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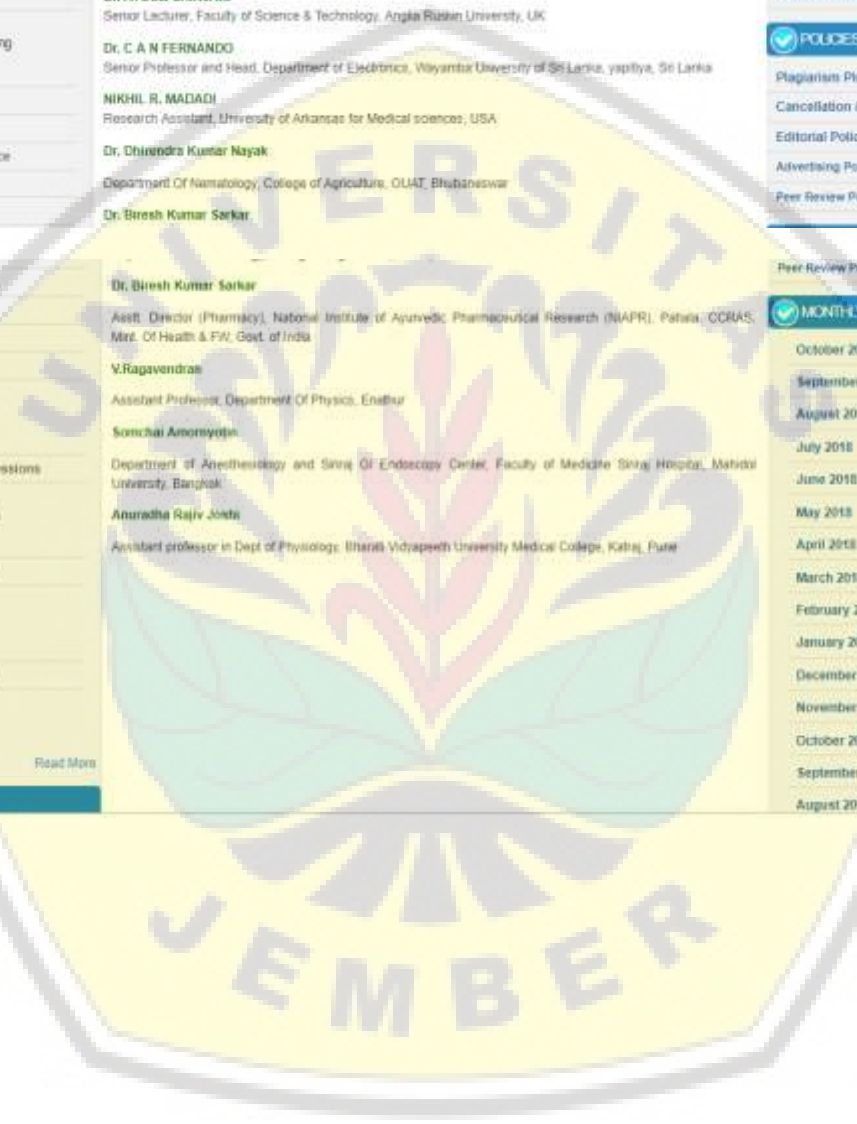
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Study of diversification of raw materials in the manufacture of biodiesel as renewable fuel

Author: DigoListyadi, Nasrullinnalik and Han Sujahono

Biodiesel is adiesel oil that comes from living things, both vegetable and animal. Biodiesel has long been known by the public and the use of diesel engines is the first time using peanut oil biodiesel. Researches on other organic materials that have the potential as biodiesel feedstocks are still being carried out, one of which uses raw materials of Candlenut seeds oil, dregs grated coconut, Used cooking oil, Kepuh seeds oil, Kapok seeds oil and Nyamplung seedoil (Calophylluminophyllum). The process of making biodiesel is very simple. Biodiesel is produced through a process called esterification reaction of free fatty acids depending on the quality of vegetable oil used as raw material or transesterification reaction of triglycerides with alcohol with the help of catalysts. The catalyst used for the esterification reaction is an acid, usually sulfuric acid (H2SO4) or phosphoric acid, while the transesterification process uses KOH. The process of making biodiesel using 1% H2SO4 catalyst, 30% methanol with a mixing time of 2 (two) hours. Transesterification process using KOH catalyst 0.5% reached 1% by weight, 30% methanol and mixing time was 60 minutes, 90 minutes and 120 minutes. The results of this study conclude that a) Candlenut seeds oil, dregs grated coconut oil, Used cooking oil, Kepuh seeds oil, Nyamplung seeds oil and kapok seeds oil are used as raw material for making biodiesel. b) The longer the reaction time, it will produce a lot of biodiesel due to the raw material for making biodiesel. b) The longer the reaction time, it will produce a lot of biodiesel due to the possibility of greater contact between substances. c) biodiesel from the ingredients of Candlenut seeds oil, dregs grated coconut oil, Used cooking oil, Kepuh seeds oil, Nyamplung seeds oil and Kapok seeds oil have a specific mass value in accordance with diesel and biodiesel specifications. d) The heat value of biodiesel produced from the Candlenut seeds oil and dregs grated coconut oil, is almost close to the heat value of diesel and biodiesel specifications, which is 9636.6 cal / g. While the heating value of biodiesel produced from used Used cooking oil, Kepuh seed oil and Kapok seed oil, than diesel specifications and Standard biodiesel, except biodiesel from Nyamplung seed oil has a higher value than diesel specifications and biodiesel standards 04- T182-2015

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STUDY OF DIVERSIFICATION OF RAW MATERIALS IN THE MANUFACTURE OF BIODIESEL AS RENEWABLE FUEL

DigdoListyadi., Nasrullminnafik and HarySutjahjono

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ABSTRACT

Biodiesel is adiesel oil that comes from living things, both vegetable and animal. Biodiesel has long been known by the public and the use of diesel engines is the first time using peanut oil biodiesel. Researches on other organic materials that have the potential as biodiesel feedstocks are still being carried out, one of which uses raw materials of Candlenut seeds oil, dregs grated coconut, Used cooking oil, Kepuh seeds oil, Kapok seeds oil and nyamplung seedsoil (*Calophyllum inophyllum*). The process of making biodiesel is very simple. Biodiesel is produced through a process called esterification reaction of free fatty acids depending on the quality of vegetable oil used as raw material or transesterification reaction of triglycerides with alcohol with the help of catalysts. The catalyst used for the esterification reaction is an acid, usually sulfuric acid (H₂SO₄) or phosphoric acid, while the transesterification process uses KOH. The process of making biodiesel using 1% H₂SO₄ catalyst, 30% methanol with a mixing time of 2 (two) hours. Transesterification process using KOH catalyst 0.5% reached 1% by weight, 30% methanol and mixing time was 60 minutes, 90 minutes and 120 minutes. The results of this study conclude that: a). Candlenut seeds oil, dregs grated coconut oil, Used cooking oil, Kepuh seeds oil, Nyamplung seeds oil and kapok seeds oil are used as raw material for making biodiesel. b). The longer the reaction time, it will produce a lot of biodiesel due to the possibility of greater contact between substances. c). biodiesel from the ingredients of Candlenut seeds oil, dregs grated coconut oil, Used cooking oil, Kepuh seeds oil, Nyamplung seeds oil and Kapok seeds oil have a specific mass value in accordance with diesel and biodiesel specifications. d). The heat value of biodiesel produced from the Candlenut seeds oil and dregs grated coconut oil, is almost close to the heat value of diesel and biodiesel specifications, which is 9536.8 cal / g. While the heating value of biodiesel produced from used Used cooking oil, Kepuh seed oil and Kapok seed oil, than diesel specifications and Standard biodiesel, except biodiesel from Nyamplung seed oil has a higher value than diesel specifications and biodiesel standards 04- 7182-2015

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INTRODUCTION

One of the most widely used solar products is biosolar. Biosolar is a mixture of diesel oil and vegetable oil biodiesel derived from plants. Biodiesel is a renewable and environmentally friendly diesel fuel. Biodiesel is defined as a mixture of monoalkyl esters from long chain fatty acids, known as Fatty Acid Methyl Ester (FAME), derived from renewable raw materials such as vegetable oils or animal fats through a process of esterification and transesterification⁽¹⁾. Researches on other organic materials that have the potential as biodiesel feedstock are still being carried out, for example using vegetable oil raw material from candlenut, nyamplung seed oil (*Calophyllum inophyllum*)⁽²⁾. Biodiesel is an alternative fuel contained in vegetable oils or animal fats

which have properties resembling diesel or diesel oil, used as the main fuel of diesel engines so that it is very prospective to be developed. Biodiesel composed of raw materials can come from a variety of vegetable resources, namely groups of oils and fats from various kinds of fatty acid esters which can be produced from plant oils such as palm oil, coconut oil, jatropha oil, rubber seed oil, kapok seed oil, hazelnut oil, neem oil, kusambi oil and there are still more than 50 kinds of Indonesian plants that have the potential to be used as a liquid form of this energy source⁽³⁾.

Biodiesel can be obtained through transesterification of triglycerides and or esterification of free fatty acids depending on the quality of vegetable oil used as raw material for making biodiesel. Transesterification reaction is an exchange reaction of triglyceride groups with alcohol groups with the help of catalyst materials. The catalyst used in the transesterification process is alkaline, usually used in the form of sodium hydroxide (NaOH) or potassium hydroxide (KOH).

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Esterification is a reaction to the conversion of free fatty acids into esters which aims to reduce levels of free fatty acid free fatty acids (FFA). The catalyst used for the esterification reaction is an acid, usually sulfuric acid (H_2SO_4) or phosphoric acid (H_3PO_4)⁽⁴⁾.

The characteristics that can be used as a benchmark for potential biodiesel are viscosity, density, flash point, cetane number, and other combustion parameters. This study aims to examine the effect of time, temperature, ratio between the weight of vegetable oil and methanol on biodiesel and glycerol produced from various vegetable oil ingredients, and determine the characteristics of the biodiesel produced.

METHOD

The research was conducted at the Energy Conversion Laboratory, Faculty of Engineering, University of Jember. The tools used in this study were four neck round flask, water bath, stirrer motor, condenser, magnetic roder. The raw materials used in this study are Candlenut seeds oil, dregs grated coconut, Used cooking oil, Kepuh seeds oil, Kapok seeds oil and nyamplung seeds oil (*Calophyllum inophyllum*), methanol, phosphoric acid, aquades, hot water.

The main raw material for nyamplung seeds oil, kapok seeds, kepuh seeds oil has a very high FFA level of about 8.63 mg KOH / mg sample, so that in the manufacture of methyl esters is carried out through three stages: degumming process, esterification reaction, and transesterification. Before going through the esterification stage, nyamplung seeds, kapok seeds, kepuh seeds oil through the first stage of treatment, namely degumming.

Degumming aims to separate pollutants from kapok seed oil in the form of gum. In the degumming process of kapok seed oil using H_3PO_4 as much as 1% by volume of oil and reacted at a temperature of 70°C for 60 minutes. The second stage is to do the esterification process, which is to convert free fatty acids into methyl ester so that the free fatty acid levels will go down by reacting oil with methanol as much as 30% of the weight of oil with the help of acid catalyst namely H_2SO_4 as much as 1% by volume of oil at 70 oC for 120 minutes.

The next step to get methyl ester is by reacting nyamplung seed oil, kapok seed, kepuh seed and methanol (transesterification) with KOH catalyst (1% of the weight of the esterification methyl ester) with the amount of methanol as much as 30% of the weight of the esterification results with reaction time 60 minutes, 90 minutes and 120 minutes at 70° C. After the process stops After the process stops, the product is purified.

Other raw materials are Candlenut seeds oil, dregs grated coconut and Used cooking oil has lower FFA levels than other ingredients, so in the manufacture of methyl esters is carried out through transesterification only. The steps to get methyl ester are by reacting the Kemiri Seed oil, used cooking oil and coconut pulp and methanol (transesterification) with KOH catalyst (1% of the weight of the esterification methyl ester) with the amount of methanol as much as 30% of the weight of the esterified product with a reaction time of 60 minutes, 90 minutes and 120 minutes at 70 ° C. After the process stops, the product is purified. The product produced from optimal conditions is allowed to stand for 24 hours to completely separate methyl esters and glycerol. The top layer of methyl

ester and the lower layer of glycerol. Methyl ester is separated from glycerol then washed with 1% vinegar mixed with water at a temperature of 120°C to remove residual alcohol, catalyst and glycerol which do not react and remain in methyl ester until the washing water has been slightly clear.

DISCUSSION

Produced Biodiesel

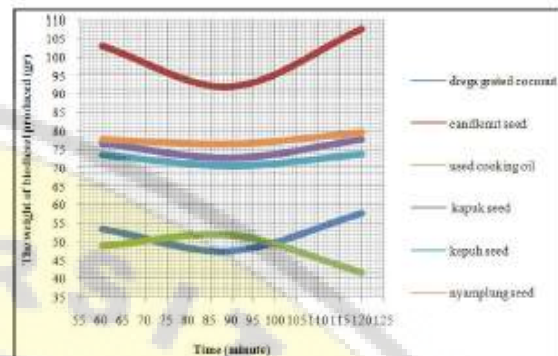


Figure 1 The relationship curve between biodiesel weight produced with time in the Transesterification Reaction

In Figure 1, there is a correlation curve between reaction time (hours) and biodiesel yield resulting from the transesterification reaction. The longer the reaction time, it will produce a lot of biodiesel due to the possibility of greater contact between substances. However, if the equilibrium reaction has been reached, then with increasing time, it will not increase the results. The results showed that used used cooking oil experienced an increase in biodiesel yield from $t = 60$ minutes to $t = 90$ minutes, but after t reaction = 90 minutes decreased to $t = 120$ minutes, at t reaction = 90 was the optimum biodiesel yield of 51.9 gram. But then that is at 120 minutes the yield decreases. This is because at $t = 90$ minutes, the reaction has reached equilibrium. The reaction can be reversible so that when it reaches the equilibrium point, the reaction will shift to the left and minimize the yield (5)Suhendra *et al.*, 2008). At $t = 90$ minutes the used cooking oil experienced an increase in biodiesel yield, because the methanol solvent still did not evaporate completely, thus increasing the amount of biodiesel produced. For other biodiesel-making ingredients, namely dregs grated coconut, Candlenut seeds oil, kapok seeds oil, Kepuh seeds oil and nyamplung seedoil on the 120-minute reaction are all still experiencing an increase in biodiesel yield, so that it can be said on these materials, the reaction has not experienced equilibrium. Candlenut seeds oil, dregs grated coconut, Used cooking oil, Kepuh seeds oil, Kapok seeds oil and nyamplung seedoil (*Calophyllum inophyllum*).

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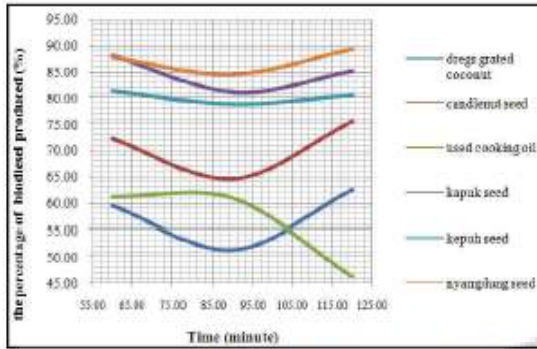


Figure 2 The relationship curve between the percentage of biodiesel yield and the time in the Transesterification Reaction

In Figure 2, there is a relationship curve between reaction time (hour) and biodiesel percentage (%) resulting from the transesterification reaction. As in Figure 1. above, in Figure 3.2 this also shows similar results, namely the longer the reaction time, the greater the yield of biodiesel will result due to the possibility of greater contact between substances. However, if the equilibrium reaction has been reached, then with increasing time, it will not increase the results. From the results of the study, it was found that, specifically for used cooking oil at t reaction = 85 minutes, the optimum biodiesel yield was 61%. But then it was decreased in 120 minutes. This is because at t = 85 minutes, the reaction has reached equilibrium. The reaction can be reversible so that when it reaches the equilibrium point, the reaction will shift to the left and minimize the yield⁽⁹⁾. For other biodiesel-making ingredients, namely Candlenut seeds oil, dregs grated coconut, Kepuh seeds oil and Kapok seeds oil and nyamplung seedoil on the 120-minute reaction are all still experiencing an increase in biodiesel yield, so that it can be said on these ingredients, the reaction has not experienced equilibrium

Glycerol Produced

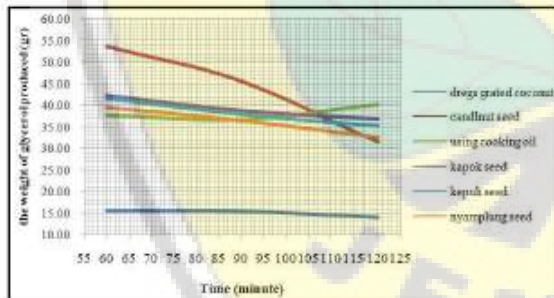


Figure 3 The relationship curve between the weight of glycerol produced with the time in the Transesterification Reaction

Figure 3 shows that the time variable affects the amount of glycerol produced. In general, glycerol decreases when the time is added from 60 minutes to 120 minutes, although there is an increase in used cooking oil. In candlenut oil a decrease in the amount of glycerol is higher than that of other ingredients. This is a reason that supports that: the longer the reaction time, it will produce a lot of biodiesel due to the possibility of greater contact between substances. However, if the equilibrium reaction has been reached, then with increasing time, it will not increase the results. In the cooking oil oil the reaction equilibrium has occurred at t reaction = 90 minutes so that at 120 minutes, fewer biodiesel is produced, but the

amount of glycerol is increased. Candlenut oil, on the contrary, contrasts with the 120 minutes of used cooking oil produced by a lot of biodiesel but the amount of glycerol decreases. Ong H. C. *et al.* (2013)⁽⁷⁾ clearly report that the contact between methanol and oil will be longer as the reaction time increases so that it converts more methyl esters. Freedman *et al.*⁽⁸⁾(1984) suggested that the addition of reaction time causes conversion to increase. At the beginning, the reaction is slow because of mixing and dispersing alcohol into oil.

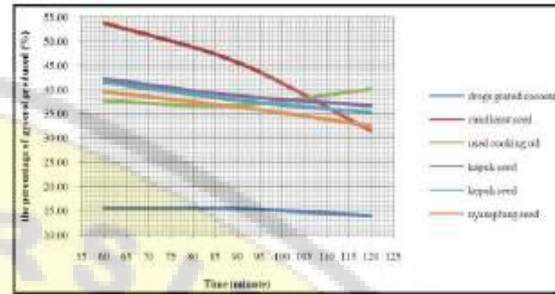


Figure 4 The relationship curve between the percentage of glycerol results with the time in the Transesterification Reaction

In Figure 4. seen the relationship curve between reaction time (hours) and the percentage of glycerol (%) resulting from the transesterification reaction. As in Figure 3. above, in figure 4. shows that the time variable affects the amount of glycerol produced. In general, the percentage of glycerol has decreased when the time was increased from 60 minutes to 120 minutes, despite the increase in cooking oil. In candlenut oil a decrease in the amount of glycerol is higher than that of other ingredients. This is a reason that supports that: the longer the reaction time, it will produce a lot of biodiesel due to the possibility of greater contact between substances. However, if the equilibrium reaction has been reached, then with increasing time, it will not increase the results. In the used cooking oil, the reaction equilibrium has occurred at t reaction = 90 minutes so that at 120 minutes, fewer biodiesel is produced, but the amount of glycerol is increased. Candlenut oil, on the contrary, contrasts with the 120 minutes of used cooking oil produced by a lot of biodiesel but the amount of glycerol decreases. Ong H.C. *et al.* (2013)⁽⁷⁾ clearly report that the contact between methanol and oil will be longer as the reaction time increases so that it converts more methyl esters. Freedman *et al.*⁽⁸⁾ (1984) suggested that the addition of reaction time causes conversion to increase. At the beginning, the reaction is slow because of mixing and dispersing alcohol into oil.

Biodiesel Analysis Test

In general, the factors that influence the transesterification reaction are stirring, temperature, catalyst, reactant ratio and reaction time⁽⁹⁾. The biodiesel produced from the transesterification reaction has specifications as listed in Table 1, while the standard specifications of Pertamina are as shown in Table 2

Table 1 Biodiesel Analysis Results

NO	Test	Materials					
		Candlenut seeds oil	dregs grated coconut	Used cooking oil	Kepuh seeds oil	nyamplung seeds oil	Kapok seeds oil
1	Heat (calories/gram)	9324,853	9319,551	9052,084	9069,172	9748,957	8641,473
2	Density (g/ml) (D 1298 / D 4052)	0,881	0,881	0,878	0,875	0,858	0,868

3	Viscosity (cst) (D445)	5,824	5,191	6,334	6,015	4,886	6,815
4	Flash point (min) (D93)	167	123	169	85	130	115

Table 2 Solar specifications and biodiesel SNI 04-7182-2015 Standard

NO	Test	Standar (solar)		Biodiesel
		min	max	
1	Heat (calories/gram)		9.536,80	9536,8
2	Density (gr/ml) (D 1298 / D 4052)	0,815	0,87	0,85 - 0,89
3	Viscosity (cst) (D445)	1,6	5,8	2,3 - 6,0
4	Flash point (min) (D93)	100	-	100

Density and Viscosity

From table 1 it can be seen that the reaction of transesterification of Candlenut seeds oil, dregs grated coconut, Kepuh seeds oil, Nyamplung seeds oil and Kapok seeds oil has a specific mass value in accordance with the specifications of diesel fuel and biodiesel SNI 04-7182-2015 Standard. The viscosity value of the biodiesel from the transesterification reaction of Candlenut seeds oil, used cooking oil, dregs grated coconut, Kepuh seeds oil, Nyamplung seeds oil and Kapok seeds oil is much smaller than the viscosity value of the diesel specification SNI 04-7182-2015 Standard. This is due to the breaking of the glycerol group from used cooking oil so that the specific gravity and viscosity become decreased. Viscosity is important in diesel fuel. Low viscosity can cause leakage in the fuel injection pump, while too high viscosity can affect the work of the fuel injection device. When compared with diesel available on the market, the biodiesel viscosity produced is greater. This is because the amount of carbon chains contained in the fatty acids that make up biodiesel is more than diesel. Solar has a maximum number of carbon chains of 16, while biodiesel from used cooking oil amounts to carbon chains up to 21. This causes the viscosity and specific gravity greater than solar. Viscosity is a number that states the amount of resistance of a liquid material to flow or the size of the amount of shear resistance of the liquid. The higher the biodiesel viscosity value, the thicker the biodiesel and the flowing ability to decrease⁽¹⁰⁾. The viscosity of a fuel becomes a very important parameter because it will affect the performance of the engine injector⁽¹¹⁾. Fuel viscosity needs to be limited because too low viscosity can cause leakage in fuel injection pumps, while too high viscosity can affect the fast working of fuel injection devices and complicate oil fuel removal⁽¹²⁾. Biodiesel from the kepuh seeds oil has a PMCC 85 Flash Point value which means that at a temperature of 85 C the biodiesel will begin to ignite. This flash point is lower than biodiesel from other materials and has not met the quality standards of the physical properties of ASME D93 biodiesel for min 100 C min. This is due to the remaining methanol in the transesterification reaction which has not been lost all during the process of refining biodiesel⁽¹³⁾.

Flash point

From table 1 it can also be seen that the transesterification reaction of Candlenut seeds oil, dregs grated coconut, Used cooking oil, Kepuh seeds oil and Nyamplung seeds oil has a Flash point value that is higher than the flash point of the SNI 04-7182-2015 Standard biodiesel specification, except for seeds kapok seed oil whose value is lower. However, when compared with the flash point of Pertamina Standard solar specifications, the flash point of biodiesel comes from

candlenut seeds and used cooking oil, the value is above the maximum value of the Specifications of diesel fuel SNI Standards 04-7182-2015. The high flash point of biodiesel is also caused by the amount of the biodiesel carbon chain that reaches 21 so that the biodiesel becomes long burned⁽¹⁴⁾.

Calorific Value

The heat value of biodiesel produced from Candlenut seed material and dregs grated coconut, is almost close to the calorific value of diesel specifications and biodiesel standard SNI 04-7182-2015, which is 9536.8 cal/g. While the biodiesel heating value produced from the Used cooking oil, Kepuh seeds and Kapok seeds is lower than the diesel and biodiesel specifications of SNI 04-7182-2015 Standard, except biodiesel from Nyamplung seed material has a higher value than the diesel specification and SNI Standard biodiesel 04-7182-2015. It can be concluded that the energy produced by biodiesel in this study is almost the same as the energy produced by biodiesel and diesel fuel. SNI 04-7182-2015

CONCLUSION

From the results of the analysis that has been done it can be concluded that:

1. Candlenut seeds, dregs grated coconut, Used cooking oil, Kepuh seeds, Kapok seeds and nyamplung seeds are used as raw material for making biodiesel.
2. The longer the reaction time, it will produce a lot of biodiesel due to the possibility of greater contact between substances.
3. Biodiesel from the ingredients of Candlenut seeds, dregs grated coconut, Used cooking oil, Kepuh seeds, Nyamplung seeds and Kapok seeds has a density value that is in accordance with the specifications of diesel fuel and biodiesel SNI 04-7182-2015 Standard.
4. The heat value of biodiesel produced from Candlenut seeds material, dregs grated coconut, is almost close to the heat value SNI 04-7182-2015 Standard Specifications which is 9536.8 cal/g. While the heating value of biodiesel produced from the ingredients of Used cooking oil, Kepuh seeds and Kapok seeds, is lower than the SNI 04-7182-2015 Standard Specifications. except biodiesel from Nyamplung seed material has a higher value than SNI Specification 04-7182-2015.

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