Temperature and Catalyst Variations for Optimal Biodiesel Oil Production from *Callophyllum Inophyllum L* using Esterification and Transesterification (ESTRANS) Process

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Received: 13.12.2016 Accepted:06.04.2017

Abstract-*Callophyllum Innophyllum L.*, called *Nyamplung* in Indonesia, is an evergreen tree whose seed oil has potential as a source of biodiesel. This is one form of alternative energy that could contribute to solve the current problem of diminishing petroleum energy and can help to reduce air pollution. This research developed a method for biodiesel production by utilize catalyst to produce methyl esters compound in nyamplung oil.This method focused on the variation in temperature and catalyst to optimize biodiesel production from *Nyamplung*, using esterification and transesterification (ESTRANS) process. The problem on producing biodiesel is how to reduce the content of free fatty acids (FFA) below 2% according to international standards. The esterification process is done in order to achieve FFA value of 1.46%, and the next process is transesterification by using solution of alkaline catalyst. This measurement uses NaOH, KOH, and MgOH catalysts with the variations in concentrations ranging from 0.5, 1, 1.5 and 2%, while the variations in temperature are 45, 55 and 65^{o}C. The results of yield and viscosity values obtained from the optimal catalyst NaOH 1% at 55^{o}C were 98.8% and 5.5 mm^{2}/s, in accordance with standard values. To determine the content of methyl ester, Gas Chromatography- Mass Spectrometry (GC-MS) was used. Results showed that, at optimal temperatures, the best product was obtained using the NaOH catalyst at 1% with a temperature of 55^{o}C. This biodiesel contained percentages of methyl palmitate, methyl oleic, and methyl stearate of 35.51, 15.45, and 28.30%; respectively, complying with current biodiesel standards.

Key words: n*yamplung*, alexandrian laurel balltree, biodiesel, esterification, transesterification, and methyl ester,

1. Introduction

The energy crisis occurred in recent decades had led the government and society to find alternative energy sources such as solar energy, wind, water, and bioenergy. This bioenergy could be derived from plants such as beans, castor, palm and seeds of *Nyamplung* or Alexandrian laurel plants balltree (*Calophyllum inophyllum* L) which can be used for biofuels thrives in Indonesia mainly in the protected forest. The tree of *Calophyllum inophyllum L* is very easy to grow and has not a significant crop pests, so it is very easy to be cultivated.[1]

Previous researched about biodiesel, by *P. Verma, et.al.*[2] studied the impact of various biodiesel on engine performance. Further, *S.T. Ubwa* et.al {3] investigated performance characteristics of petrol/bio-ethonal blends for engines. The developing of biofuel plan and its implementation through the production of ethanol from palm sap. The cultivators of oil palm were examined for the potential palm sap that can be derived [4]. And other investigation focused on the control and management of the production of active and reactive powers of a wind farm [5].

Other investigation of biodiesel from Algal [6], Jatropha, vegetable oil, and *Nyamplung* oil indicate that biomass is an alternative biodiesel that has significant potential to contribute the green energy. The potential of *Nyamplung* to be produced as biodiesel, were 20 tons/ ha per year[7].The oil content was relatively high of 40-73%, compared to 46-54% and 40-60% for palm oil and jatropha oil. For example, one liter of *Nyamplung* could be produced from 2.5 kg of seeds, while for one liter of castor oil needs 4 kg of seeds[8].

Biodiesel which contains methyl ester using transesterification reaction of triglycerides is derived from oil *Nyamplung*. The advantage of biodiesel as an alternative fuel is that this material has a high octane value, little SOx, good lubrication characteristics, slightly exhausted emissions and relatively clean burning characteristic.The content of the octane in this plant was higher than the octane content of diesel, and it made emission level of carbon, nitrogen, and sulfur in the combustion low [9].

M. Canakci et.al (2001) researched the biodiesel oil, and conversions of methyl ester were carried out by the esterification process using acid catalyst, [10] a transesterification reaction alkali catalytic to convert the remaining triglycerides. The oil has a high acidity level of less quality because there will be lathering cause of corrosion in the engine. The content of original *Nyamplung* could be seen in Table 1. It shows the contents of saturated fatty acid of 29,415% weight, and unsaturated fatty acid of 70,325%.[7]. The problem of producing biodiesel is to reduce the content of fatty acid of *Nyamplung* seed.

Table 1. Seed content of *Calophyllum Inophyllum L*

No	Component	Weight Percentage (%)
1	Saturated fatty acids	29,415
	Palmitic acid	14,318
	stearic acid	15,097
2	Unsaturated fatty acids	70,325
	Palmitoleic acid	0,407
	Oleic acid	35,489
	Linoleic acid	33,873
	Linolenic acid	0,557

This study explore the process of nyamplung fruit to become biodiesel oil. In this case, dry seed of Nyamplung is blended and pressed by hydrolic press, then filtered to generate crude oil. Then the dirt or sapand water content inside the oil that will be separated by degumming process. In this process, the oil cruide is heating and stearing in centrifuse with a magnetic stirrer. Furthermore, the free fetty acid (FFA) will be released by esterification method using an acid catalyst, thus the content will be less than 2% according to the standard [11]. Later, diesel oil that contained methyl ester was produced using transesterification process with methanol and alkaline catalyst. A biodiesel oil with good quality contains methyl ester more than 87%. Testing the content of methyl ester was conducted using Gas Chromatography Mass Spectrometry (GC-MS). The physical properties of *Nyamplung* oil such as yield and viscosity were measured to acquire a high-quality biodiesel. This research used a variation of temperature, concentration, and variation of alkaline catalyst in the process of transesterification such as NaOH, KOH, and MgOH. The study provides the information of characteristics of methyl ester in *Nyamplung* oil.

2. Materials and Methods

Nyamplung seed used in the research was from the District of Pinrang regency in South Sulawesi province, Indonesia. The Chemicals used include methanol, ethanol (C_2H_5OH) 96% hydrochloric acid (HCl) 37%, catalyst sodium hydroxide (NaOH) KOH and MgOH respectively 1% each, indicator phenol phetalin 0.1% phosphoric acid (H_3PO_4), $NaHCO_3$ 0.01% and 0.01% CH_3COOH. The equipments used in this research were a tool hydraulic press, blender, oven, burette digital scales, measuring cups, magnetic stirrer, upright cooler, water bath, hot plate stirrer, thermometer, pycnometer, ostwald viscometer and GC-MS. The activities were including crude oil, producing biodiesel, Esterification, and transesterification process.

2.1 Biodiesel Processing of Nyamplung Oil

The step of producing biodiesel oil is the dry seeds comprised of grounding and squeezing using hydraulic press at a pressure of 8-13 tons, then filtering to generate the crude oil. Furthermore, degumming process aims to remove dirt or sap that is in the oil, then filtered by means of a vacuum filter in warm conditions. The results of compression process is performed on a hot plate heating until the temperature reached 65°C while stirring it with a magnetic stirrer. H_3PO_4 solution is added to the amount of 5% (v/v) of *Nyamplung*oil in a beaker, then stirred using a magnetic stirrer for an hour and let stand for 24 hours.

The procedure is done to separate oil from the resin (gum) or mucus found in *Nyamplung* oil, the oil is then heated until 60^{o}C, the phosphoric acid is added and stirred for a certain time, and separation between oil and latex takes place. Furthermore, the oil obtained from the degumming is washed with hot water until the pH of the waste water process that is neutral. The Oil neutralization results are then calculated by means of their weights and Free Fatty Acid (FFA) of oil production.[12]

a. Esterification Process

The esterification process is done to reduce the levels of FFA. The process is shown in Figure 1. The step of oil degumming process is to weigh methanol to be reacted with acid catalyst of HCl. And compound is then stirred using magnetic stirrer and heated in varying temperatures. The steps of esterification process of layer that is formed consisting of the upper layer is a residual methanol that reacts with water, while the bottom layer is a methyl ester that is washed with water containing $NaHCO_3$ to bind excess HCl that can affect the acid number. The results will form the NaCl salt leaching. Methyl esters are formed, computed, weighted and analyzed by FFA using the same steps for the catalyst NaOH and MgOH with temperature variation such as in Figure 1.

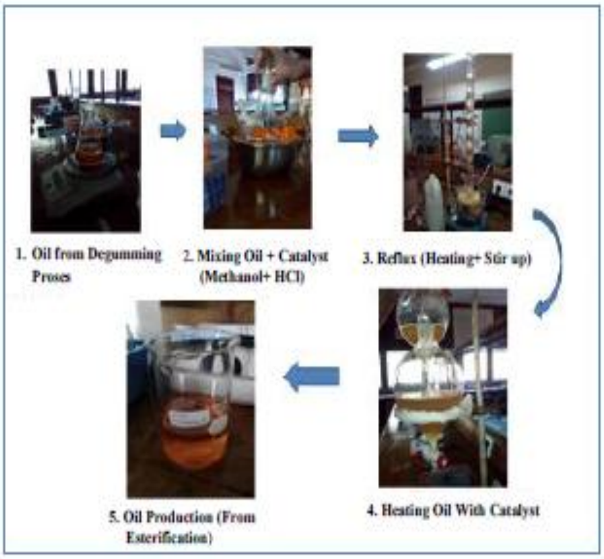


Fig. 1. Esterification process to reduce the Free Fatty Acid (FFA)

The last step is to mix *Nyamplung* oil with methanol at mole ratio of 20: 1 (w/w) and 10% HCl for oil in a double-mouthed Erlenmeyer flask. Double-mouthed pump in mounted on the condenser functions to condense the methanol vapor to enter back into the Erlenmeyer. The reaction was performed at 60^0C with stirring 300 rpm for an hour. After the esterification process is completed, the mixture is put in a test tube, deposited for 8 hours and then measured the levels of FFA on the bottom layer. If the levels of FFA obtained is still above 2%, the esterification process may be repeated until it is achieved FFA of level below 2%.

b. Trans-esterification Process

The oil is formed in the esterification process, by reacting it with methanol, using a catalyst NaOH, and stirring such as in Figure 2. The reaction product is separated and allowed to stand for separating the glycerol and methyl ester. Further, methyl ester is washed by water containing acetic acid CH_3COOH to bind the excess NaOH Drying process of methyl ester is done by heating to a temperature of 110-120^0C. The remaining water in the methyl ester is absorbed using Na-sulfate anhydrous.

Nyamplung oil esterification results including in the double-mouthed flask of 500 ml was added methanol mole ratio of 6: 1 and dissolved in methanol 0.5% NaOH double mouth flask mounted to condense the methanol vapor in order to get back into the Erlenmeyer. The reaction is conducted at a temperature of 45° C with stirring 400 rpm for 1, 2 and 3 hours.

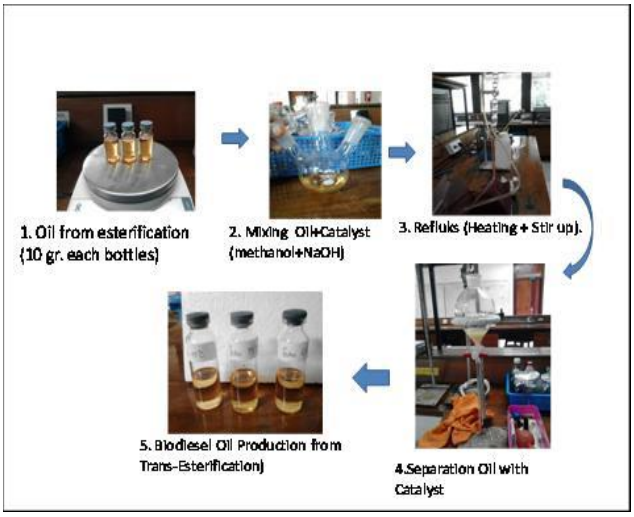


Fig. 2.Trans-esterificastion process for producing Methyl ester.

After the transesterification process is complete, the mixture is inserted in the separating funnel, then deposited for 12 hours. After that, the glycerol will settle on the bottom of the separating funnel so it is easy to be separated. Biodiesel that is formed then it is washed with hot water until pH neutral and dried by heating at a temperature of 55^oC and 65^oC. Perform the same steps above for the transesterification process using NaOH and MgOH. Furthermore, the methyl ester is calculated weights, this two-step process known as esterification and transesterification (ESTRANS) [13].

c. Gas Chromatography Mass Spectrometry (GC-MS)

Measuring the content of methyl esters using the GC-MS to view the content of methyl ester contained in the *Nyamplung* oil by supporting program of GC-MS. Chromatography is a method of analysis for the separation, identification and determination of a compound in the mixture. Using two methods of analysis of compounds that gas cromatography (GC) to determine the amount of compound, and a mass spectrometer (MS) to analyze the molecular structure. In determining the composition of the constituent fatty acid triglyceride oils *Nyamplung* used gas chromatography followed by mass spectrometer [14], and measuring the highest yield from the process of transesterification process.

d. Measuring of Viscocity and Yield

The viscosity of fluid shows the resistance of fluid flow, due to friction in the liquid that moves from one place to another which affect fuel injection to the combustion chamber, resulting in the deposition formed on the machine. High viscosity or more viscous fluid causes the flow rate and lower then flow rate,that the degree of atomization of the fuel will get reduced in the combustion chamber. To overcome this issue the chemical process needs to be done to lower the viscosity values to approach the viscosity of diesel fuel[15]. The viscosity of a fluid (liquid) can be measured by Ostwald viscometer and this measurement of viscosity values is calculated by the formula[16].

$$v = \frac{\mu}{\rho} \tag{1}$$

Where: v is kinematic viscosity, and μ is dynamics viscocity coefficient in Poise or gr/Cm s, and ρ: is the density of the sample (gr/Cm^3).

Furthermore, the yield measurement is detemined by the ratio between the mass of biodiesel produced using the ESTRANS method than the *Nyamplung* crude oil. The oil yield can be calculated as:

$$Yield\ (\%) = \frac{Biodiesel\ \ mass\ \ (gr)}{crude\ \ Oil\ mass\ \ (gr)}\ x\ 100\% \tag{2}$$

The quality of biodiesel is determined by the value of high yield in Equation 2.This formulation shows the value of the percentage of biodiesel oil produced from the ESTRANS processing then compared with the crude oil produced.

3. Results and Discussion

Biodiesel manufacture of fruit *Nyamplung* was done through extortion phase to produce crude oil. Degumming process is performed to separate the oil content of the sap with biodiesel. At degumming process, free fatty acid content was measured at 3.65%, that the esterification process will reduce the free fatty acid content to less than 2%. The results obtained in the first esterification process is 2.92% of FFA. The value is still high in which theesterification process is repeated to obtain the FFA values less than 2%. The process of the second stage resulted FFA of 1.46%, as inTable 2:

Table 2. Free Fatty Acid (FFA) value using esterification process

No.	Processing	FFA
1	Degumming	3.65%
2	Esterification 1	2.92%
3	Esterification 2	1.46%

Results of FFA by 1.46% in step 2 is continued at step on trans-esterification process using methanol and alkaline catalyst to produce methyl ester as a raw material of biodiesel. The process of transesterification on this study is conducted in three phases, namely: using a catalyst NaOH 1% with temperature variations, comparing three catalysts: NaOH, KOH, and MgOH at concentrations of 1%, and using catalyst of NaOH with concentration variation of 0.5, 1, 1.5 and 2% respectively. The results obtained of the highest yield value was measured to examine the content of methyl esters using GC-MS method.

The measurement with the yield value using NaOH catalyst 1% at temperature variations 45^o, 55^o and 65^o is shown in Figure 3a. The optimal obtained yield was at 98.80% and 55^{o}C of temperature, the result measures the content of methyl esters using GC-MS as in Figure 4.

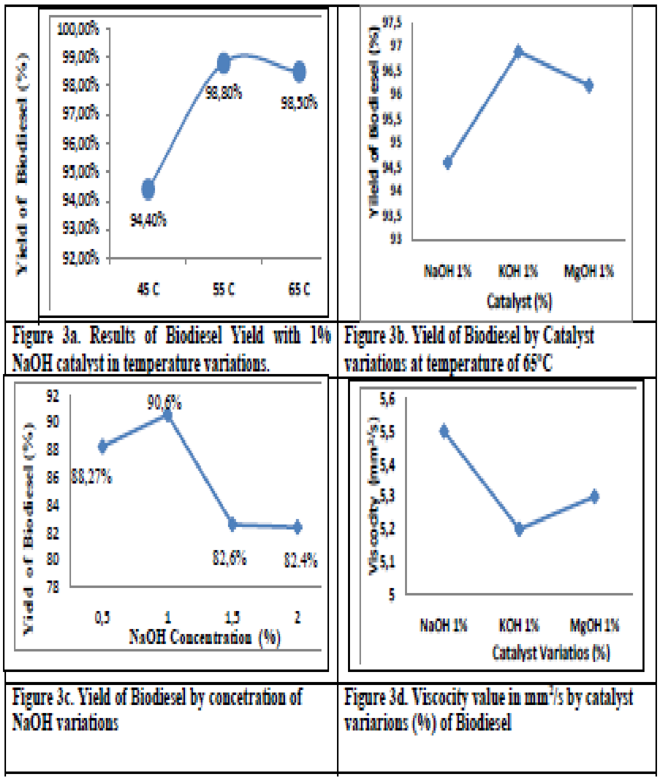


Figure 3a. Results of Biodiesel Yield with 1% NaOH catalyst in temperature variations.

Figure 3b. Yield of Biodiesel by Catalyst variations at temperature of 65°C

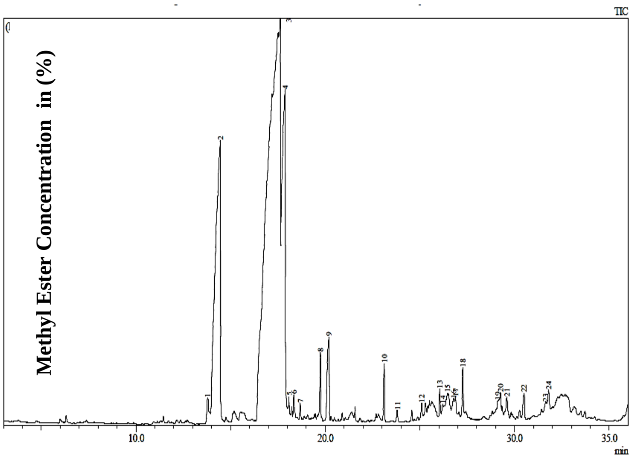
Figure 3c. Yield of Biodiesel by concetration of NaOH variations

Figure 3d. Viscocity value in mm²/s by catalyst variarions (%) of Biodiesel

Fig. 3. Measurement of Yield and Viscocity of *Nyamplung* Biodiesel in Temperature and Catalyst Variations.

The next step of the research is to utilize the catalyst variations using KOH and MgOH at the concentration of 1%. The result was of highest yield of 97% using KOH at 65^{o}C then using NaOH and MgOH as shown in Fig. 3b. The optimal value of *Nyamplung* oil with the KOH catalyst at 1% was measured by the contents of methyl ester using GC-MS in Figure 5. Furthermore, the research was conducted to determine the optimal value of the yield of biodiesel with each variation of the catalyst NaOH at concentrations of 0.5, 1, 1.5, and 2%. The result of the highest yield values of 90.6% is obtained at a concentration of 1% NaOH catalysts as shown in Figure 3c.Viscosity measurement is done using some variation of the catalyst NaOH, KOH and MgOH. The result obtained was the highest viscosity value of the catalyst NaOH of 5.5 mm^2/s. The viscosity is in accordance with the standards in the range between 2.3 to 6.0 mm^2/s, the number matches with the standards as shown in Figure 3d.

Results with high yield was analyzed by GC-MS to determine the content of methyl ester in *Nyamplung* oil. The GC-MS scanning of *Nyamplung* biodiesel uses NaOH 1% catalyst as the higher yield as the following Figure 4.



Retention Time (minute)

Fig. 4. Gas Chromatography methyl ester on the Concentration 1% of NaOH

The spectral analysis indicated in Figure 4 has 24 peaks and only thirteen peaks which contains methyl esters with a total percentage of 90.93%. The results of scanning the content of methyl ester in Figure 4 are gathered to take substances that includes a group of methyl ester such as palmitate, oleate and streate, illustrated in Figure 5.The components methyl ester which can be identified by the molecular weight of the fragmentation pattern at the second peak indicates the presence of methyl palmitate with a percentage of 35.51% and retention time of 14.45 minute,the third peak indicates the methyl oleate of 15.45%, and the fourth indicates the presence methyl stearate of 28.30% in retention time of 17.87 minute. The spectral analysis of GC-MS is showed in Figure 5 as follow.

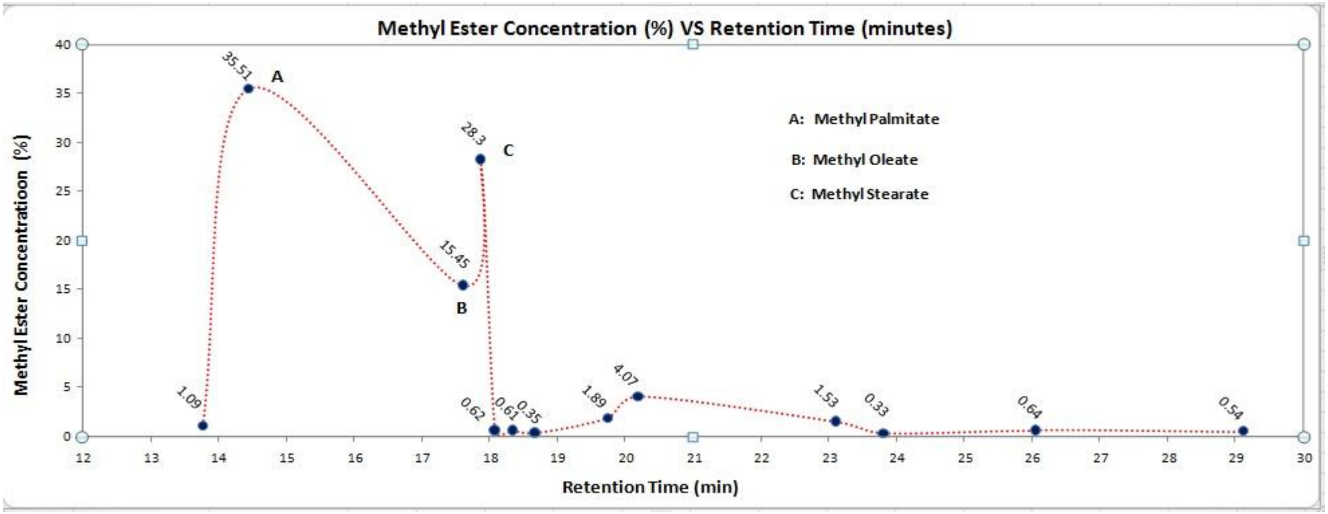
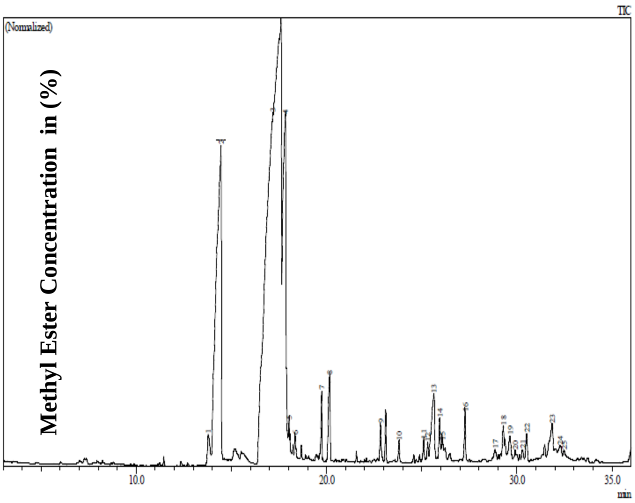


Fig. 5. The spectral analyze of Methyl ester concentration of 1% NaOH vs. Retention Time (minute) as result of GC-MS Methyl Ester content of *Nyamplung* Oil

The result of GC-MS analysis in Fig. 5 above has 20 peaks spectra, despite that methyl ester only contained 8 peaks at 48.35% of methyl ester. The highest content of methyl ester contained 27.59% in the third peaks of with a retention time of 17:17. Furthermore, GC-MS analysis of *Nyamplung* oil uses KOH catalyst of 1% in the trans-esterification process as shown in Figure 6 at the right side.

The second GC-MS spectral results showed that the content of methyl ester in the highest NaOH catalyst is equal to 35.51% with a total percentage of 90.93% of methyl ester content, while at the KOH catalyst for total content of methyl ester is obtained at 48.35% and the highest at 27.59% such as in Figure 6. These results suggest the use of NaOH catalyst which has a methyl ester content of greater than with the use of KOH catalyst.



Retention Time (minute)

Fig. 6 Gass chromatography of methyl ester using catalyst of 1% KOH.

4. Conclusion

The research carried out in this paper is the concluded.The biodiesel component has been investigated with the highest yield value of 98.8% using a catalyst of 1% NaOH at a temperature of 55°C. The esterification process reduces the value of free fatty acid (FFA) by 1.46%, biodiesel from oil *Nyamplung* through transesterification process is carried out using a catalyst in a variation of NaOH, KOH, and MgOH. From this research it is obtained that the yield value of NaOH is 1% amounting to 98.80% at 55^oC, and at a temperature of 65^oC the highest yield on catalyst of 1% KOH is 97%, while the value of viscosity is 5.5 mm^2/s using NaOH 1% as a catalyst. This value is in accordance with the viscosity standard, with the highest yield value was checked using the GC-MS to determine the content of methyl ester. The results show the maximum of methyl ester at NaOH with catalysts of 1%, it has been identified from the fragmentation pattern. The second peak indicates the presence of methyl palmitate of 35.51%, the third peak shows the presence of methyl oleate with a percentage of 15.45% and the fourth peak indicates the presence of methyl stearate with a percentage of 28.30%. These results indicate the optimal composition of the methyl ester in the use of 1% NaOH.

Aknowledgement

The authors would like to thanks to PMC Group and Rector of Hasanuddin University, Makassar, South Sulawesi, Indonesia for partial supportson this research.

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