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BIODIESEL PRODUCTION FROM SARDINE FLOUR USED COOKING OIL USING ONE STEP TRANSESTERIFICATION TECHNIQUES

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Abstract. *Diesel oil demand an energy source in the industrial, transportation and electric generating sector is increasing and it resulted in the decreasing of fossil energy source backup. Biodiesel as an alternative energy source to substitute diesel oil can be utilized from used fried oil of sardine flour. The purpose of this research was to develop the technology to convert used fried oil of sardine flour to become biodiesel using a step trans-esterification technic as an alternative of renewable energy source and also to utilize waste of used oil. Biodiesel made using one step trans-esterification technic with NaOH catalyst concentration 0.5; 1.0; 1.5; 2.0 (% m/m) from total weight of oil and methanol. Trans-esterification process runs for 30, 60 and 90 minutes at 65℃ temperature. The biodiesel obtained was analyzed using gas chromatography and mass spectrometer (GC-MS). The quality was determined by comparing its physicochemical properties and compared to the SNI standard 04-7182-2015. The result of GC-MS showed 10 peaks corresponding to ten methyl ester (biodiesel): octanoic acid methyl ester; decanoic acid methyl ester; dodecanoic methyl ester; tridecanoic acid, 12-methyl-, methyl ester; pentadecanoic acid methyl ester; hexadecatrienoic acid methyl ester, 9-hexadecenoic acid methyl ester, 9-hexadecenoic acid methyl ester, trans-13-octadecenoic acid methyl ester, hexadecanoic acid methyl ester. The biodiesel obtained has a density of 908 kg/m^3, viscosity of 3.13 mm^2/s, an acid value of 0.29 mg-KOH/g found in treatment 1.5% NaOH and time process of 60 minutes. Viscosity and acid value were in a good agreement with SNI standard 04-7182-2015. The research shows that the used fried oil of sardine flour has the possibility as a biodiesel source.*
Keywords: *Biodiesel, sardine flour used cooking oil, trans-esterification*

1. Introduction

Limited oil resources and the domestic refinery capacity cause the fulfillment of fossil-based fuel oil (BBM) that needs to be done through imports. Solar, as one of the backbones of the transportation, industrial and electricity generation sectors, is estimated at 16.2 million kiloliters throughout 2018 (Satrianegara, 2018). National scale fuel consumption that is very large is not comparable with the potential and reserves owned. This becomes a problem that needs special attention and must be addressed immediately. The effort that can be taken is to immediately substitute BBM with renewable alternative fuels, namely biodiesel, which has many raw materials for this matter in the country (Darmanto & Sigit, 2006).

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Biodiesel is a methyl ester compound resulting from the esterification or trans-esterification process of vegetable oil or animal fat. Biodiesel has the same physical properties as diesel oil so that it can be used as an alternative fuel for diesel-engine vehicles. According to Haryanto (2002) and Wang et al (2009), the advantages of biodiesel compared to non-toxic petroleum fuel, has a high level of energy, can reduce carbon monoxide, hydrocarbon and NOx emissions, which are present in the liquid phase and can be degraded biologically.

Used fried oil of sardine flour has the potential as a raw material for biodiesel. Glyceride content and free fatty acids in sardine frying oil can be converted to biodiesel through an esterification / trans-esterification process. The use of used frying oil as raw material also has advantages because the amount is abundant and will never run out. Based on the feasibility evaluation, the used frying oil is most suitable for use as biodiesel feedstock (Ruhyat & Firdaus, 2006).

Suirta (2009), researched on the preparation of biodiesel from palm oil used cooking oil using 2 stages, esterification and trans-esterification, producing six methyl ester (biodiesel) compounds with physical and chemical properties according to German standards DIN 51606. Some researchers point out that this 2-stage process has a disadvantage in consuming methanol twice, while the biodiesel yield also decreases by 20% to 30% and requires longer reaction times and affects the quality of the biodiesel produced ((Ajala, Aberuagba, Olaniyan, Ajala, & Sunmonu, 2017); Jaruyonan & Wongsapai, 2018). Making one-stage biodiesel is done by Buchory (2009) with a non-catalytic cracking process that takes place at high temperatures and pressures so that it requires large energy. Saifuddin et al (2009) developed an enzymatic process technique in processing biodiesel from used cooking oil, but the required production costs were high and the reaction time was long. Cheap and appropriate pretreatment alternatives are needed to reduce high free fatty acids in used cooking oil before the trans-esterification stage.

Microfiltration was chosen for the pretreatment process of used sardine frying oil. Microfiltration is an easy, simple and inexpensive technique to reduce free fatty acids and eliminate suspended solids from used fried oil of sardine flour (Nasir et al., 2002) as well as a substitute for the esterification process, so that the process of converting used fried oil of sardine flour can be done with one trans-esterification stage. The purpose of this study was to develop a technology to convert used sardine frying oil into biodiesel with a one-stage trans-esterification technique as an alternative to renewable energy and the use of used oil waste. The biodiesel produced was analyzed by gas chromatography and mass spectrometer (GC-MS). Quality is determined by analysis of physical and chemical properties and then compared with biodiesel quality standards SNI 04-7182-2015.

2. Materials and Methods

Materials

The materials used in this study include: used fried oil of sardine flour, crystal NaOH, methanol 96%, ethanol 95%, phenolphthalein, KOH 0.02 N and bleaching earth.

Tools

The tools used include: filter paper with pore size 16 µm, vacuum pump, hot plate, stirring, analytic balance, incubator, centrifuge, GC-MS.

Method

This research was conducted in one step trans-esterification techniques. Pretreatment of used fried oil of sardine flour was done by the microfiltration process with filter paper 16 µm to reduced free fatty acid content. For one step trans-esterification techniques, there are two variables. The first variable is concentration of NaOH in sodium methoxide with 3 treatment levels namely 0.5%, 1.0%, 1.5% and 2.0%. The second variable is stirring time during the trans-esterification process in 30, 60 and 90 minutes with stirring temperature 65°C. The study was conducted with 3 repetitions. Biodiesel product from the trans-esterification process was purificated by adding 1% bleaching earth.

The analysis process was carried out on GC-MS to determined methyl ester (biodiesel) and then analysis of quality biodiesel by physic and chemical properties and compared with biodiesel quality standards SNI 04-7182-2015.

Research Procedure

Microfiltration

Microfiltration is a pretreatment process for used fried oil of sardine flour. Microfiltration was carried out using a 16 µm paper filter with the help of a 1.5 bar pressure vacuum pump to remove suspended solids and reduce free fatty acids. Used oil of fried sardine flour before and after the microfiltration process was tested for free fatty acid based on SNI 01-3555-1998 method.

Transesterification

The trans-esterification process was carried out first to make sodium methoxide solution by dissolving NaOH in methanol with a variation of NaOH concentration 0.5;

1.0; 1.5; 2.0 (% m/m) of the total weight of used fried oil of sardine flour and methanol. Used fried oil of sardine flour is heated to temperatures reaching 50°C. After the temperature is reached, the sodium methoxide solution is added to used sardine frying oil while stirring at 200 rpm and heating the temperature 65°C for 30, 60 and 90 minutes. Separation of biodiesel and glycerol was carried out by settling the mixture for 12 hours at room temperature then centrifuged 1100 rpm for 10 minutes at 64°C.

Purification

Biodiesel produced from the trans-esterification process of sardine frying oil used by refining bleaching earth 1% (m/v) of the total volume of used fried oil of sardine flour biodiesel. Absorbents are added to biodiesel. Stir for 15 minutes at 55°C. Separated between biodiesel and adsorbent using filter vacuum pump. The refined biodiesel was analyzed for methyl ester (biodiesel) by gas chromatography and mass spectrometer (GC-MS) and quality of biodiesel for acid numbers (mg-KOH/g) method SNI 01-3555-1998, viscosity (mm^2/s) and density (kg/m^3), then compared to determine the feasibility of sardine frying oil biodiesel based on SNI 04-7182-2015.

3. Results and Discussion

Raw Material Analysis

The used fried oil of sardine flour used in this study came from 8 times the frying process of sardines (*Sardinella lemuru*) which were added. According to Sopianti *et al* (2017), the oil used for frying more than 7 times has no longer met SNI quality standards. Microfiltration is carried out to reduce the free fatty acid content of used sardine frying oil. The smaller the content of free fatty acids, the less saponification reaction (soap formation) and vice versa the formation of methyl ester (biodiesel) is greater.

In this study, the levels of free fatty acids before microfiltration were 0.24%. The porous membrane used in the microfiltration is 16 μm in size. The free fatty acid content of used frying oil of sardine flour after microfiltration is 0.17%, so that the percentage of free fatty acid purification obtained from the results of microfiltration is 29%. According to Yoeswono *et al*. (2007) in Sahubawa (2010), animal oil that is trans-esterified must have a free fatty acid content of less than 1.0%. The results of the calculation of free fatty acids provide instructions for carrying out a one-stage trans-esterification reaction.

The Results of Biodiesel Conversion

The conversion of used fried oil of sardine flour into biodiesel was carried out using a one-stage trans-esterification technique. The process of removing suspended solids and decreasing the free fatty acids contained in used sardine frying oil is done using the microfiltration technique. High free fatty acids can interfere with the conversion process because free fatty acids can react with the catalyst to form soap. Microfiltration produces clear oil. One step trans-esterification process is continued on microfiltration oil. Trans-esterification was carried out using a NaOH base catalyst at a concentration of 0.5; 1; 1.5; 2 (% m/m) for 30, 60 and 90 minutes at 65°C. The result, obtained a product consisting of two layers, consisting of a lower layer which is glycerol and the top layer which is biodiesel.

Identification of Biodiesel by GC-MS

Products produced from the transesterification process were identified by GC-MS to ensure that the results obtained were biodiesel (methyl ester). The results of the biodiesel analysis are shown in Figure 1. The type of methyl ester compound, retention time and chromatogram peak area in Table 1.

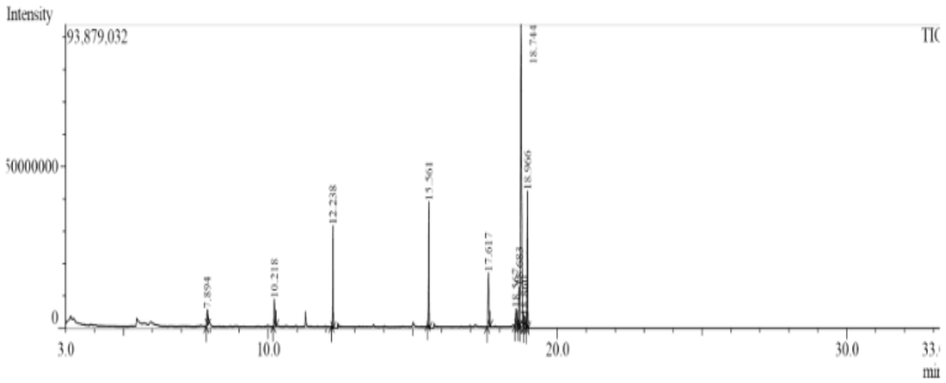

Figure 1. Chromatogram of biodiesel from GC-MS analysis

Table 1. Composition of methyl ester sardine frying oil

No.	Peak area (%)	Retention time	Compound
1	8.826	7.894	Octanoic acid, methyl ester
2	6.207	10.217	Decanoic acid, methyl ester
3	9.207	12.237	Dodecanoic acid, methyl ester
4	14.745	15.560	Tridecanoic acid, 12-methyl-, methyl ester
5	11.871	17.617	Pentadecanoic acid, methyl ester
6	1.539	18.569	Hexadecatrienoic acid, methyl ester
7	2.832	18.683	9-Hexadecenoic acid, methyl ester
8	28.133	18.745	9-Hexadecenoic acid, methyl ester
9	1.641	18.864	trans-13-Octadecenoic acid, methyl ester
10	14.991	18.964	Hexadecanoic acid, methyl ester

From Table 1 it can be seen that the composition of methyl ester from sardine flour used cooking oil is dominated by 9-Hexadecenoic acid or another name palmitoleinic acid of 28.133%. According to Taufiqurrahmi et al (2011), used frying oil has a fatty acid composition consisting of palmitic acid 21.47%, stearic acid 13%, oleic acid 28.64%, linoleic acid 13.58%, linoleneic acid 1.59%, myristic acid 3.21%, 1.1% lauric acid and others 9.34%. Based on research from Estiasih & Ahmadi (2004), the composition of fatty acids of fish oil was dominated by palmitic acid 33.91%, oleic acid 20.92% and total omega 3 fatty acids of 21.23%. Fatty acids react with methoxide to form methyl esters. It can be seen from the composition of methyl ester sardine flour used cooking oil.

Analysis of Biodiesel Acid Number

Figure 2 show the number of biodiesel acids at various of NaOH concentration and trans-esterification time reaction at temperatures of 65°C. The acid number is expressed in mg-KOH which is needed to neutralize free fatty acids in 1 (one) gram of biodiesel. The acid number is one indicator of the quality of biodiesel.

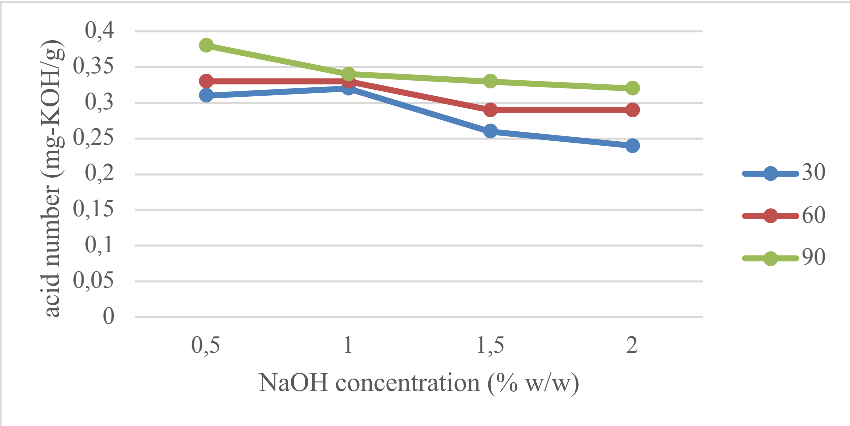

Figure 2. Biodiesel acid number

The value of the biodiesel acid number in the trans-esterification process ranges from 0.24-0.38 mg-KOH/g. The biodiesel quality standard according to SNI 04-7182-2015 is a maximum of 0.5. The resulting biodiesel acid number is below 0.5 so that from the acid number, the biodiesel produced from each treatment meets the biodiesel quality standard. Low acidic numbers indicate that the content of free fatty acids in biodiesel is also low. From the graph it can be seen that there is a trend of decreasing acid numbers along with the increasing number of catalysts added. This is caused by the higher number of catalysts, the greater the free fatty acids that experience saponification so that the acid number decreases. Aziz et al (2012), states that most fatty acids are free to react with catalysts to form soap which is characterized by the formation of emulsions when washing biodiesel with water. Acid biodiesel numbers affect the strength of the corrosion of the engine if it is used as fuel (Laila & Oktavia 2017).

The Density Of Biodiesel

The results of biodiesel density analysis at various catalyst concentrations of NaOH and reaction time are shown in Figure 3.

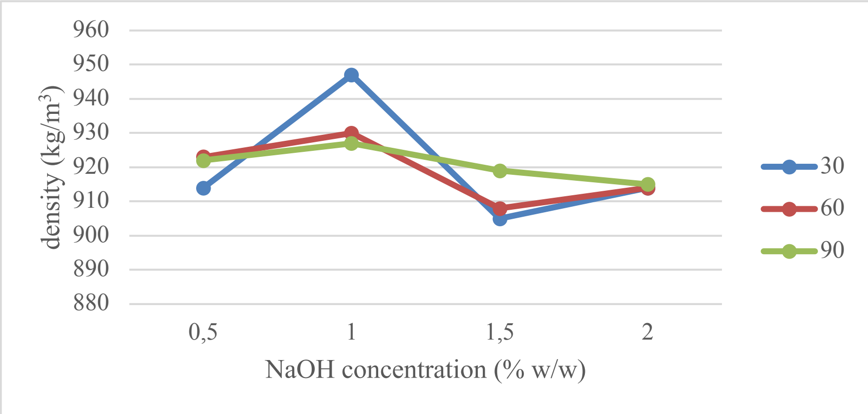

Figure 3. The density of biodiesel

In Figure 3 shows that the highest peak density is at the same NaOH concentration, which is 1%. The highest density value was got at 30 minutes trans-esterification process and the lowest at 90 minutes trans-esterification process. The longer incubation time, at the same NaOH concentration, the density became lower, because chemically, trans-esterification takes the fatty acid complex, neutralizes free fatty acids, removes glycerol, and forms alkyl esters (biodiesel).

The density of biodiesel produced in the study ranged from 905-947 kg/m^3. Provisions of SNI 04-7182-2015 are a maximum of 850-890 kg/m^3. Figure 3 showed that the density produced is more than the maximum limit of the SNI standard. According to Affandi et al 2013, the density of biodiesel is affected by unfavorable purification stages resulting in varying density. Density is an indicator of the amount of impurities such as soap and glycerol as a result of saponification, fatty acids not converted to biodiesel, water, residual sodium hydroxide, or the remaining methanol contained in biodiesel (Pramitha et al., 2016). The density that exceeds the provisions should not be used because it will increase engine wear and cause engine damage (Nurfadillah , 2011).

The Kinematic Viscosity of Biodiesel

The results of biodiesel kinematic viscosity at 40°C analysis at various catalyst concentrations of NaOH and reaction time are shown in Figure 4.

Figure 4 shows the viscosity of biodiesel ranging from 3.13-30.87 mm^2/s. The biodiesel SNI standard 07-182-2015 requires kinematic viscosity at 40°C ranging from 2.3 to 6.0 mm^2/s. From Figure 4 it can be seen that the treatment of 1.5% and 2% NaOH concentrations that meet SNI requirements. In general, the viscosity of biodiesel shows a downward trend with the increasing concentration of NaOH added. The NaOH concentration which produced the lowest viscosity in the treatment of 1.5% NaOH concentration and 60 minutes process duration, ie 3.13 mm^2/s. Viscosity is an important parameter because the fuel that is too thick makes it difficult for flow, pumping and ignition. While fuels that are too runny make it difficult to spread the fuel so that it is difficult to burn and cause leaks in the injection pipe (Setiawati & Edwar, 2012).

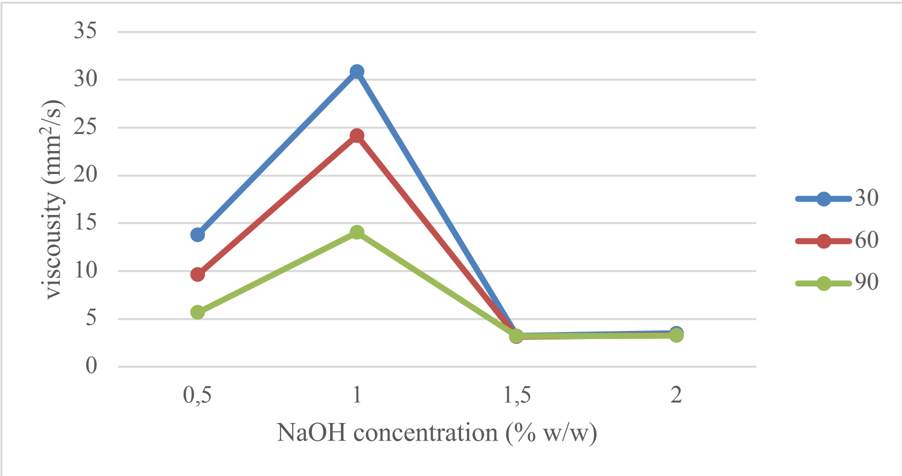

Figure 4. The kinematic viscosity of biodiesel

4. Conclusions

Based on the analysis of GC-MS showed 10 peaks corresponding to ten methyl ester (biodiesel): octanoic acid methyl ester; decanoic acid methyl ester; dodecanoic methyl ester; tridecanoic acid, 12-methyl-, methyl ester; pentadecanoic acid methyl ester; hexadecatrienoic acid methyl ester, 9-hexadecenoic acid methyl ester, 9-hexadecenoic acid methyl ester, trans-13-octadecenoic acid methyl ester, hexadecanoic acid methyl ester. The biodiesel obtained has a density of 908 kg/m3, a viscosity of 3.13 mm^2/s, an acid value of 0.29 mg-KOH/g was found in treatment 1.5% NaOH and time process of 60 minutes. Viscosity and acid value were in a good agreement with SNI standard 04-7182-2015.

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