples were esterified at varied stirring speed 500, 600 and 700 rpm, with constant transesterification operation condition. The samples were prepared at oil-to-methanol molar ratio of 1:6, 2% H₂SO₄ acid catalyst used for esterification and 2% NaOH as alkaline transesterification catalyst. Temperature and time in the transesterification were 60 °C and 60 min, respectively. The effect of stirring speed on the biodiesel conversion can be seen in Figure 3.

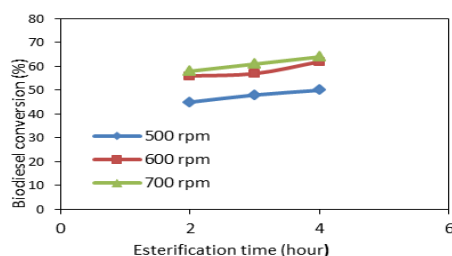


Figure 3. Effect of stirring speed and time on biodiesel conversion.

Figure 3 shows that the increasing stirring speed and esterification time resulted an increased the conversion of biodiesel from transesterification product. An increased of conversions 47.19%, 48.06%, and 49.58% were observed with increased of esterification time 2, 3 and 4 hours at stirring 500 rpm. An increasing stirring speed to 600 rpm leads to an increased the conversion of 56.05%, 58.42%, and 66.09% at 2, 3, 4 h respectively, compared to that at 500 rpm. At 700 rpm, the highest conversion 57.88%, 62.32% and 68.03% were observed.

D. Effect of the type alkali catalyst

To study the effect of alkaline type catalyst in transesterification, the operation condition for the first step of esterification was kept constant such as the the ratio of with methanol of 6:1, the catalyst used 2% H₂SO₄, temperature 60 °C and the time for 60 minutes. After the esterification reaction was completed, it was followed by a transesterification reaction using three different types of alkaline catalysts: NaOH, KOH, and K₂CO₃ at 60 °C and stirring at 600 rpm. The result of biodiesel conversion at different alkali catalyst types is shown in Figure 4:

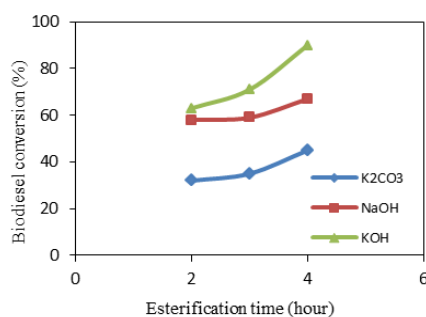


Figure 4. Effect of the type of alkaline catalyst in the transesterification on biodiesel conversion.

From Figure 4 it can be seen biodiesel conversion at various alkali catalyst used during the transesterification process. The highest biodiesel was obtained using KOH catalyst for 2, 3, 4 hours reaction times yielded conversion of 63.35%, 72.49%, and 89.99%, respectively. Meanwhile, when using NaOH catalyst the lower conversion 57.88%, 58.42%, and 66.09% were obtained for a reaction time of 2, 3, 4 hours, respectively than that of KOH. However, the lowest biodiesel conversion was obtained for the transesterification reaction by using K₂CO₃ which yielded 29.11% , 32.67% and 43.48% for 2, 3 and 4 hours, respectively. The lowest bioediesel yield was caused by the formation by product of soap from reaction between triglyceride and alcohol. Based on the result that KOH was the best catalyst, this was due to the formation of soap

could be minimized. According to studied conducted by Encinar et al. (2005) the production of biodiesel from used cooking oil, conversion of 95% could be reached using KOH catalyst for at 65 ° C at a reaction time of 100 minutes. The results concluded that in a process of methanolysis of used frying oil, potassium hydroxide was the best catalyst compared with NaOH.

From the Figure 4, it can be seen that the yield of biodiesel increased with increasing time during esterification reaction first stage process. This is due to the longer the esterification time, the amount of number of fatty acids content in the oil is lower. The highest biodiesel yield was obtained when the esterification was conducted for 4 hours this result suggested that little amount of the free fatty acids was existed so that the soap formation could be minimized and the transesterification reaction can be improved. According to Encinar et al. (2005) the use of an alkaline catalyst for the transesterification would cause a side reaction between alkaline and free fatty acids in the oil. The high free fatty acid content will reduce the results of biodiesel as fatty acid can react with alkaline catalyst to form soap. The reduction of free fatty acid content in the oil was carried by the esterification reaction, then followed by transesterification reaction using the oil product that has low free fatty acids (Loterio et al. ,2005 and Zahidah and Fitri, 2005). Ramdhas (2005) found that the high content of FFA in rubber seed oil could be reduced to lower than 2% by means of esterification, then the low FFA oil could be used as the raw material of biodiesel production by transesterification.

4. CONCLUSION

Oil from fish waste can be used as raw material for biodiesel, the process of which is carried out in two stages. The first stage is the esterification process with an acid catalyst (H_2SO_4) to lower the acid value oil and the second one is transesterification process with alkaline catalyst (NaOH, KOH, K_2CO_3) to change the oil into biodiesel.

Temperature, stirring speed, the type of alkali catalyst are the factors that affect the conversion of biodiesel. The optimum conversion of 66.09% was obtained in varying temperature and time variation at 60 ° C for 4 hours and the optimum condition was achieved in the stirring speed of 700 rpm and time variation of 4 hours with a conversion of 68.03%, while the optimum conversion of 88.99% in varying alkaline catalyst and time with KOH as alkaline catalyst and varying alcohol type for 4 hours and in the term of time.

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