# Variation of Process Conditions of Transesterification on Biodiesel Shyntesis from Rubber Seed (*Heveabrasiliensis*) as Catalyst

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***Abstract-*** Biodiesel synthesis with rubber seed as raw material had been done. The purposes of this research are to know 1). characters of biodiesel (density, kinematics viscosity, pour point, flash point and heat of combustion ) at various temperature and time process, 2). are the characters of biodiesel suitable based on SNI 04-7182-2006. There are three steps to synthesis of biodiesel, the first step is pressing process with hydraulic presser to take rubber seed oil, after this, decolorization process used active carbon to take clear oil and followed by degumming process to remove gum. The second step is esterification process, to reduce the FFA of rubber seed oil (using18 M of $H_2SO_4$ and methanol, at 60 $^0$C and 60 minutes) , and the third step is production biodiesel from rubber seed oil by transesterification process, use methanol and KOH as catalyst with (ratio of methanol/oil) = 8/1). Transesterification process was going on various temperature of : 45, 65, and 85 $^o$C , and at various of process duration of: 60 and 120 minutes. The characters of biodiesel from rubber seed oil at various process conditions : 45, 65 and 85 $^0$C and time 60 and 120 minutes are:Density value of biodiesel $B_1$, $B_2$, $B_3$, $B_4$, $B_5$ and $B_6$, are: 902,8; 901,7; 887,6; 902,7; 897,9 and 886,93 kg/m$^3$ respectively. Except $B_3$ and $B_6$, the density value of all biodiesel are not suitable with SNI Standard, ( 850 – 890 kg/m$^3$). Viscosity value of biodiesel $B_1$, $B_2$, $B_3$, $B_4$, $B_5$and $B_6$ , are: 21.6032; 22.8623; 18.1665; 16.7291; 19.7945 and 20.7268cSt, respectively, the value are higher than value of SNI Standard (2.3 – 6.0 cSt). Pour point value of biodiesel $B_1$, $B_2$, $B_3$, $B_4$, $B_5$ and $B_6$ are: 0; 3; 6; 0, 6; and0$^0$C., respectively, so all of biodiesel are suitable with SNI Standard. ( (-15) - 13 $^0$C). Flash point of biodiesel $B_1$, $B_2$, $B_3$, $B_4$, $B_5$ and $B_6$ are:174; 196; 198; 208; 198 and 184 $^0$C. Flash points of all biodiesel are suitable with SNI Standard. ( minimal100$^0$C). Heat of combustions of biodiesel $B_1$, $B_2$, $B_3$, $B_4$, $B_5$ and $B_6$ are : 9421.3905; 9724.1315; 9501.3474; 9821.6535; 9023.50 and 9216.280 cal/g, respectively, except $B_4$, all of the value of heat combustion are less then value of SNI Standard (10160 – 11000 Cal/g).

## INTRODUCTION

Diesel Fuel is one of fuel that has important role in Indonesia Economy. In fact, crude oil refinery ability to produce diesel fuel is not increase, while diesel fuel demand was increase, so Indonesia must import biodiesel fuel , and in 2006, Indonesia has imported 5-6 thousand million liter of biodiesel fuel[1]. According to this fact, efforts are required to find sources of fuel that has characters like diesel fuel. Biodiesel is biofuel that made from oil seed plant. There are three steps to make biodiesel from oil seed plant, there are : taking oil from seed, esterification process to reduce of free fatty acid and then followed by transesterification process. [2, 3, 4,5].Biodiesel can use as alternative fuel for diesel car in many concentrations with diesel fuel (10 or 20 %)[5,6].

There are many plant seeds that can be use as biodiesel resources, for examples: castor, avocado, rubber, coconut, kemiri, cotton seed, bintaro, and nyamplung[1,4,5,7].The reason why we choice rubber seed as biodiesel resources because rubber seed oil is not an edible oil, and has about 40 – 50% of oil [4,5,8].Besides of this, there are about 301,777.75 ton per year rubber seed that not optimized use yet[6]. Biodiesel is one of monoester compound of fatty acids that yield from transesterification process of plant oil with alcohol and alkaline use acid or alkali as catalyst.[2, 4, 5].Almost the plant oil has high of acid number, so before converted to biodiesel, acid number must be reduce by esterifications process. Free fatty

acid will react with alkali catalyst form soap, among of alkali catalyst will reduce, this is caused not efficiency, and reduce rendement of biodiesel . Besidesof this, soap can caused difficulty on washing process of biodiesel that yield[4,5].

A new things in this research are: obtain oil from rubber seed was done by pressing method [3], and in esterification reaction used 18 M of $H_2SO_4$ solution, during 60 minutes with temperature variation in transestrification process are : 45, 65 and 85 $^0$C, wit time variation are: : 60 and 120 minute, and ratio of methanol/ oil is 8/1.

# EXPERIMENTAL PROCEDURES

## Materials

Materials that used in this research are rubber seeds, KOH, methanol, aquadest 0,1 N of Sodium Hydroxide (aq), 18 M of $H_2SO_4$ solution, activated carbon, phenolphtalen indicator, 96% of ethanol, 20% of phosphoric acid.

## Procedure

Preparation of sample. Rubber seed was obtain from PTP IX, Tuntang, Semarang, Indonesia. Rubber seed sample were dried under sun, along 7 days, and then to be pressed under 180 kN to obtain the crude rubber seed oil. The rubber seed oil was decolorized by mixed with activated carbon with ratio of (oil/activated carbon) is 1: 100, and shakes the mixture until homogenous , then let it along 48 hours. After that oil was filtered with paper filter, and to be degummed at 80 $^0$C on hot plate stirrer, using $H_3PO_4$ of 20%, with ratio (phosphoric acid/oil) : 0.3% and stirred along 30 minutes. After that, the oil was washed with water until pH is neutral, then to be heated until 120 $^0$C to remove the water from oil[5].

The next step is esterification process to up down value of free fatty acid of the oil. Esterification process was done at hot stirrer at 60 $^0$C. Make mixture of 18 M of sulfuric acid solution with methanol, (ratio methanol/oil is 8/1), and add this mixture to the oil in three necks flask. Esterification process was done along 60 minutes. After that oil was separate from aqueous phase by centrifuge apparatus [6, 8].

The last process is transesterification. One hundred and twenty grams of clear rubber seed oil was heated in three necks flask until 45 $^0$C, while stirred with magnetic stirrer. Prepare solution of KOH (1.2 g) with 21.53 g of methanol 99%, then pour this mixture into the flask, and react along 60 minutes. After that the yield of reaction let along 24 hours, and separate biodiesel from glycerol ( biodiesel is in upper layer and glycerol in up down layer). After that, wash biodiesel with aquadest and let it along 24 hours. The next steps is heated biodiesel at 110 $^0$C[9].

Repeat step (3) with temperature 65 and 85 $^0$C. Repeat step (3) and (4) with process time is 120 minutes and we obtain several data as shown Table 1.

Table 1. List of Biodiesel Code at Various Experiment Variables

| No | Temperature ($^o$C) | Time (minutes) | Biodiesel Code |
|---|---|---|---|
| 1 | 45 | 60 | $B_1$ |
| 2 | 65 | 60 | $B_2$ |
| 3 | 85 | 60 | $B_3$ |
| 4 | 45 | 120 | $B_4$ |
| 5 | 65 | 120 | $B_5$ |
| 6 | 85 | 120 | $B_6$ |

## CHARACTERIZATION OF BIODIESEL

**FTIR Analysis of Biodiesel**

Prepare biodiesel sample of $B_1$, $B_2$, $B_3$,$B_4$, $B_5$, $B_6$ to characterized with FTIR Spectroscopy.

**Determination of Biodiesel characters**

**Density:** Density of biodiesel was determined by equation:

$$\rho_b = \frac{M_x - M_0}{V_p}$$

Where: $\rho_b$ = density of biodiesel (g/mL)
$V_p$ = picnometer volume (mL)
$M_x$ = mass of (picnometer + aquadest) (gram)
$M_0$ = mass of empty picnometer (gram)

Clean picnometer and dried, then weigh (mass= Mo). Fill in biodiesel to picnometer and weigh it (mass = $M_x$). Repeat this step for $B_2$until $B_6$.

**Viscosity**

Viscosity of biodiesel were determined by Ostwald Apparatus, with equation bellow[10]:

$$\eta_1 = \frac{\eta_2 \rho_1 t_1}{\rho_2 t_2}$$

Where: $\eta_1$ = Viscosity of biodiesel (CSt or $mm^2/s$)
$\eta_2$ = Viscosity of water (CStor $mm^2/s$)
$\rho_1$ = Density of biodiesel ($kg/m^3$)
$\rho_2$ = Density of water ($kg/m^3$)
$t_1$ = Flowing time of biodiesel through capillary pipe (second)
$t_2$ = Flowing time of water through capillary pipe (second)

**Pour Point :**Fill in the sample to chamber and heated it by water bath until 115$^o$F then cooled until 90$^o$F. After that fill in to *Pensky-Martensclosed up* apparatus, and temperature start up down. Check grade of frozen every 5 $^o$F temperature. If fog was arise in the inner of the apparatus wall, this temperature is noted as pour point.

**Flash point:** Flash point was determined with Cleveland and Pensky Martens apparatus.

**Heat of Combustion :**Heat of combustion of biodiesel was determined by Bomb Calorimetry apparatus

## RESULT AND DISCUSSION

### Characterization by FTIR

Spectrum of Rubber Seed Oil and each of biodiesel were showed at Figure 1 until 7, and at Table 2.

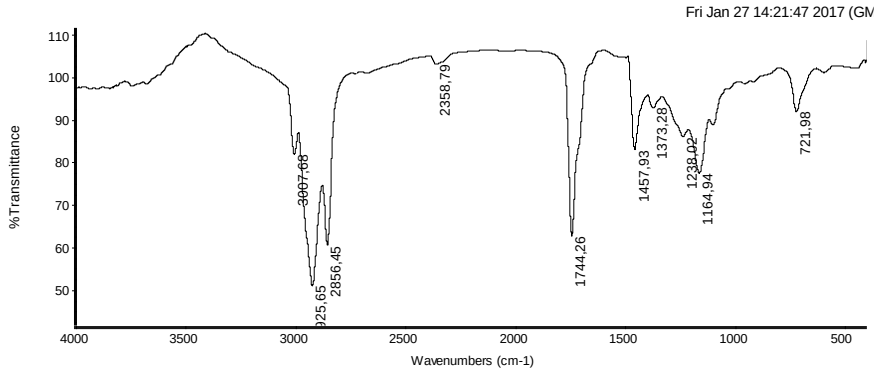



Figure 1.IR Spectrum of Rubber Seed Oil

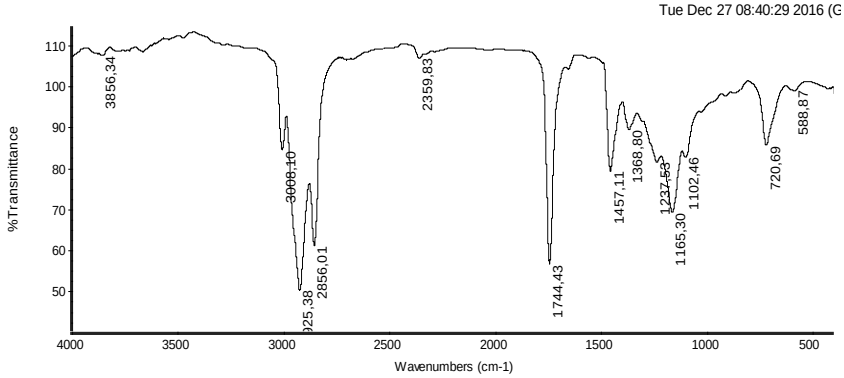



Figure 2. IR Spectrum of Biodiesel $B_1$

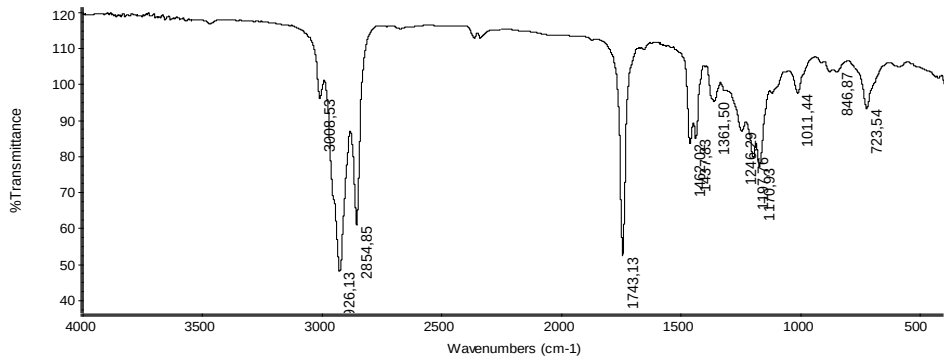



Figure 3. IR Spectrum of Biodiesel $B_2$

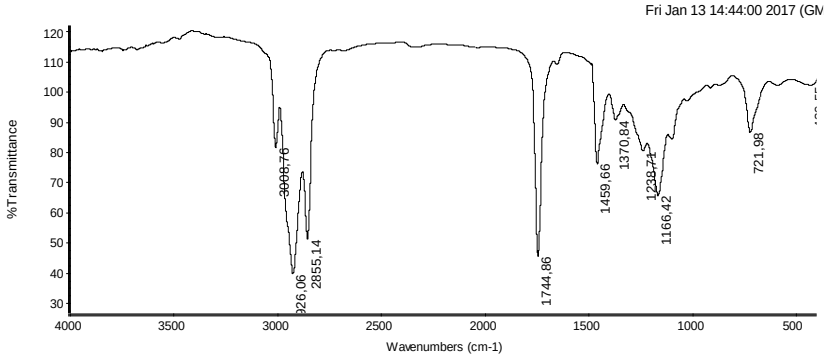
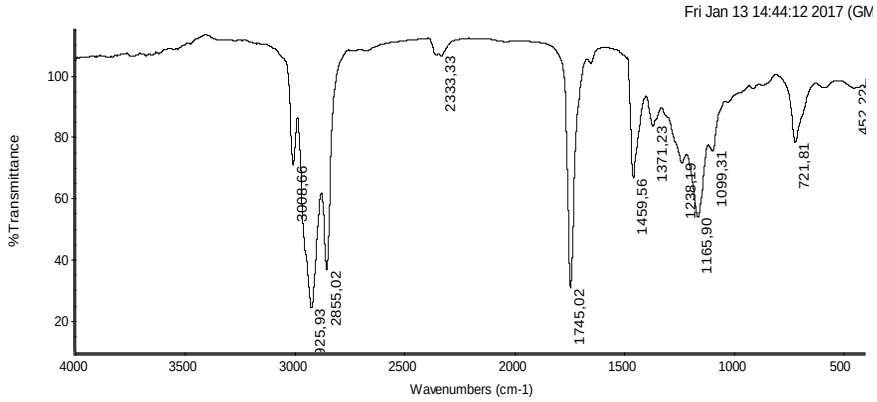



Figure 4. IR Spectrum of Biodiesel $B_3$



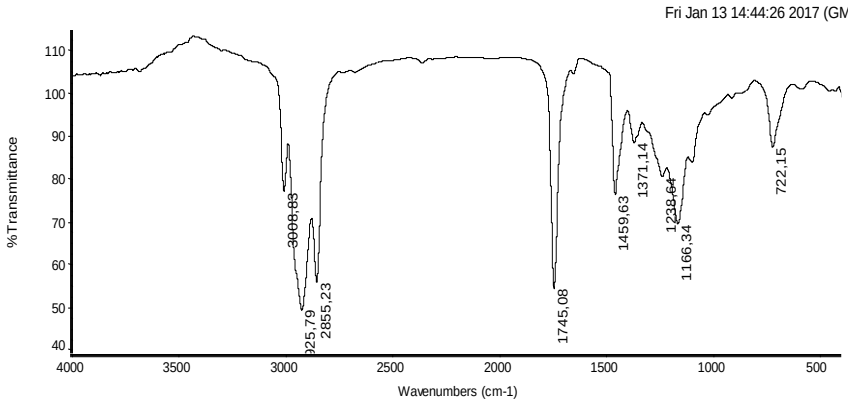




Figure 6. FTIR Spectrum of Biodiesel $B_5$

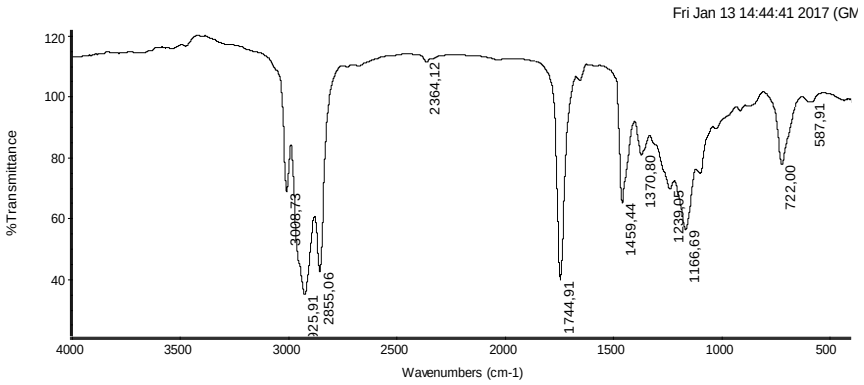



Figure 7. IR Spectrum of Biodiesel $B_6$

Table 2.FTIR Analysis of Rubber Seed oil and Biodiesel[11].

| Material's Name | Wave's number ($cm^{-1}$) | Character of Group |
|---|---|---|
| MinyakBijiKaret | 1744,26 | Strong absorption as carbonyl C=O group |
| | 1164,94 and 1238,02 | Weak absorption as C-O ester |
| | 2925,65 and 2856,45 | Weak absorption as ester of fatty acid |
| | 3007,68 | Sharp adsorption as alkyl, methyl and methylene groups |
| | | Medium absorption as C-H aliphatic |
| Biodiesel $B_1$ | 1744,43 | Strong absorption as carbonyl C=O group |
| | 1237,53 | Weak absorption as C-O ester |
| | 1165,30 | Weak absorption as ester of fatty acid |
| | 2925,38 and 2856,01 | Sharp adsorption as alkyl, methyl and methylene groups |
| | 3008,10 | Medium absorption as C-H aliphatic |
| Biodiesel $B_2$ | 1745,28 | Strong absorption as carbonyl C=O group |
| | 1238,37 | Weak absorption as C-O ester |
| | 1166,24 | Weak absorption as ester of fatty acid |
| | 2926,37 and 2855,10 | Sharp adsorption as alkyl, methyl and methylene groups |
| | 3008,00 | Medium absorption as C-H aliphatic |
| Biodiesel $B_3$ | 1744,86 | Strong absorption as carbonyl C=O group |
| | 1238,71 | Weak absorption as C-O ester |
| | 1166,42 | Weak absorption as ester of fatty acid |
| | 2926,06 and 2855,14 | Sharp adsorption as alkyl, methyl and methylene groups |
| | 3000,70 | Medium absorption as C-H aliphatic |
| Biodiesel $B_4$ | 1745,02 | Strong absorption as carbonyl C=O group |
| | 1238,19 | Weak absorption as C-O ester |
| | 1165,90 | Weak absorption as ester of fatty acid |
| | 2925,93 and 2855,02 | Sharp adsorption as alkyl, methyl and methylene groups |
| | 3006,60 | Medium absorption as C-H aliphatic |
| Biodiesel $B_5$ | 1745,08 | Strong absorption as carbonyl C=O group |
| | 1238,64 | Weak absorption as C-O ester |
| | 1166,34 | Weak absorption as ester of fatty acid |
| | 2925,79 and 2855,23 | Sharp adsorption as alkyl, methyl and methylene groups |
| | 3000,08 | Medium absorption as C-H aliphatic |

Table 2. FTIR Analysis of Rubber Seed oil and Biodiesel….(continue)

| Material's Name | Wave's number ($cm^{-1}$) | Character of Group |
|---|---|---|
| Biodiesel $B_6$ | 1744,91 | Strong absorption as carbonyl C=O group |
| | 1239,06 | Weak absorption as C-O ester |
| | 1166,69 | Weak absorption as ester of fatty acid |
| | 2925,91 and 2855,06 | Sharp adsorption as alkyl, methyl and methylene groups |
| | 3000,73 | Medium absorption as C-H aliphatic |

Figure 1 until 7 were shown that each biodiesel spectrum have different spectra compare with rubber seed oil spectrum. It is indicated that transesterification process was on going and yield methyl ester as biodiesel. FTIR analysis of rubber seed oil and biodiesel was shown in Table 2.

## Characterization of density, viscosity, pour point, flash point and heat of combustion

Characterization of density, viscosity, pour point, flash point and Heat of Combustion were shown on Table 3.

Table 3. Value of Density, Viscosity, Pour Point, Flash Point and Heat of Combustion of Biodiesel at Various Temperature and Time Process

| **Biodiesel** | **Biodiesel Characters** | | | | |
|---|---|---|---|---|---|
| | **Density at $60^0$F ($kg/m^3$)** | **Viscosity at $40^0$C (cSt)** | **Pour Point ($^0$C)** | **Flash Point ($^0$C)** | **Heat of Combustion (cal/g)** |
| 60 minute: | | | | | |
| $B_1$ ( $45^0$C) | 902,80 | 21,6032 | 0 | 174 | 9421,3905 |
| $B_2$ ($65^0$C) | 901,70 | 22,8623 | 3 | 196 | 9724,1315 |
| $B_3$ ($85^0$C) | 887,60 | 18,1665 | 6 | 198 | 9501,3474 |
| 120 minute: | | | | | |
| $B_4$ ($45^0$C) | 902,70 | 16,7291 | 0 | 208 | 9821,6535 |
| $B_5$ ($65^0$C) | 897,90 | 19,7945 | 6 | 198 | 9023,6500 |
| $B_6$ ($85^0$C) | 886,93 | 20,7268 | 0 | 184 | 9216,2800 |
| SNI | 850 - 890 | 2,3 – 6,0 | -15 – (13) | Min. 100 | 10160 – 11000 (Fuel Oil) |

**Density**. According to yield of experiment, density value of biodiesel $B_1$, $B_2$, $B_3$,$B_4$, $B_5$, and $B_6$ respectively are : 902.8; 901.7; 887.6; 902.7; 897.9 and 886.93 $kg/m^3$. Only $B_3$, and $B_6$that suitable with SNI Standard, but for another biodiesels have density not suitable with SNI Standard. Most of biodiesel from plant seed have density less then SNI Standard

**Viscosity.**The viscosity value of biodiesel $B_1$, $B_2$, $B_3$,$B_4$, $B_5$, and $B_6$ are: 21.6032; 22.8623; 18.1665; 16.7291; 19.7945 and20.7268cSt respectively, and all of biodiesels have viscosity higher than Standard SNI. This is caused by in this experiment esterification process was going along 1 hour, and commonly, for biodiesel from rubber seed oil has viscosity higher than viscosity of diesel oil, so biodiesel was mixed with diesel fuel oil to reduce viscosity of biodiesel[5,6].

**Pour Point.** Pour point is the lowest temperature that biodiesel can flow if was cooled on certain condition (8)According to this experiments, obtain that value of pour point of biodiesel $B_1$, $B_2$, $B_3$,$B_4$, $B_5$, and $B_6$respectively were : 0; 0; 6, 3, -3 and $0^oC$ . All of biodiesel have value pour point as suitable as SNI (-15 sd $13^0$C).

**Flash point.**Flash point is the lowest temperature that the surface of fuel oil can burn if near by flame. Flash point need to safety in handling of fuel from burning dangerous.According to this analysis, obtain that value of flash

point of biodiesel $B_1$, $B_2$, $B_3$,$B_4$, $B_5$, and $B_6$ respectively were: 109; 115, 127, 113, 181 and 153ºC. All of biodiesel have value flash point as suitable as SNI (min $100^0$C).

**Heat of combustion.**Heat of combustion is number that show among of heat that arised if fuel oil was burn witoxygen [12]. According to this experiment, value of heat of combustion's biodiesels $B_1$, $B_2$, $B_3$,$B_4$, $B_5$, and $B_6$respectively were: 9421.3905; 9724.1315; 9501.3474; 9821.6535; 9023.650 and9216.280 cal/g, and all biodiesels have heat of combustion less than value of SNI Standard ( 10160 – 11000 Cal/g). So to take a reach burning, biodiesel must be mixed with diesel fuel oil with necessary ratio[5,6].

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## CONCLUSSION

The characters of biodiesel from rubber seed oil at various process condition : 45, 65 and 85 $^0$C and time 60 and 120 minutes are:Density value of biodiesel $B_1$, $B_2$, $B_3$, $B_4$, $B_5$ and $B_6$, are: 902.8; 901.7; 887.6; 902.7; 897.9 and 886.93 kg/m$^3$ respectively. Except $B_3$ and $B_6$, the density value of all biodiesel are not suitable with SNI Standard, ( 850 – 890 kg/m$^3$). Viscosity value of biodiesel $B_1$, $B_2$, $B_3$, $B_4$, $B_5$and $B_6$ , are: 21.6032; 22.8623; 18.1665; 16.7291; 19.7945 and 20.7268CSt, respectively, the value are higher than value of SNI Standard (2.3 – 6.0 CSt). Pour point value of biodiesel $B_1$, $B_2$, $B_3$, $B_4$, $B_5$ and $B_6$ are: 0; 3; 6; 0, 6; and$0^0$C respectively, so all of biodiesel are suitable with SNI Standard. ( (-15) - 13 $^0$C). Flash point of biodiesel $B_1$, $B_2$, $B_3$, $B_4$, $B_5$ and $B_6$ are:174; 196; 198; 208; 198 and 184 $^0$C. Flash points of all biodiesel are suitable with SNI Standard. ( minimal$100^0$C). Heat of combustions of biodiesel $B_1$, $B_2$, $B_3$, $B_4$, $B_5$ and $B_6$ are : 9421.3905; 9724.1315; 9501.3474; 9821.6535; 9023.50 and 9216.280 cal/g, respectively, except $B_4$, all of the value of heat combustion are less then value of SNI Standard (10160 – 11000 cal/g).

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