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The Effect of NaOH Concentration and Length of Trans-esterification Time on Characteristic of FAME from *Reutealis trisperma* (Kemiri Sunan)

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***Abstract*— Biodiesel (FAME) is biofuel as a result from conversion process of triglycerides (oil) into FAME (Fatty Acid Methyl Esther). *Reutelis trisperma* (Kemiri Sunan) is one of the plant that contains triglycerides, which is inedible oil due to its high poisonous component (alpha oleostearic acid), therefore this plant can be used as the nature source of biodiesel production. The research aimed to study the effect of NaOH concentration and length of trans-esterification time on the yield and FAME characteristic. The experiment was arranged in Completely Randomized Design with two replicated. The result indicated that 0.75% NaOH in two hours trans-esterification produce the highest yield of FAME with density 0.8703 g/cm^3, kinematic viscosity 5.325 cSt, acid value 0.552 mg KOH/g and iodine value 46.6972 g I_2/g.**

***Keywords*— NaOH, trans-esterification, FAME, Kemiri Sunan**

I. INTRODUCTION

Limitation of the unrenewable fuels in the world leads to find out the renewable fuels resources. Some researches has been done in development of potential natural resources from plant and animal to be the raw materials of the renewable fuels called bio energy [1] – [3].

Biodiesel as one of the bio energy, is described as the mono alkyl esters either methyl and ethyl ester of vegetable and animal oils fatty acid (FAME or FAEE). This is used for diesel engines (compression-ignition). Besides it is renewable, compared to petroleum based diesel, biodiesel has many advantages include biodegradable, non-toxic and has a more favourable combustion emission profile [1].

Vegetable oil that usually used as the feedstock of biodiesel is from palm oils [4]. The supply abundance and the fuel yield per hectare are the main reasons of utilisation of palm oil as the energy source. Other vegetable oils such as soybean, sunflower, safflower, cotton, rapeseed, Jatropha and Karanj oil can be used for the production of biodiesel either [5]. However, the high cost of production due to the cost of virgin vegetable oils is the main obstacle of biodiesel commercialization [1]. This high cost of vegetable oils is caused by the competition with the food utilization or land efficiency. Therefore, it is needed to find out the potential vegetable oils which is low price in order to minimise the production cost.

Reutealis trisperma (Kemiri sunan) is a conservation tree that grow in Indonesia mainly in West Java, which produce seed with vegetable oil content about 50-56%. This oil can't be used as the oil food because of its poisonous content (alpha oleo stearic acid). Therefore, this seed has potential as the feedstock of biodiesel.

Biodiesel is produced from vegetable oils by trans-esterification process of triglycerides and form FAME (Fatty Acid Methyl Esther) or FAEE (Fatty Acid Ethyl Esther). In this process, triglycerides are converted to FAME or FAEE and glycerine by alcohol and a strong base catalyst [5]. Some factors that influence the trans-esterification process are the concentration of base catalyst and length of trans-esterification time.

The study aimed to find out the effect of concentration of base catalyst (NaOH) and length of trans-esterification time on the yield and characteristic of biodiesel from *Reutealis trisperma* (kemiri sunan).

II. MATERIAL AND METHOD

Reutealis trisperma (kemiri sunan) dried kernel was obtained from region of Garut, West Java. The experiment was conducted with randomized complete design factorial pattern, with two replicate. Treatments are concentration of base catalyst (NaOH 0.75%, 1 % and 1.25%) and trans-esterification reaction time (1 hour and 2 hours).

The oils were produced from dried kernel with mechanical pressed. Esterification reaction of the oils was done prior to trans-esterification due to the high Free Fatty Acid content in the Kemiri Sunan oils. After esterification reaction, the oils were mixed with methanol and NaOH in proper proportion. The trans-esterification process was conducted at a temperature of 60°C and stirred at 350 rpm. After the reaction, the mixture was settled down for about 60 minutes, and the glycerol at the bottom layer was separated from the kemiri sunan methyl esters.

The properties of oils and its methyl esters were determined by Standard Industry Indonesia (SNI 04-7182-2006). The oils as well as its methyl esters properties measured were density, kinematic viscosity, acid number, I_2 number and water content. Chemical analysis of the methyl esters was conducted with Shimadzu GCMS QP2010 Ultra at column oven temperature of 60°C, injection temperature of 280°C, column flow of 1.61 mL/min and total flow of 326.3 mL/min.

A. Density

Relative The pycnometer was cleaned by filling it with ethanol, emptied and dried carefully with dry air, permitted to stand for 30 minutes and weighed accuracy (a). Then the pycnometer was filled with distilled water, placed it in a water bath at 25°C for 30 minutes. It was dried and weighed (b). The pycnometer was cleaned by filling it with ethanol and diethyl ether again, emptied and dried carefully with dry air, permitted to stand for 30 minutes and weighed accuracy (c). Then the pycnometer was filled with the sample, placed it in a water bath at 25°C for 30 minutes, dried and weighed (d). Density was (d-c)/(b-a).

B. Kinematic viscosity

The kinematic viscosity of the oil as well as its methyl esters were measured by Ostwald viscometer. The tube was filled with sample, then it is measured the time to run from one point to another point.

C. Acid number

The sample of 2 gram was weighed accuracy in the saponification flask (Erlenmeyer). 10 ml alcohol and 3 drops of phenolphthalein solution were added in the flask. The sample was titrated with KOH 0,1 N. The first appearance of a red coloration was considered the end point.

D. I2 number

The sample of 0.5 g was weighted in the flask accurately, mixed with 10 mL chloroform, added with 10 mL Hanus reaction solvent and stirred until dissolved perfectly. The mixture was settled down for 1 hour, then it is added with 10 mL of potassium iodide 15%, stirred and mixed with 100 distilled water. The mixture was titrated with sodium thiosulphate 0.1 N then added with 2 mL of starch 1% and titrated again until the blue colour varnished.

III. Result and Discussions

Properties of *Reutealis trisperma* (kemiri sunan) oils as well as its methyl esters were determined for its density, kinematic viscosity, acid number and I_2 number. While, determination of the material composition with GCMS was used for methyl esters only.

A. Properties of the Reutealis trisperma oils

The properties of *Reutealis trisperma* oil were shown in Table 1. The value of all properties of *Reutealis trisperma* oil produced from mechanical pressed in this study nearly the same as the oil of previous study except of I_2 value [6]. The value of each properties of the oil were used to compare with the same properties of its methyl esters. The density illustrated the weight of a unit volume of the oil, which depends on the fatty acid content and the oil purity as well. Kinematic viscosity determined internal friction of the oil to flow, which decreased with increasing of the temperature. Acid number is a measure of free fatty acid in the oil. The I_2 value of the oil was quite different from previous study, this may due to different storage condition.

TABLE I
PROPERTIES OF KEMIRI SUNAN OIL

Properties	Value
Density, 25°C (g/cm^3)	0.9347
Kinematic viscosity (cSt)	35.20
Acid number (mg KOH/g)	18.85
Water content (%)	0.5080
I_2 value (g I_2/100 g)	48.6352

B. Yield of Biodiesel

Yield is defined as the ratio of methyl esters to the oil, which is its value between 41.04 – 61.1 %. The yield of methyl esters from each treatment was shown in Figure 1 and the result of Duncan test was represented in Table 2. From the figure we can point out that increasing the NaOH concentration decreasing the yield of its biodiesel.

Some factors that influence the biodiesel yield include molar ratio of triglycerides to alcohol, reaction temperature, reaction time, water content, free fatty acid content, soap content , catalyst type as well as concentration of catalyst [7]. The higher free fatty acid, the higher concentration of catalyst will be needed. According to [5], if the acid value that reflected the free fatty acid (FFA) is greater than 1, to neutralize its FFA, more alkali is required. In this study the FFA value of the oil after esterification was 0.12%. therefore, the increasing NaOH concentration did not increase the yield but decreased it. Moreover, the excess of alkali concentration during reaction may cause saponification that lead to interrupt the reaction and produced in lower yield.

Table 2 showed that the longer reaction time, the higher of the biodiesel yield except for 1.25% alkali concentration. This due to the longer reaction time would give time to reaction process of the conversion of triglyceride to be methyl esters.

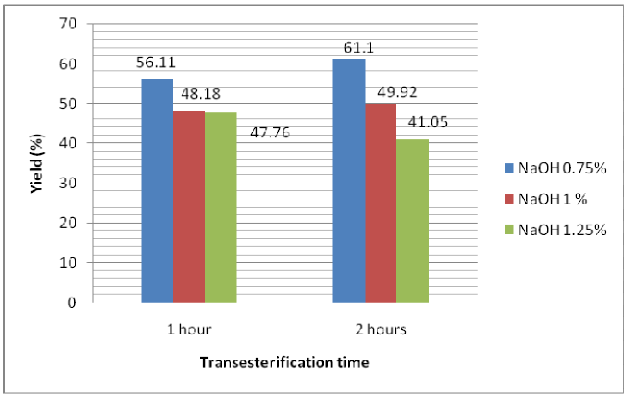

Fig. 1 Yield of biodiesel from each treatment

TABLE II
DUNCAN ANALYSIS OF BIODIESEL YIELD

NaOH Concentration	**1 Hour**	**2 Hours**
0.75% (a_1)	56.11 A (a)	61.10 B (a)
1% (a_2)	48.18 A (b)	49.92 B (b)
1.25% (a_3)	47.76 B (b)	41.05 A (c)

C. Properties of biodiesel

Properties of biodiesel for all treatment were determined to find out the effect of alkali concentration and reaction time on each properties.

1) *Density* : The density of biodiesel produced from kemiri sunan oils was between 0.8703 – 0.8754 g/cm^3, which is in the range of SNI standard (04-7182-2006). The density value of each treatment was shown in Fig. 2 and the Duncan analysis was shown in Table 3. The density increased along the increasing alkali concentration. The density was reflected the component inside the materials, the lesser carbon chain and the lesser unsaturated molecule, the molecule weight will be higher and the density will be bigger. In accordance with the biodiesel yield discussed above, the yield was decreased along the increasing of alkali concentration, and caused the increasing of density.

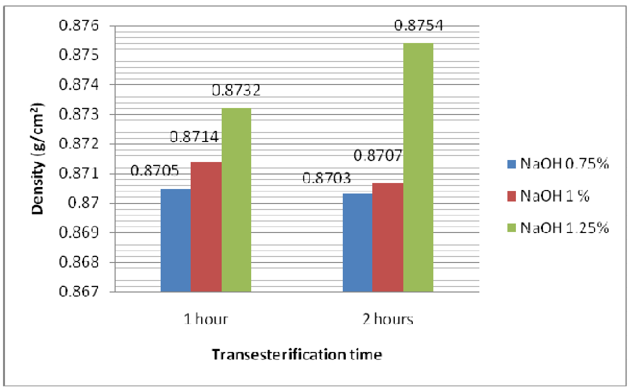

Fig. 2 Density of biodiesel from each treatment

TABLE III
DUNCAN ANALYSIS OF BIODIESEL DENSITY

NaOH Concentration	**1 Hour**	**2 Hours**
0.75% (a_1)	0.8705 A (b)	0.8703 A (b)
1% (a_2)	0.8714 A (b)	0.8707 A (b)
1.25% (a_3)	0.8732 A (a)	0.8754 B (a)

2) *Kinematic viscosity* : The kinematic viscosity of biodiesel in this study was in the range of 5.325 – 5.596 cSt. The viscosity of each treatment was shown in Fig 3 and the Duncan analysis was shown in Table 4. This value indicated the resistance of the fluid to flow. In comparison with the viscosity value of the oil, the viscosity value of oil methyl esters was lower than the oil itself. The viscosity value of biodiesel standard according SNI is 2.3 – 6 cSt. The Kemiri sunan methyl esters was fulfilled that standard. While, the viscosity value of diesel engine is 2.76 mm2/s. In contrast with the diesel engine, the oil methyl esters seems slightly viscous. The viscosity value of the biodiesel is the most important property because it affect the fuel injection equipment. The higher viscosity, the poorer atomization of the fuel spray [8].

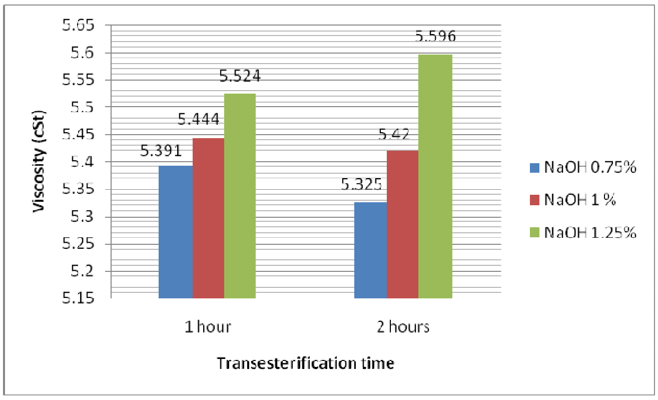

Fig. 3 Viscosity of biodiesel from each treatment

TABLE IV
DUNCAN ANALYSIS OF BIODIESEL VISCOSITY

NaOH Concentration	**1 Hour**	**2 Hours**
0.75% (a_1)	5.391 A (b)	5.325 B (a)
1% (a_2)	5.444 A (b)	5.420 A (b)
1.25% (a_3)	5.524 A (a)	5.596 B (c)

3) *Acid number :* Acid number of *Reutealis trisperma* biodiesel were 0.55 mg KOH/ g sample (Fig 4). In comparison with the acid value of *Reutealis trisperma* oil, acid number of biodiesel is very low. This number decreased sharply during trans-esterification, since the free fatty acid in the oil was changed to be methyl esters. The SNI standard of acid number is max 0.8 mg KOH/g. Compare to this standard, the biodiesel from *Reutealis trisperma* is in the range of the standard.

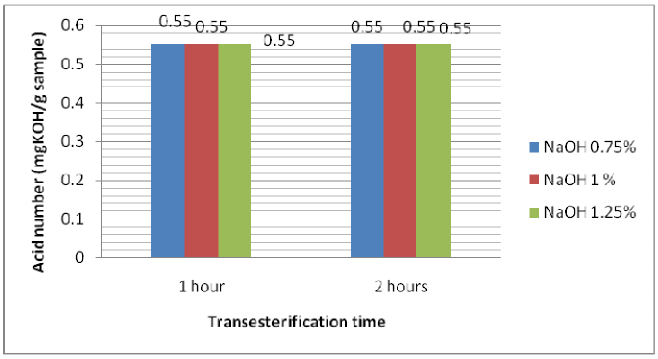

Fig. 4 Acid number of biodiesel from each treatment

4) *I_2 number :* Iod number of the *Reutealis trisperma* methyl esters were between 45.16 – 46.7 g I_2/ 100 g sample. The Iod number of each treatment was shown in Fig 5 and the Duncan analysis was shown in Table 5. The SNI standard for Iod number of biodiesel is max 115 g I_2/ 100 g sample. Compare to the standard, the Iod number of *Reutealis trisperma* methyl esters are in the range of the standard. The Iod number indicates the unsaturated chain of the biodiesel component. This number decreased along the increasing the alkali concentration. This caused by faster breakdown of the unsaturated chain by high alkali concentration [9].

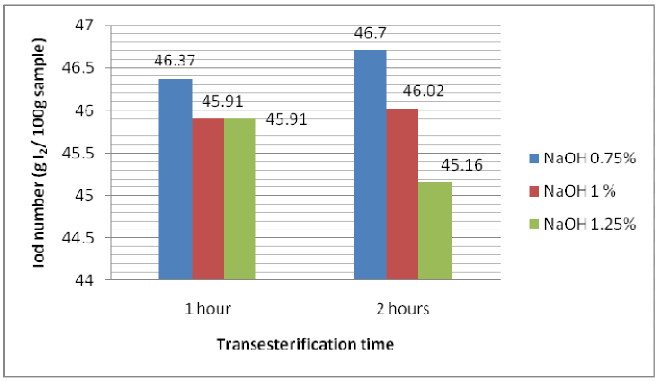

Fig. 5 Iod number of biodiesel from each treatment

TABLE V
DUNCAN ANALYSIS OF BIODIESEL I_2 NUMBER

NaOH Concentration	Iod Number (g I_2/100 g)
a_1	46.5327 a
a_2	45.9633 b
a_3	45.1760 c
Reaction time	
b_1	45.9594 a
b_2	45.8219 a

5) *Water content :* Water content of the *Reutealis trisperma* methyl esters were between 0.0435 – 0.0453 %. The water content of each treatment was shown in Fig 6 and the Duncan analysis was shown in Table 6. The SNI standard for water content of biodiesel is max 0.05%. Compare to the standard, the water content of *Reutealis trisperma* methyl esters are in the range of the standard. The water content of the biodiesel is an important property. The availability of water in the biodiesel above standard will cause hydrolysis reaction with the methyl esters and bring about corrosion of the engine machine.

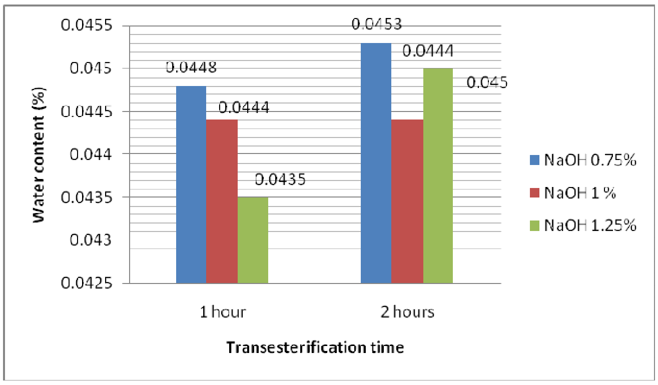

Fig. 6 Water content of biodiesel from each treatment

TABLE VI
DUNCAN ANALYSIS OF BIODIESEL WATER CONTENT

NaOH Concentration	Water content (%)
a_1	0,0450 a
a_2	0,0444 a
a_3	0,0420 a
Reaction time	
b_1	0,0442 a
b_2	0,0434 a

D. Composition of Reutealis trisperma methyl esters

Methyl esters composition was determined by Gas Chromatography Mass Spectroscopy. The Table 7 showed the *Reutalis trisperma* methyl esters composition. Linoleic acid methyl ester is the most component of biodiesel from *Reutalis trisperma* (63.02%), followed by Oleic acid methyl ester (15.36%), Palmitic acid methyl ester (12.67%) and Stearic acid methyl ester (7.93%).

IV. CONCLUSIONS

The study showed an interaction between alkali catalyst concentration and reaction time on the biodiesel yield, density and kinematic viscosity. Sodium hydroxide catalyst concentration affected the yield, density, kinematic viscosity and Iod number. Treatment of 0.75% NaOH in two hours trans-esterification produced the highest yield of FAME with density 0.8703 g/cm^3, kinematic viscosity 5.325 cSt, acid value 0.552 mg KOH/g and iodine value 46.6972 g I_2/g. The major methyl esters contained in the biodiesel were Linoleic acid, Oleic acid, Palmitic acid, and Stearic acid methyl esters.

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