Jurnal Teknologi

Full Paper

THE BIODIESEL PROCESSING FROM OIL OF YELLOWFIN TUNA [*Thunnus albacares* (Bonnaterre, 1788)] OFFAL USING ACID CATALYST

Article history
Received
6 November 2015
Received in revised form
26 January 2016
Accepted
26 February 2016

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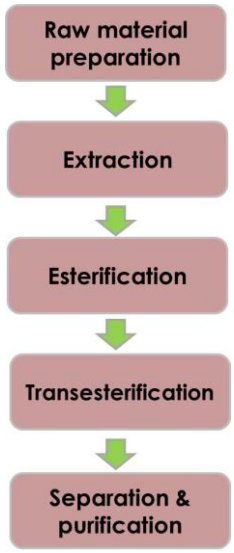
Graphical abstract



Abstract

Biodiesel is one of the alternative fuels to meet the need of the diesel fuel in Indonesia. One of potential animal oil/fat to be utilized as biodiesel raw material is offal from yellowfin tuna. The objective of the study is to know the free fatty acid (FFA) levels of raw material, influence of the H_2SO_4 concentration as catalyst on biodiesel conversion, composition of the main Fatty acid compounds from biodiesel, and physical characteristics of biodiesel through esterification and transesterification reaction. In transesterification phase, the variabel is H_2SO_4 concentration 1.25 %, 1.50% and 1.75 % at 60 °C and 65 °C with oil to methanol molar ratio of 1:9. Based on experiment results, the know that: FFA content from oli of yellowfin tuna offal amounted to 2.33 %, the largest conversion of methyl ester from spectra of H-NMR, FT-IR, GC-MS and ASTM was produced from the treatment with 1.50 % H_2SO_4 at 65 °C, with an average yield of 89.09 % and the conversion value of methyl ester was 52.63 %. The main compounds of Fatty acids that formed biodiesel were palmatic acid (43.64 %) and oleic acid (32.08 %). The physical characteristics of biodiesel according to the national standards of Indonesia (NSI) were specific density of 0.8637 60/60 °F g mL^{-1} kinematic viscosity of 2.555 mm^2 s^{-1}, pour point is -3 °C and cloud point of 25 °C, while flash point of 25 °C and water content of 0.20 % was not consistent with the SNI.

Keywords: Acid catalyst, biodiesel, esterification, transesterification, temperature, offal, yellowfin tuna [*Thunnus albacares*(Bonnaterre, 1788)]

1.0 INTRODUCTION

Indonesia is one of the largest fossil oil producers in the world but is still importing fuel to meet domestic needs in the transportation and energy sectors. The value of crude oil imports in the third quarter of 2014 was approximately USD 9.93 × 10^9 and exports of oil in the third quarter of 2014 was US$ 3.59 × 10^9[1]. Government Regulation No. 79 in 2014 on national energy policy was issued to address the nation's energy problems. These regulations set targets of the energy conditions that must be met by 2025 (23 % for new and renewable energy, 25 % for oil, 30 % for coal and 22 % for natural gas) and in 2050 (31 % for new and renewable energy, 20 % for petroleum, 25 % for coal and 24 % for natural gas). This policy is very interesting because of the use of new and renewable energy with a very large number where biodiesel is also included. According to the Directorate General of New Renewable Energy and Energy Conservation, total biodiesel requirement in 2025 is expected to reach 15 × 10^6 kL yr^{-1} and in 2035 reached 27.4 kL yr^{-1}, while the total biodiesel production in 2013 only 2.2 × 10^6 kL yr^{-1} [2].

Related to the issue about alternative energy sources (biodiesel), the Ministry of Maritime Affairs and

Fisheries published a regulation on improving the added value of wastes from fishing industry into non consumption fisheries products that have an important economic value [3]. In the period from 2013 to 2014, Directorate of Non Consumption Fishery Products, Ministry of Marine Affairs and Fisheries, prioritize the processing of non consumption products of the fishing industry by products, such as gelatin, collagen, organic fertilizer, flour and fish feed, biodiesel, craft leather products, chitin and chitosan.

Indonesia fishery potential is enormous because Indonesia is the largest archipelago country in which two third of it is the ocean. One of the abundant marine resource is tuna. Tuna fish production in Indonesia reached 613 575 t yr^{-1} with a value of IDR 6.3 × 10^{12}. In 2008 the government restricted the export of fish in an intact form, then it is spurring the growth of fish processing units that could potentially produce waste. Waste generated from fishing activity is still quite high, around 20 % to 30 % [4]. Utilization of oil from fish waste is a very appropriate choice because it is a non-food product that is constantly generated in the production process. Types of waste containing oil in bulk is offal, head and skin. The results of observations on the tuna and marlin loin industry show that tuna weighing 75 kg to 90 kg produces approximately 5 kg offal, marlin weighing 90 kg to 100 kg produces 7.5 kg offal and skipjack weighing 12 kg produces approximately 1.0 kg offal. This waste contain the oil that has the potential to be utilized as raw material for biodiesel [5].

The quality of biodiesel depends on the content of FFA. Production of biodiesel from oils with a high free Fatty acid content requires a two-stage process that is esterification reaction and transesterification reaction [6]. The esterification reaction serves to convert FFA to methyl ester in the early stage of the reaction, followed by a transesterification reaction at a later stage. When oils with a high free Fatty acid content, is directly converted into biodiesel by transesterification reaction using an base catalyst, most of the catalyst will react with the fatty acid to form soap [7]. This reaction leads to the saponification reaction pathways and esterification reaction.

Esterification and transesterification reaction can be used as a catalyst. Super acid catalyst SO_4^{2-}/ZnO with a conversion of 78.00 % [8]. Conversion of biodiesel from oils flour sardines by 45.34 % using NaOH catalyst [9]. Ash empty fruit bunches yield biodiesel with the acquisition of 84.12 % [10]. The processing of biodiesel using alkaline catalysts have some drawbacks that form side products such as soaps which are difficult to be separated from the main product so the effectiveness of the catalyst decrease and these conditions will decrease the yield of biodiesel [11]. In contrast, the process of making biodiesel using an acid catalyst does not form soap. Therefore the choice of processing biodiesel from yellowfin tuna offal using acid catalyst (H_2SO_4) is expected to increase biodiesel conversion.

2.0 EXPERIMENTAL

2.1 Material and Apparatus

Yellowfin tuna [*Thunnus albacares* (Bonnaterre, 1788)] offal was obtained from KUB Fresh Fish, Bantul, Yogyakarta. Hexane (technical), methanol (pro analysis; Merck), sulfuric acid (pro analysis; Merck), Na_2SO_4 anhydrous (pro analysis; Merck), distilled water, ethanol (pro analysis; Merck), phenolphthalein pH indicator, NaOH (pro analysis; Merck) were used for chemical process. Three-neck flask (500 mL; Pyrex), thermometer (Pyrek), magnetic stirrer (1.5 cm), turning cooler (spiral shapes; Pyrek), analytical balance (320 g × 0.01 g, Shimadzu; and 1 000 g × 0.1 g, Tanita), hot plate stirrer (maximum temperature 400 °C and the stirrer max 10 per BSI), evaporator (Heidolph), pipette, measuring cups (250 mL, 100 mL; Pyrex), funnel separator (250 ml; 500 ml per Herma), water pump (400 L · h^{-1}; Aquila), H-NMR (500 MHz per aligent), FT-IR, GC-MS (Shimadzu QP-2010S), ASTM D (1298; 93; 445; 95; 97; 2500) were used in this experiment.

2.2 Methods

2.2.1 Oil Preparation

Samples were prepared based on previously developed method [12]. Tuna fish offal was filtrated using filter paper until pulp was removed. Hexane form oil extract was evaporated using evaporator to obtain pure oil. FFA was examined using following formula (1) follow reference [13]:

$$\text{FFA}(\%) = \frac{a \times M \times 282 \times 100}{g \times 1000} \quad (1)$$

a : NaOH volume (ml)
M : NaOH molarity
g : Sample weight (g)
282: The molecular weight of oleic acid (g · mol^{-1})

2.2.2 Esterification Reaction

Esterification reaction process begins with the heating oil at 70 °C for 1 h with the aim of eliminating the water content in the material, allowed to stand up to a temperature at 60 °C, the preparation of esterification [14]. The esterification reaction is done by setting up oil extracted from tuna fish offal as much as 300 g and methanol as much as 7.17 g. Both ingredients were mixed, then 10 % of H2SO4 was added. Reflux system was prepared by heating it at 65 °C for 1.5 h. Then, oil was poured into the separating funnel. This process was able to separate oil from dirt and water.

2.2.3 Transesterification Reaction

Transesterification reaction carried out by reacting with a solution of H_2SO_4 fish oil in accordance with the treatment, which was dissolved in methanol at a

temperature of 60 °C and 65 °C for 1.5 h at reflux system. The process of settling (separation) is performed to separate between biodiesel and glycerol produced, settling time depends on the clear separation (biodiesel on the upper surface and soap or glycerol on the bottom surface). The separation process using a funnel separator. Biodiesel was washed with distilled water in order to dissolve the methanol, glycerol and soap that were still ending up after the separation process. Washing was done approximately three times or until distilled water was clear. The addition of anhydrous Na_2SO_4 was useful to absorb the water content which may still present in order to obtain pure biodiesel. Biodiesel filtration was useful to separate the dirt mixed in pure biodiesel, thus, biodiesel that was clean from dirt and dust of anhydrous Na_2SO_4 was obtained.

2.2.4 Conversion of Methyl Ester

The conversion of fish offal oil yellow fin tuna as methyl esters (biodiesel) is done with 1H-NMR methods [17] using the following formula (2).

$$C_{ME} = 100 \times \frac{5 \times I_{ME}}{(5 \times I_{ME} + 9 \times I_{TAG})} \quad (2)$$

C_{ME} : Conversion of methyl ester (%)
I_{ME} : Integration of peak methyl ester (%)
I_{TAG} : Integration of peak triacylglycerol (%)

The percentage results of the transesterification reaction can be calculated based on the percentage of proton spectra on the type of bond proton spectra glycerides and methyl esters. Factor five and nine are the result of the fact that glycerol in triglyceride has five protons and three methyl ester produced from a triglyceride has nine protons [17].

Identification of the compound methyl ester biodiesel test conducted by FT-IR. Analysis of the composition of fatty acid compound forming biodiesel tested GC-MS. The biodiesel quality tested with ASTM standards, include specific density, flash point, kinematic viscosity, water content, pour point, and could point.

2.3 Treatment

The treatments transesterification reaction is a variation of H_2SO_4 catalyst concentration of 1.25 %, 1.50 % and 1.75 % of the total weight of the oil and methanol (w/w), with a mole ratio of oil: methanol was 1:9 at 60 °C and 65 °C. The ratio of 1:9 produces the largest biodiesel yield. The boiling point of methanol 65 °C [15, 16].

2.4 Statistics Analysis

ANOVA test is used to determine the effect of treatment on the quality and characteristics of biodiesel from yellowfin tuna offal. If the treatment is tested significantly, there will be a further test with the DMRT (Duncan Multiple Ranges Test) [18]. The data that tested is the yield value of the transesterification reaction by treatment with H_2SO_4 catalyst at a concentration of 1.25 %, 1.50 % and I.75 % with the temperature at 60 °C and 65 °C.

3.0 RESULTS AND DISCUSSION

3.1 Extraction oil of Yellowfin Tuna Offal

Oil yield obtained from the extraction is 16.58 %, lower compared to the [18] and [19], rather larger compared with [20] and [21]. Oil yield from the various research results can be seen in Table 1. The resulting oil yield varied because ratio of raw materials (oil) and solvent at the time of extraction and solvent polarity level are different. The greater the level of solvent comparison used the greater the yield generated [23]. Oil yield increases when the solvent used has a degree of polarity and low boiling point [24].

3.2 Free Fatty Acid

Averages FFA content of oil tuna Offal amounted to 2.33 %. The resulting percentage is too high so as to get rendemen of biodiesel a lot more must go through two stages of reaction is the reaction of esterification and transesterification reactions. Oil with high FFA content requires two steps reaction, namely the esterification and transesterification reactions [25]. Esterification process serves to convert the free fatty acids to methyl ester in the early stages. FFA results the obtained when compared with lower [8] and [26]. Percentage FFA of various research results are shown in Table 2.

FFA rate differences caused by the composition of the oil. CPO has a high FFA values as contained in the CPO is not only oil, but there are other substances such as water. The presence of water in the oil will increase the value of FFA due process of hydrolysis during storage, triglycerides will react with the water to form glycerol and free Fatty acids [26]. FFA values were very low in the process of making biodiesel because it can improve biodiesel conversion. In the oil of yellowfin tuna offal, FFA generated little value, this is due to other substances such as water and impurities are not entrained into the oil.

Table 1 The yield of oils extracted from various research results

Description	Research of Oil Extraction					
	[39]	[18]		[19]	[20]	[21]
Raw Material	Offal of yellowfin tuna fish	Meat of lemuru fish		Offal and skin of black tilapia fish	Offal and head of carp fish	Meat of swangi fish
Solvent	*n*-hexane	ether	chloroform	methanol 96%	heksane	Aquadest
Ratio of oil : solvent (v/v)	1:2	1: 5	1:5	1:2	-	1: 2
Yield (%)	16.58	68.55	60.09	30.99	13.62	1.23

Table 2 FFA percentage of different raw materials

No	Description	The Percentage of FFA		
		[9]	[24]	[39]
1	Raw material	Oil of sardines fish meal	CPO	Oil of yellow fin tunal
2	FFA (%)	3.80	5.20	2.33

3.3 Esterification Reaction with Acid Catalyst (H_2SO_4)

Oil extracted from tuna fish offal wastes are esterified with methanol amounted to 300 g. Methanol and oil mole ratio of 9:1, assuming a molecular weight of free fatty acids amounting to 282 g mol^{-1}, the weight of the methanol used as much as 7.17 g. Results obtained from 300 g of oil produces an average of 248 g (94.67 %). Using biodiesel derived from waste offal and black tilapia skin to obtain yield of 91.89 % and 81.38 % with oil and methanol mole ratio of 1:6 [20]. The difference is caused by the mole ratio of methanol and oils. Oil and methanol mole ratio of 1:9 can produce methyl ester yield more because on the whole the ratio of triglycerides have been exhausted converted into biodiesel [10] and [15]. Excessive use of methanol which aims to make the water formed from the reaction can be absorbed by methanol, so as not to hinder the course of the conversion reaction of the free fatty acids into methyl ester [28].

3.4 Transesterification Reaction with Acid Catalyst (H_2SO_4)

Methyl ester obtained from the esterification reaction was taken as much as 50 g, which use temperature is 60 °C and 65 °C with each treatment was 1.25 %, 1.50 % and 1.75 %. Based on the results of analysis show that the catalyst concentration of 1.5 % H_2SO_4 at 65 °C showed the greatest yield with a mean value of 89.09 %, followed by the result of the concentration of 1.75 % H_2SO_4 catalyst with a temperature at 65 °C with a mean of 84.50 % (Figure 1). At 1.75 % H_2SO_4 catalyst concentration decreased yield of biodiesel because biodiesel product that adsorbed into the catalyst [29]. When the acid catalyst is added too much resulting mixture of catalyst and reactant becomes thick, so the impact on the yield generated [8].

ANOVA analysis results showed that the conversion of biodiesel resulting from the treatment (60 °C concentration of 1.25 % ≠ concentration of 1.50 % ≠ concentration of 1.75 %, so does the temperature at 65 °C, concentration of 1.25 % ≠ concentration of 1.50 % ≠ concentration of 1.75 %), meaning that from each treatment were tested there is a difference, to determine the best average rank test based on further namely DMRT (Duncan Multiple Range Test). From the results of DMRT known that the best treatment was obtained from the catalyst concentration of 1.5 % at 65 °C with a yield of 89.09 %, followed by the results of the treatment catalyst concentration of 1.75 % at 65 °C with a yield of 84.50 % view.

The yield obtained when compared with the other researcher is greater, by contrast when compared with other studies obtained a smaller yield [9, 16, 31]. The yield of the transesterification reaction results from various research results are shown in Table 3. From the results of the research it can be concluded that the oil and methanol mole ratio of 1:9 is the best ratio for triglycerides that has completely reacted with methanol to form methyl esters. Good catalyst was used in the manufacture of biodiesel is a catalyst capable of converting triglycerides into methyl ester in large amounts and relatively quickly [29]. The temperature is best used does not exceed the boiling point of methanol at 65 °C because if the temperature used is higher than the methanol evaporated more than reaction with triglyceride to form methyl esters.

3.5 Biodiesel Conversion with ^{1}HNMR Methods

Based on the ^{1}HNMR methods, the highest biodiesel conversion resulting from the treatment of the catalyst concentration of 1.5 % at 65 °C, is 52.63 %, followed by the result of a concentration of 1.5 % and 1.75 % at 60 °C is 39.32 %. Increased catalyst concentration followed by increased conversion of methyl ester produced until the optimum concentration of 1.5 % (Figure 2). The addition of 1.75 % catalyst at 60 °C and 65 °C decreased biodiesel conversion of 39.32 %. This is due to biodiesel produced that is absorbed into the catalyst. The addition of excess catalyst results in a mixture of catalysts and reactants so it is difficult to separated [29]. If compared with result of other researcher they are lower because of the type of catalyst used have different reaction rates [9, 10, 29].

The transesterification reaction using alkaline catalyst is faster than the acid catalyst because in an alkaline solution, carbonyl directly attacked by the nucleophilic without prior protonation [30]. By contrast in comparison with other researcher conversion is greater (Table 4) [9, 15, 19]. The main factors which are most influential in making biodiesel is FFA feeds tock, a high FFA content results in the saponification reaction to the content of FFA in the material should be as minimal as possible.

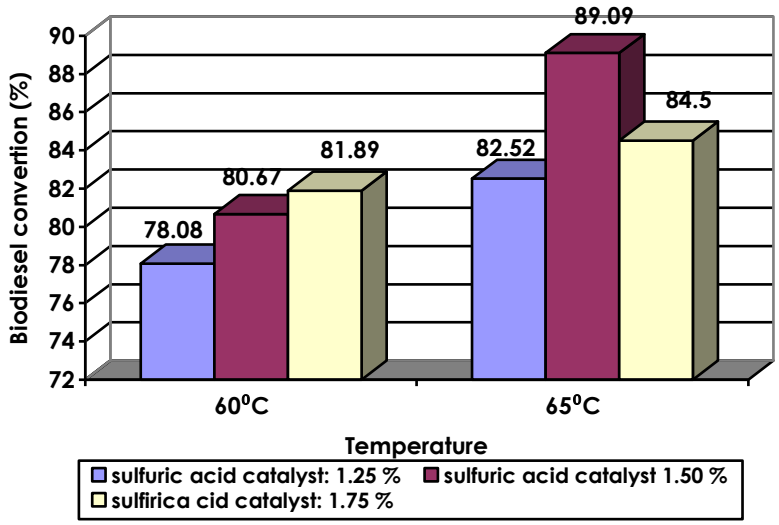


Figure 1 The effect of temperature and catalyst concentration on the biodiesel yield

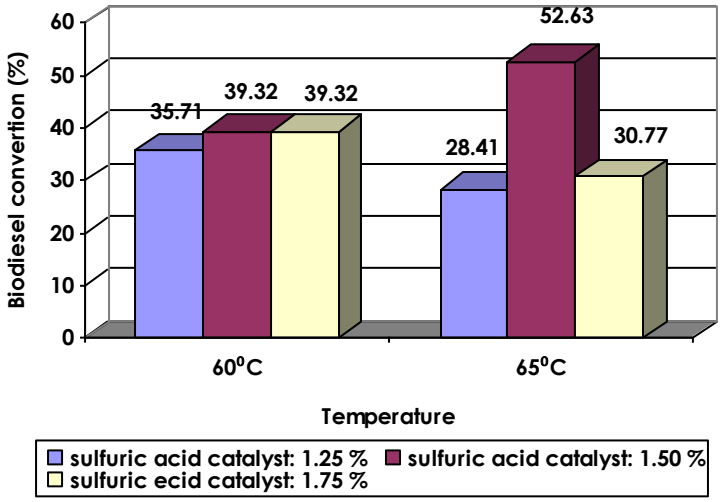


Figure 2 The effect of catalyst concentration and temperature on the biodiesel conversion

Table 3 Biodiesel conversion value of transesterification reaction from various research

Description	**Biodiesel conversion value from any research**						
	[9]	**[30]**	**[15]**	**[29]**	**[10]**	**[19]**	**[39]**
FFA(%)	3.80	5.17	4.86	2.33	-	-	2.33
Mole ratio methanol : oil	6:1	22 % (w/w)	9:1	9:1	9:1	6:1	9:1
Times (hours)	2	1	2	1,5	2	2	1,5
Types of catalyst	NaOH	Ash bunches	KOH	CaO	Ash bunches	NaOH	H_2SO_4
Catalyst concentration (%)	1.5	2.0	1.5	1.5	15 in 75 mL methanol	1.5	1.5
Conversion (%)	45.34	65.60	43.08	100	84.12	40.50	52.63

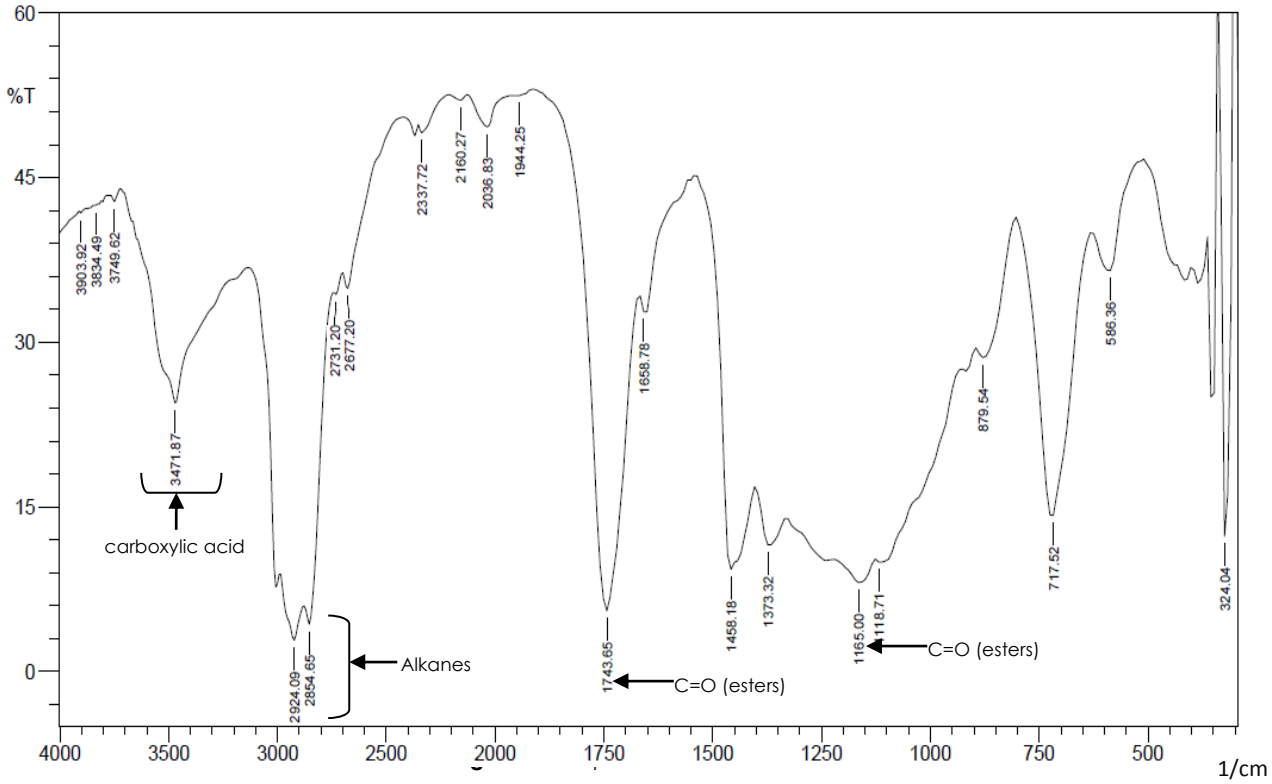


Figure 3 FTIR spectra of biodiesel

3.6 Identification of Methyl Ester Kinds

The resulting spectra showed the presence of a strong absorption in the region 1 743.65 cm^{-1} which is the characteristic absorption for the carbonyl group C=O ester. Ester formation is also reinforced by a sharp uptake in the area of 1 165 cm^{-1} which showed the presence of CO ester bond. According to reference [13], the ester group contained in the catchment area from 1 080 cm^{-1} to 1 300 cm^{-1} and 1 690 cm^{-1} to 760 cm^{-1}. Sharp uptake in the area of 2 924.09 cm^{-1} and 2 854.65 cm^{-1} is an absorption for the group alkanes (Figure 3). Based on the distribution of these spectra, indicated that the methyl esters resulting from the transesterification reaction containing hydrocarbon chain with an ester group at the chain terminal. A strong absorption was obtained at 1 743.65 cm^{-1} region [9, 33].

3.7 Composition of Fatty Acid Compounds Former Biodiesel

GC-MS test is used to determine the composition of methyl ester-forming compound. Analysis by GC-MS carried out on a sample of biodiesel that has the greatest yield of conversion is the catalyst concentration of 1.5 % H_2SO_4 at 65 °C. The conversion of biodiesel taken from the H-NMR test results. GC analysis results are shown in Figure 4. GC chromatogram analysis results showed eight peaks were detected as fatty acid methyl esters. A compound is said to be similar to the standard compound if it has the same molecular weight, and the price of SI (Similarity Index) is high. Results of the gas chromatography analysis by the catalyst concentration H_2SO_4 1.5 % at 65 °C can be seen in Table 5.

Based on the results of GC-MS analysis, it was concluded that the content of methyl ester biodiesel is the highest in methyl palmitate (43.64 %) followed by methyl oleic (32.08 %) can be seen in Table 4. Biodiesel from oil flour waste sardines have a main fatty acid component forming biodiesel is methyl palmitate (20.31%) and methyl oleate (13.93 %) [9]. Biodiesel from tuna fish offal have primary fatty acid is methyl palmitate (43.79 %) and methyl oleate (39.32 %) [30]. Oil that are commonly used as the base material of biodiesel are triglycerides containing palmitic acid, stearic acid, and oleic acid [29].

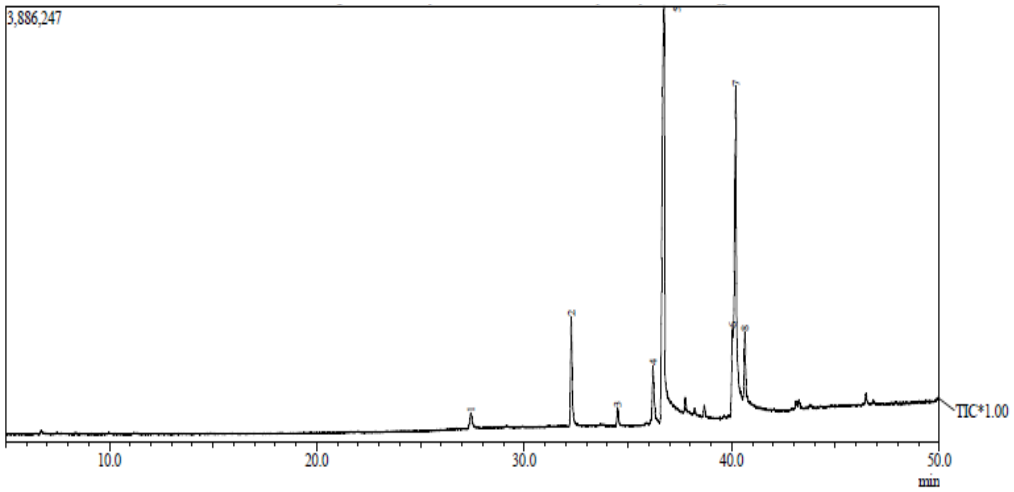


Figure 4 Chromatogram of methyl ester mixture

Table 4 The results of gas chromatographic analysis with catalyst concentration $H_2SO_4$1.5 % at a temperature of 65 ºC

No	Retention Time (Minutes)	Peak	Compound (%)	Compound types
1	27.419	1	1.00	Methyl laurate
2	32.158	2	7.05	Methyl myristate
3	34.496	3	1.06	Pentadecanoic acid
4	36.200	4	3.92	Methyl palmitoleic
5	36.739	5	43.64	Methyl palmitate
6	40.033	6	5.34	Methyl linoleic
7	40.196	7	32.08	Methyl oleate
8	40.633	8	5.93	Methyl stearate

3.8 Physical Quality of Biodiesel

The physical characteristics of biodiesel from yellowfin tuna offal will be compared with the ISO standard, diesel oil 48 and ASTM-D 6751 (Table 5). The physical properties were analyzed, which consists of: specific density, flash point, kinematic viscosity, water content, pour point and cloud point.

3.8.1 Specific Density

The value of the specific density of biodiesel produced by 0.8637 °F (mg·L^{-1}), shows that the value of the specific density of biodiesel oil yellow fin tuna fish offal already meet the standard specifications of diesel oil. Previous research reported study to obtain a specific density value respectively by 0,8080 °F (mg·L^{-1}), 0,8885 °F (mg·L^{-1}) and 0,8914 °F (mg·L^{-1}) [9, 16, 30]. Specific density value can be used to calculate the heat of combustion. High heat of combustion that shows the quality of the combustion of fossil fuels, the better [38].

3.8.2 Flash Point

The resulting flash point of 25 °C, do not achieve the quality requirements of biodiesel (ISO, ASTM and diesel). Low flash point was caused by the compounds contained in biodiesel. Based on the test results, the GC-MS is the main component of palmitic acid. Palmitic acid is a saturated fatty acid with a bond that has a high octane number and flammable. According to [39], biodiesel contains high unsaturated bond is biodiesel that is resistant to oxidation and has a high octane number. Flash point is related to security and safety, especially in handling and storage. Previous study scored a flash point 180 °C respectively, 104.5 °C and 172.5 °C [9, 15, 19]. This value already meets the standard specifications of diesel oil, so it is safe to use during storage, handling and transportation. High flash point indicates low volatility/steam and Flammability of a fuel [39].

3.8.3 Kinematic Viscosity

The value of the kinematic viscosity of 2.55 cSt in this study has been allowed to meet the specifications (ISO, ASTM standards, and diesel). Viscosity of 4.113 cSt and 3.079 cSt was obtained from other study [9, 19]. Too high viscosity can complicate the flow, pumping and lighting. Otherwise the viscosity is too low value fuel difficult to burn and will cause leaks in the injection pipe [39].

Table 5 Comparison of the physical properties of biodiesel from yellowfin tuna offal with ISO standards, diesel oil 48 and ASTM D 6751

No	Physical Characteristics	[39]	Standards					
			[33]		[40]		[41]	
		H_2SO_4	min.	max.	min.	max.	min.	max.
1	Specific density 60/60 °F. (mg/L)	0.864	0.850	0.890	0.820	0.870	0.840	0.920
2	Flash Point (°C)	25	100	-	60	-	130	-
3	Kinematic viscosity 40 °C, (cSt)	2.555	2.3	6	1.6	5.8	4.5	7
4	Water content % (wt)	0.20	-	0.05	-	0.05	-	0.05
5	Pour point (°C)	-3	-15	13	-	18	-	
6	Cloud point (°C)	0	-	18	-		Reported	

3.8.4 Water Content

The water content in the oil is one measure of the quality of the oil. The resulting moisture content of 0.20 % indicates that very high of water content does not comply with ISO, ASTM standards or diesel oil. The high water levels caused by the washing process is less than perfect so that the water left in biodiesel. The value of water content of trace (where very little water) [9, 15]. The presence of water in the biodiesel can enlarge the hydrolysis reaction which can lead to increased levels of free fatty acids. The water content in the fuel can also result in lower heat of combustion, foamy and corrosive reaction with sulfur because it will form the acid. The presence of water since the beginning of the reaction is undesirable because it can interfere with the formation of biodiesel.

3.8.5 Pour Point and Cloud Point

Diesel fuel must be able to flow freely at the lowest possible temperature of the atmosphere when the fuel is used. Lowest temperature at which diesel fuel can still flow is called pour point. Low pour point has the advantage; that is, biodiesel does not easily freeze at low temperatures. Pour point value generated at -3 °C, has met the biodiesel specification (ISO, ASTM standards or diesel). Haze point occurs when the oil is cooled to form a sort of haze caused by crystal formation and solidification [37]. Cloud point value generated at 0 °C, has met the specifications of biodiesel. Low cloud point value can affect the smooth flow of fuel, so it is easy to flow inside the filter, pump and injector machines. In contrast cloud high point value can clog fuel flow.

4.0 CONCLUSION

FFA content from oil of yellowfin tuna offal amounted to 2.33 %, the largest conversion of methyl ester from spectra of H-NMR, FT-IR, GC-MS and ASTM was produced from the treatment with 1.50 % H_2SO_4 at 65 °C, with an average yield of 89.09 % and the conversion value of methyl ester was 52.63%. The main compounds of fatty acids that formed biodiesel were palmatic acid (43.64 %) and oleic acid (32.08 %). The physical characteristics of biodiesel that according to the national standards of Indonesia (NSI) were specific density is 0.8637 60/60 °F (mL g^{-1}), kinematic viscosity is 2.555 $mm^2 \cdot s^{-1}$, pour point is -3 °C and cloud point is 25 °C, while flash point is 25 °C and water content is 0.20 % do not according to the SNI.

Acknowledgements

Acknowledgements submitted to the honorable: Juju Junengsih, Ridwan Latif Fauzi, laboratory/ technician on Fish Technology Laboratory, Animal Feed and Nutrition Laboratory, Department of Fisheries Science, Faculty of Agriculture, Gadjah Mada University who has helped smooth the study, and also the Research Institute for Community Service, Gadjah Mada University, Yogyakarta.

References

[1] Alhusain. 2014. Dynamics of World Oil Prices. [Online]. From http://documen.dpr.go.id/assessment/files/shor_info/Info%20short-VI-24-II-P3DI-Dec-. [Accessed on 3 February 2014].

[2] Sugiyono, A., Anindhita, M. S. Boedoyo, and Adiarso. 2014. *Indonesia Energy Outlook*. Jakarta: Agency for the Assessment and Application of Technology.

[3] Ministry of Energy, Resources and Mineral, Republic of Indonesia. 2012. *New Renewable Energy and Energy Conservation in Indonesia* [Statement of Directors]. Jakarta: Directorate Oil and Gas, Ministry of Energy, Resources and Mineral, Republic of Indonesia.

[4] Institute for Research and Development Ministry of Marine Affair and Fisheries Jakarta. 2015. The First in the History of the CTF Success Make Tuna Spawning. [Online]. From http://www. Balitbang-kp.kkp.go.id/ read-more-10038.aspx. [Accessed on 4 June 2015].

[5] Sahubawa, L. 2012. Biofuel Production and Quality Optimization Results Esterification and Transesterification Reactions Storey with Natural and Chemical Catalysts [Lecturer Notes]. Yogyakarta: Gadjah Mada University.

[6] Patil, P. D. and S. Deng. 2009. Transesterification of *Camelina sativa* Oil Using Heterogeneous Metal Oxide Catalysts. *Journal of Energy and Fuels*. 1(23): 4619–4624.

[7] Akhirudin. 2006. *College Keen Biodiesel*. [Online]. From: http:// disperindag.jabarprov.go.id/. [Accessed on 20 July 2014].
[8] Utami, I., R. Solikhah, and I. Istadi. 2012. Synthesis Catalysts Super Acid SO2-4 / ZnO for Biodiesel Production from Palm Oil. *Journal of Chemical Industrial and Technology*. 1(2): 69–78.
[9] Sahubawa, L. and D. P. Ningtyas. 2013. Pengaruh Penggunaan Katalis NaOH pada Reaksi Transesterifikasi terhadap Kualitas Biofuel Limbah Minyak Teping Ikan Sardin [The Effect of Using NaOH Catalyst in Transesterification Reactions on the Biofuels Quality from Sardine Flour Oil Waste]. *Jurnal Saintek Perikanan*. 7(1): 88–93 [Bahasa Indonesia].
[10] Sibarani, J., S. Khairi, Yoeswono, K. Wijaya, and I. Tahir. 2007. Pengaruh Abu Tandan Kosong Kelapa Sawit pada Transesterifikasi Minyak Kelapa Sawit Menjadi Biodiesel [Effect of Palm Empty Bunch Ash on Transesterification of Palm Oil into Biodiesel]. *J. Chem*. 2(7): 314–319. Bahasa Indonesia].
[11] Santoso, H., Y. Yunus, and T. M. Anggraini, 2011. Efek Gula dalam Katalis Biodiesel dari Minyak Goreng [*Performance Sugar in Catalysts Biodiesel from Used Cooking Oil*] [Research Report]. Bandung: Parahyangan Catholic University. [Bahasa Indonesia].
[12] Folch, J., M. Lees, and G. M. S. Stanley. A Simple Method for the Isolation and Purification of Total Lipids from Animal Tissue. *Journal of Biological Chem*. 2 (226): 497–509.
[13] Destianna, M., A. Zandi, Nazef and A. Puspasari. 2007. Fisisologi Tumbuhan dan Lingkungan [*Plant Physiology and Environmental*]. Lecture Notes. Yogyakarta: Gadjah Mada University. [Bahasa Indonesia].
[14] Awaluddin, A., Saryono, S. Nelvia and Wahyudi. 2008. Faktor-Faktor yang Mempengaruhi Produksi Biodiesel dari Minyak Sawit Mentah Menggunakan Katalis Padat Kalsium Karbonat yang Dipijarkan [Factors Affecting Production of Biodiesel from Crude Palm Oil Using Incandescent Calcium Carbonate Solid Catalyst]. *Journal of Natural Indonesia*. 3(11): 129–134. [Bahasa Indonesia].
[15] Pamungkas, A. 2013. *Pengaruh Konsentrasi Katalis Kalium Hidroksida dalam Reaksi Transesterifikasi terhadap Rendemen dan Konversi Biodiesel dari Limbah Minyak Ikan Sardin* [The Effect of The Concentration of Potassium Hydroxide Catalyst In The Transesterification Reaction on The Yield and Conversion of Biodiesel from Waste of Sardine Fish Meal Oil]. Research Report. Yogyakarta: Gadjah Mada University. [Bahasa Indonesia]
[16] Knothe, G. 2000. Progressing Transesterification Reaction Monitoring a Fiber–Optic by Near Infrared Spectroscopy with Correlation to Nuclear Magnetic Resonance Spectroscopy. *JAOCS*. 2(77): 489–493.
[17] Besral. 2012. One Way ANOVA in SPSS In Data Processing and Analysis-1 Use SPSS. [Online]. From: http://www.statiskian.com/2012/11/one-way-ANOVA. [Accessed on 9 July 2009].
[18] Mudawamah, U. 2007. Isolasi Asam Lemak dari Minyak Ikan Lemuru (*Sardinella longiceps*) dengan Berbagai Pelarut dan Identifikasinya Menggunakan Gas Chromatography–Mass Spectroscopy (GC–MS) [Isolation of Fatty Acids in Fish Oil Lemuru *(Sardinella longiceps)* with Variation Solvent and Identification Using Gas Chromatography–Mass Spectroscopy (GC–MS)]. Research Report. Malang: Islamic University of Malang. [Bahasa Indonesia].
[19] Kurniawan, C. B. 2012. *Biodiesel dari Organ Dalam dan Kulit Ikan Tilapia HItam* [Biodiesel from Offal and Leather of Black Tilapia] [Research Report]. Yogyakarta: Gadjah Mada University. [Bahasa Indonesia].
[20] Kaban, J. and Daniel. 2005. Synthesis of N-6 Fatty Acid Ethyl Esters of Some Fresh Water Fish Oil. *Journal of Communication Research*. 2(17): 16–23.
[21] Huli, L., A. S. H. Suseno, and J. Santoso. 2014. Kualitas Minyak Ikan dari Kulit Ikan Swangi [Fish Oil Quality of By-product (Fish Skin) from Swangi Fish]. *Journal PHPI*. 3(17): 233–242. [Bahasa Indonesia].
[22] Parth, N. P., M. P.Krupa, S. C. Dhaval, G. P. Khushboo, A. H. Henil, D. K. Chandni, *et al*. 2011. Extraction of Herbal Aroma Oils from Solid Surface. *Pharmacie Globale IJCP*. 2(9): 1–10.
[23] Guenther, E. 1987. *Essential Oils*. Ed. 1, Volume 1. Jakarta: UI Press.
[24] Kurniati, Y. and W. H. Susanto. 2015. *Pengaruh Kandungan Basa NaOH dan Kandungan ALB CPO terhadap Kualitas Minyak Kelapa Sawit Pasca Netralisasi* [Effect of NaOH Bases and Content of Free Fatty Acid (FFA) on CPO to the Quality of Post-neutralization Palm Oil]. *Journal of Food and Agro–industry*. 1(3): 193–202. [Bahasa Indonesia].
[25] Junengsih, J. 2015. *Pembuatan Biodiesel dari Organ Dalam dari Tuna Sirip Kuning Menggunakan Katalis Asam* [Biodiesel Processing of Yellow Fin Tuna Offal Using Acid Catalyst] [Research Report]. Yogyakarta: Gadjah Mada University. [Bahasa Indonesia].
[26] Soerawidjaja, T. H. 2006. *Minyak dan Produk Kimia Lain dari Kelapa* [Oil and Other Chemical Products from Coconut] [Lecturer Handouts]. Bandung: Bandung Institute of Technology. [Bahasa Indonesia].
[27] Zhu, H. and W. U. Zongbin. 2006. Preparation of Biodiesel Catalyzed by Solid Super Base of Calcium Oxide and Its Refining Process. *Chinese Journal of Catalysis*. 27(5): 391–396.
[28] Zappi, M., M. Hernandez, D. Spark, J. Horne, and M. A. Brough. 2003. A Review of the Engineering Aspects of the Biodiesel Industry. Mississippi: Missisippi State Universty.
[29] Fauzi, R. L. 2014. *Biodiesel dari Organ Dalam Tuna Sirip Kuning Menggunakan Katalis CaO dengan Metode Transesterifikasi* [Biodiesel from Yellow Fin Tuna Fish Offal Using CaO Catalyst with Transesterification Method] [Research Report]. Yogyakarta: Gadjah Mada University. [Bahasa Indonesia]
[30] Sahubawa, L. and Mastori. 2010. Influence of Catalysts on the Biodiesel Quality of Sardine Fish Meat Oil on a Transesterification Reaction Stage. *Journal of Human and Environment*. 3(17): 12–30.
[31] Nur, M. A. and H. Adijuwana. 1989. *Spectroscopy in Analysis of Biological Analysis*. Bogor: Bogor Agriculture Institute.
[32] Sudarmadji, S., B. Haryono, and Suhardi. 1996. *Analisis Pangan dan Pertanian* [Analysis of Food and Agriculture]. 1st Ed. Yogyakarta: PT. Liberty. [Bahasa Indonesia].
[33] Badan Standarisasi Nasional. 2006. Standar Nasional Indonesia (SNI). SNI-04-7182-2006. Persyaratan Mutu Biodiesel [Quality Requirement of Biodiesel]. Dewan Standarisasi Indonesia. Jakarta. [Bahasa Indonesia].
[34] Turboman. 2013. The Power of Catfish: Biodiesel from *Pangasius djambal* [Online] From: http://forum.o-fish.comviewtopic.phpf=68&t=17249&p=182263. [Accessed on 2 December 2013].
[35] Fina, A. 2012. *Pemanfaatan Limbah Minyak Ikan Sardin sebagai Biodiesel Menggunakan Katalis KOH* [Utilization of Waste Oil Sardine Fish Meal and Biodiesel Using KOH Catalyst]. Research Report. Yogyakarta: Gadjah Mada University. [Bahasa Indonesia]
[36] Oktakarno. 2008. Pengaruh H-Zeolite sebagai Katalis terhadap Total Asam Lemak Bebas dan KOnversi Biodiesel pada Minyak Goreng [*The Effect of H-Zeolite as a Catalyst on the Total of Free Fatty Acids and Biodiesel Conversion in the Cooking Oil*]. Research Report. Yogyakarta: Gadjah Mada University. [Bahasa Indonesia].
[37] Gultom, T. 2001. *Handbook of Biochemistry*. Yogyakarta: Yogyakarta State University.
[38] Hardjono, A. 2001. *Handbook of Petroleum Technology* [Lecturer Notes]. Yogyakarta: Gadjah Mada University.
[39] Sahubawa, L., J. Junengsih, and Ustadi. 2015. *Pembuatan Biodiesel dari Organ Dalam Tuna Sirip Kuning Menggunakan Katalis Asam* [The Biodiesel Processing from Oil of Yellowfin Tuna Offal Using Acid Catalyst] [Research Report]. Yogyakarta: Gadjah Mada University. [Bahasa Indonesia].
[40] Director General of Oil and Gas. 2006. *Decree on Specifications Fuel of Solar Types Oil, Type 48 and 51, No. 3675 K/24/DJM/2006, Dated 17 March 2006*. Jakarta:

Ministry of Energy, Resources and Mineral of the Republic of Indonesia.
[41] ASTM-D 6758. 2003. *American Standar Testing Method of Biodiesel*. USA: Standard Test Method for Measuring Stiffness and Apparent Modulus of Biodiese by an Electro-Mechanical Method.