



The Effect of Methanol Volume and H₂SO₄ Catalyst to the Indonesian Standard of Biodiesel

Handono Sasmito^{1*}, Sudjito², Pratikto², Bambang Dwi Argo³

¹Doctoral Program of Mechanical Engineering, Faculty of Engineering, University of Brawijaya, Malang

²Lecturer of Mechanical Engineering, Faculty of Engineering, University of Brawijaya, Malang

³Lecturer of Agricultural Faculty, University of Brawijaya, Malang
(INDONESIA)

ABSTRACT

Biodiesel could be produced from rubber plant (*Hevea brasiliensis*) through transesterification reaction. The aim of this study was to analyze the effect of using H₂SO₄ catalyst and methanol volume for producing the Indonesian standard of biodiesel. The effect was due to the characteristic of biodiesel which included density, viscosity, cetane Index, calorific value, and flash point. These factors would influence the burning process of biodiesel. It had been observed experimentally. Result showed that higher volume of H₂SO₄ catalyst and methanol would produce higher density, viscosity, and flash point but it would decrease calorific value and cetane index. This condition was approximate to the Indonesian national standard of biodiesel.

Keywords: biodiesel, transesterification, H₂SO₄ catalyst, methanol

INTRODUCTION

Biodiesel production was importantly analyzed due to scientific articles and regional standard or patents. A critical analysis was described on the most used oil sources, the catalysts and the methods to verify the transesterification yields. The predicted shortage of fossil fuel encouraged the search for substituting petroleum derivatives. This search resulted in an alternative fuel [1] called "biodiesel". Some definitions considered biodiesel as any mixture of vegetable oil and fossil diesel, while others took into account only mixtures of alkyl esters of vegetable oils or animal fats and diesel. In other word, biodiesel was as alkyl ester of fatty acids which made by the transesterification of oils or fats, from plants or animals with short chain alcohols such as methanol and ethanol. Consequently, a by-product from biodiesel was glycerine.

There were several choices for vegetable oil sources [2]. The possibility of using vegetable oils as fuel had been recognized since the beginning of diesel engines. The diesel engine could be fed by vegetable oils, and that this possibility could help the agricultural development in the countries where this engine would be used. Esters from vegetable oils were the best substitutes for diesel because they do not demand any modification in the diesel engine and had a high energetic yield. Besides, vegetable oils naturally fixed the solar energy and did not contain sulphur [3].

Stock of gasoline in Indonesia was more and more decreased. It was predicted only enough for supplying 15 years later. The assumption was due to consumption growth at the level of 5-6% per-year [4]. It was caused that gasoline was as one of the unrenewable resources. So that was needed alternative energies, one of them was biodiesel. The raw material of biodiesel was rubber seed oil, which had great percentage of fatty. Therefore, it was needed to decrease the fatty until the percentage was $\leq 2\%$. It could be carried out by continuing the reaction of transesterification [5].

Indonesia had the greatest rubber horticulture in the world. There was about 3 millions hectares of rubber horticulture and it was predicted to be able to produce rubber seed oil of 2,5 millions liter/ year [6]. The content of rubber seed was included 40-50% of oil. It showed that rubber seed had great potency to be the source of vegetable oil.

Performance of biodiesel was influenced by some factors such as volume and type of alcohol and catalyst, content of free fatty acid, temperature, water content, and time of reaction process. However, catalyst was very big influenced. Catalyst was defined as an essence which could accelerate the velocity of chemical reaction at the certain temperature. Alcohol was used as the reactan on the process of esterification. Based on the reasons as above, this research intended to trial suitable volume of H₂SO₄ catalyst and methanol so that was produced qualified biodiesel which was approximate to Indonesian standard of biodiesel..

*Correspondence Author: Handono Sasmito, Doctoral Program of Mechanical Engineering, Faculty of Engineering, University of Brawijaya, Malang, Indonesia. Email: handonosasmito@gmail.com

MATERIALS AND METHODS

This research used experimental method. It was conducted at 3 laboratories. The laboratories were as follow:

1. Laboratory of Chemical Engineering (Politeknik Negeri Malang), it was used to carry out esterification and trans-esterification of rubber seed oil.
2. Combustion Motor Laboratory of Mechanical Engineering (Engineering Faculty, Brawijaya University), it was used to measure Calory Value of biodiesel.
3. Laboratory of Pelumas Pertamina Production Unit (Surabaya), it was used to measure density, viscosity, and Cetane Index of biodiesel.

Instalation of research was as in Figure 1 below.

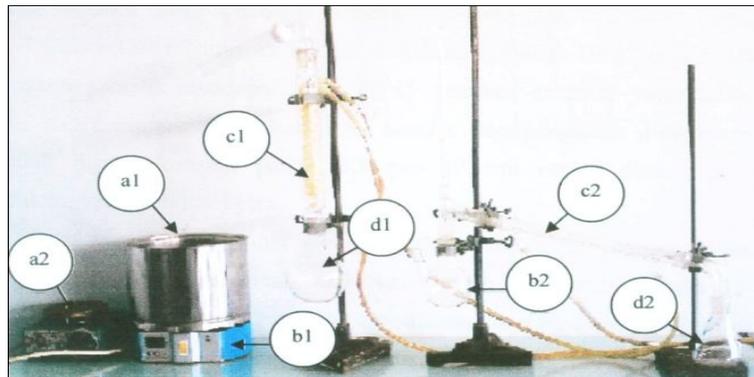


Figure 1. Instalation of research

Note:

1. Re-flux: a1 oil bath; b1. Heater; c1. Re-flux condensor ; d1. Round pitcher
2. Destilator: a2. hot plate; b2. Round pitcher; c2. Destilation condensor; d2. Erlemeyer tube

The steps of research were as follow:

1. To enter 90% of 300 ml rubber seed oil into beker glass.
2. Then, to mix 10% of 300 ml of methanol and 0,25% of total weight (± 2 gram) of H_2SO_4 into erlenmeyer tube and then whip slowly during about ± 15 minutes.
3. To enter the mixture of methanol and H_2SO_4 into beker glass
4. To do the process of esterifikasi at the temperature of $60^\circ C$.
5. After finishing process of reaction, taking it during 1 hour.
6. Then, to separate oil and water by heating biodiesel until the temperature of $\pm 100^\circ C$ during ± 10 minutes.
7. After that, it was continued with process of transesterification by doing reaction process between oil (result of esterifikasi) and 20% of methanol volume with catalyst of 0,5% calium hydroxide (KOH) weight at the temperature of $60^\circ C$.
8. To make again the process of biodiesel from rubber seed oil at the temperature of $60^\circ C$, 0,5% and 1% of sulfate acid volume. Then it was continued with variation of the other methanol volume (15%; 20%; 25%; and 30%) at sulfate acid volume of 0,25%; 0,5% dan 1%.

Biodiesel

Biodiesel was defined as mono alkyl ester of fatty acid long chain that come from plantation oil or animal oil. Biodiesel was used as alternative raw material of diesel combustion [7]. Biodiesel was as renewable resources because its raw material could be plantationed. Otherwise, compared with solar, biodiesel did not pollute environment. The use of biodiesel would decrease emission of dangerous gas such as CO , NO_x , and SO_2 .

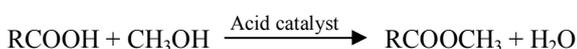
Rubber seed oil

Rubber seed oil (*Hevea Braciliensis*) consisted about 40-50% of brown hard skin and 50-60% of yellow- white cernel. Cernel of rubber seed consisted 40-50% of oil, 2,71% of ash, 3,71% of water, 22,17% of protein, and 42,21% of carbohydrate. It showed that rubber seed had great potency as the source of vegetable oil. But the high water content of rubber seed could increase tri-glyceride hydrolisis into FFA. So that was needed drying before pressing. Rubber seed was as agriculture waste that did not had economic value, did not need fertile area, intensive maintainance, and more supplying [8]. The advantages of using rubber seed as raw material of biodiesel were as follow:

1. Physical and chemical characteristic was suitable to use as raw material of biodiesel.
2. There was no competition with food interest.
3. Rubber seed could grow in any conditions and any kind of area and was able to perform forest ecology which was generally in dry area with wet season. Therefore, rubber was good enough to control critical area.

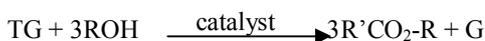
Estherification

Estherification was the step of conversion of free fatty acid to ester. Estherification was carried out to process reaction of fatty oil with alcohol. The suitable catalyst was acid character. The reaction of estherification was as follow:

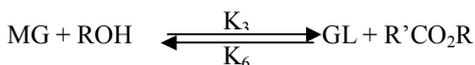
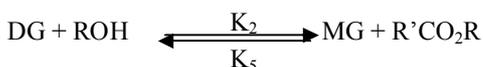
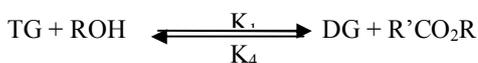


Transesterification

Transesterification was a process by using alcohol (methanol, ethanol, and buthanol) that was mixed with catalyst like sodium hydroxide or potasium hydroxide. It was intended to break the molecule from oil (tri-glyceride) chemically into metyl or etyl ester and glycerol. Reaction of transesterification and its steps were as follow: (TG= tri-glyceride, DG = di-glyceride, MG = mono-glyceride)



The steps of reaction were:



Cetane Index

Cetane Index was a parameter of burning quality at combustion material of diesel motor. Burning quality of diesel material combustion could be meaned as time used for combustion material so that could flash in combustion room and it was neasured after flashing. Cetane Index was a value determined by analysis due to distilation temperature at recovery of 50% volume and oil density at the temperature of 15° C. The formula of Cetane Index was as follow:

$$\text{Cetane Index} = 454,74 - 1641,416D^2 - 0,554B + 97,803(\log B)^2 \quad (1)$$

Note:

D = density at the temperature of 15°C, (g/ml)

B = distilation temperatue of 50% oil volume (°C)

Calorific Value

Calorific Value was a character which showed a number of heat energy in the mass or volume of combustion material through the process of perfect combustion. Calorific Value was classified as higher

heating value (HHV) and lower heating value (LHV). Calorific Value could be measured with calorimeter. It was expressed in kilo-calory per-kilogram (kcal/kg). The formula of HHV dan LHV was as follow:

$$\text{HHV} = 8080 C + 34460 (H-O/8) + 2250S \text{ kkal/Kg} \quad (2)$$

Note:

C = content of carbon in combustion material

H = content of hydrogen in combustion material

O = content of oxygen in combustion material

S = content of sulfur in combustion material

$$\text{LHV} = \text{HHV} - x\text{LH} \quad (2-2) \quad (3)$$

Note:

X = mass of H₂O performing in combustion process (mass unit of combustion material)

LH = latent heat of vapour of H₂O

= 600 kkal/kg H₂O

RESULTS AND DISCUSSION

Relation between variation of methanol volume and H₂SO₄ volume due to density of biodiesel at the esterification of rubber seed oil was described as in Figure 2 below.

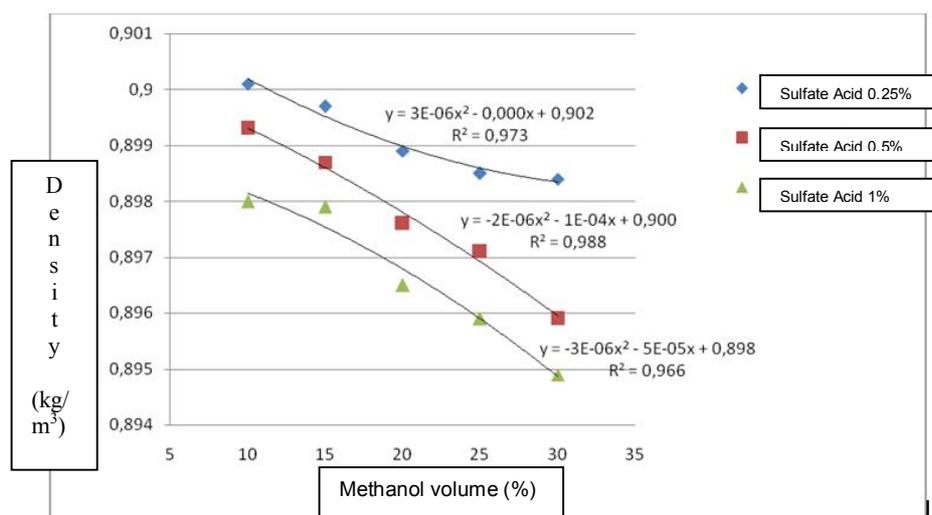


Figure 2. Relation between methanol volume and density of biodiesel

Figure 2 described the relation between density of biodiesel and methanol volume at esterification of rubber seed oil with H₂SO₄ volume of 0.25%, 0.5%, and 1%. The curve showed that the highest density was 900.1 kg/m³. It was produced from esterification process at methanol volume of 10% with H₂SO₄ catalyst volume of 0.25%. The lowest density was 894.9 kg/m³. It was produced from 30% of methanol volume and 1% of H₂SO₄ catalyst volume. High density could be caused by non perfect of esterification process so that biodiesel conversion was not maximal. Low conversion was caused by fatty acid had not reacted with methanol at the time of esterification so that in the transesterification, non conversion fatty acid was gathered with basa catalyst and performed soap and pursued the breaking of tri-glyceride to metyl eter.

Figure 3 described the relation between variation of methanol volume and H₂SO₄ volume at the esterification of rubber seed oil due to the viscosity of biodiesel.

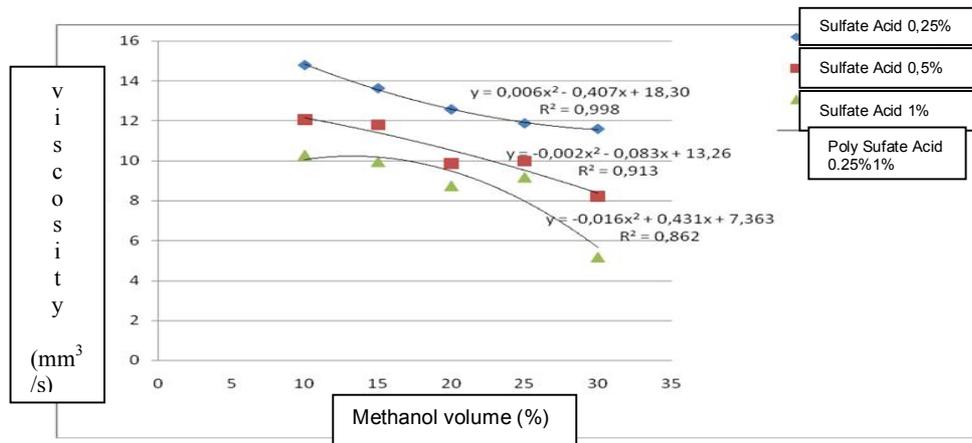


Figure 3 Relation between mathanol volume to the viscosity of biodiesel

Figure 3 showed that the highest viscosity was 14.8 mm²/s. It was produced from 10% mathanol volume with 0.25 % H₂SO₄ catalyst volume. The lowest viscosity was 5.165 mm²/s. It was produced from 30% of methanol volume and 1% of H₂SO₄ catalyst volume. High viscosity could be caused by non perfect esterification process so that biodisel conversion was less maximal. Low conversion was caused by fatty acid which had not rectioned with methanol at the time of esterification. It meanted that non conersion fatti acid was gathered with basa catalyst and performed soap, so that pursued breaking reaction tri-glyceride to metyl ester. At 0.25% of H₂SO₄ volume, viscosity decreased between 14.8 – 11.59 mm²/s foolowed by increasing of methanol volume. The other curves showed that viscosity decreased between 12.07 – 8.225 mm²/s for the 0.5% of H₂SO₄ volume and 10.28 – 5.185 mm²/s for 1% volume. It was concluded that the more increasing of methanol volume and H₂SO₄ catalyst volume would produce lower viscosity.

Figure 4 described the relation between mthanol volume and H₂SO₄ volume at the esterification of rubber seed oil due to flash point of biodiesel.

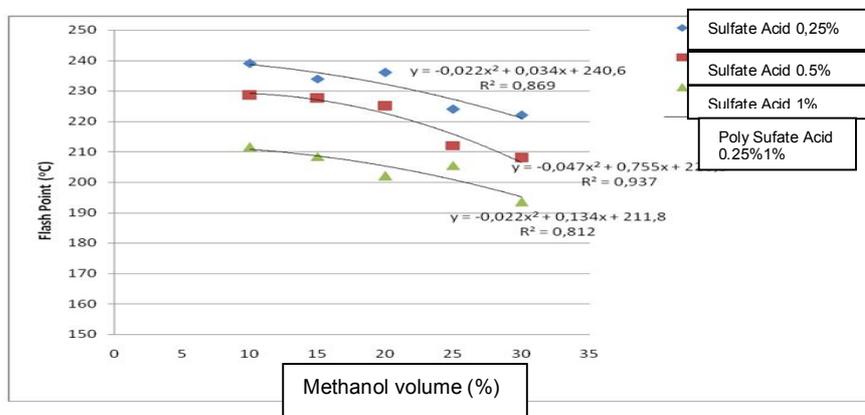


Figure 4 Relation between methanol volume to the flash point of biodiesel

Figure 4 showed that the highest flash point was 239° C. It was produced from 10% methanol volume and 0,25% H₂SO₄ catalyst volume. The lowest flash point was 193.5° C. It was produced from 30% methanol volume and 1% H₂SO₄ catalyst volume. High flash point could be caused by non perfect esterification process so that biodisel conversion was less maximal. At low conversion of biodiesel, there were tri-glyceride bonds so that was needed bigger energy to cut down the bonds. It was difference with optimized conversion of rubber seed oil. The optimized conversion one, needed less energy to cut down the bonds at the time of combustion, so that the flashing was trended lower.

Figure 5 described the relation between variation of methanol volume and H₂SO₄ volume at the esterification of rubber seed oil due to Calorific Value of biodiesel.

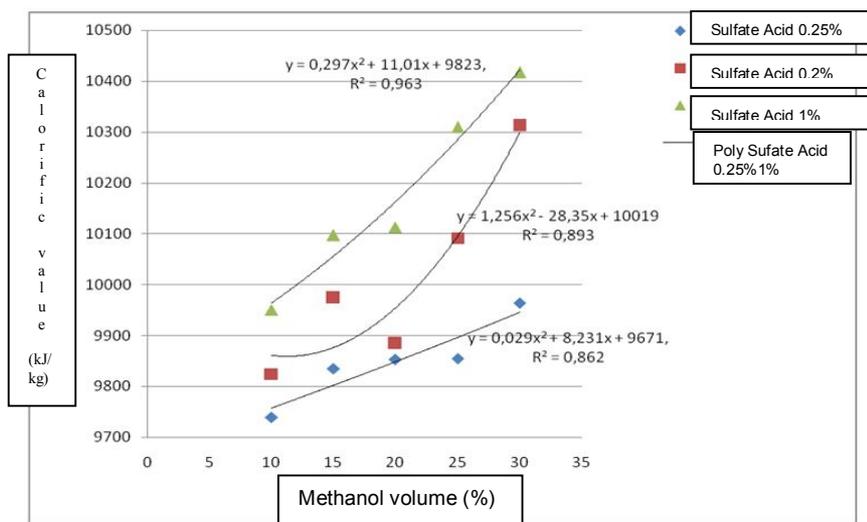


Figure 5 Relation between mathanol volume to the Calorific Value of biodiesel

Figure 5 showed that the highest of Calorific Value was 10,417.49 kJ/kg. It was produced from 30% methanol volume and 1% H₂SO₄ catalyst volume. The lowest of Calorific Value was 9,739.261 kJ/kg. It was produced from 10% methanol volume and 0.25% H₂SO₄ catalyst volume. High Calorific Value was caused by esterification process was perfect so that biodiesel conversion could be maximal.

Figure 6 described the relation between variation of methanol volume and H₂SO₄ volume at the esterification of rubber seed oil due to Cetane Index of biodiesel.

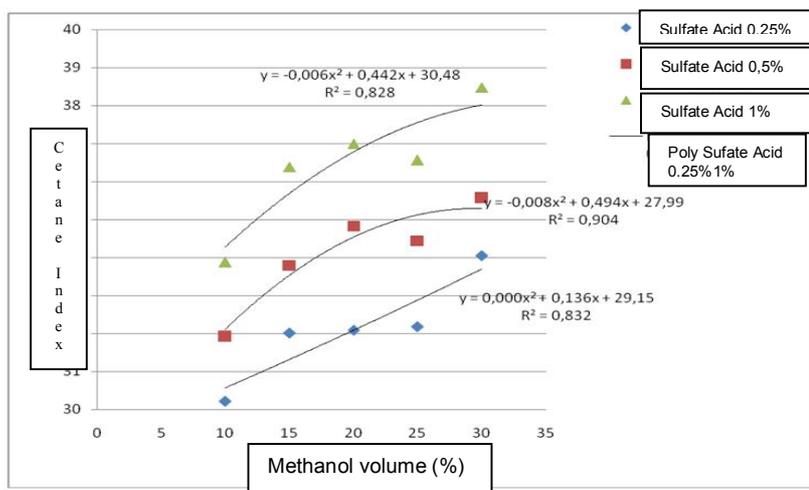


Figure 6 Relation between mathanol percentage to the Cetane Index of biodiesel

Figure 6 showed that the highest Cetane index was 38.48. It was produced from 30% methanol volume and 1% H₂SO₄ catalyst volume. The lowest of Cetane index was 30.22. It was produced from 10% methanol volume and 0.25% H₂SO₄ catalyst volume. Based on the formula, Cetane Index was proportional with density of biodiesel and proportional too with distillation temperature at recovery 50% of volume. It was meanted that Cetane Index was proportional with the ease of evaporating of combustion material. Perfect conversion of biodiesel had less number of tri-glycerides, so that the boiling point was relatively little compared to non perfect conversion of biodiesel.

CONCLUSION

Based on the analysis as above, it was concluded that the higher of H₂SO₄ catalyst volume and methanol volume at the esterification of rubber seed oil, would produce better physical characteristic of biodiesel. It could be described that this condition was also due to the more decreasing of density, viscosity, and flash point but the more increasing of Calorific Value and Cetane index. At the 1% H₂SO₄ catalyst volume and 30% methanol volume, it produced the physical characteristic of biodiesel was as follow: density = 894.9 kg/mm³; viscosity = 5.165 mm²/s; Calorific Value = 10,417.49 kJ/kg; Cetane Index = 38.48; and flash point = 193,5° C. These results was near to Indonesian national standard of biodiesel.

REFERENCES

1. Highina, B.K.; Bugaje, I.M.; and Umar, B. 2011. Performance of Biodiesel Compared to Conventional Diesel Fuel in Stationary Internal Combustion Engines. *Journal of Applied Technology in Environmental Sanitation*, Vol, 1 No, 2: 199-205
2. Sá Filho, H. L.; Rotenberg, B.; Albuquerque, S. F.; Mendonça, M. C. G.; Medeiros, P. R. S.;. 1979. *Informativo do INT*, 12, 292.
3. Meher, L. C.; Sagar, D. V.; Naik, S. N.1999. *Renew. Sustain. Energy Rev.* (in press, available on line at www.sciencedirect.com)
4. Admin. 2009. Sisa Cadangan Minyak Indonesia 15 Tahun. Palangkaraya: Indomigas. <http://www.indomigas.com/sisa-cadangan-minyak-indonesia-15-tahun/> (diakses 24 Desember 2009)
5. Cartwright, Hugh. 2010. Hands-on Science (H-Sci) Project: Chemical Safety Database. England OX1 3QZ: Physical and Theoretical Chemistry Laboratory, Oxford University. http://cartwright.chem.ox.ac.uk/hsci/chemicals/hsci_chemicals_list.html (diakses 2 Agustus 2010)
6. Soerawidjaja, Tatang H. 2006. *Fondasi-Fondasi Ilmiah dan Keteknikan dari Teknologi Pembuatan Biodiesel*". Handout Seminar Nasional "Biodiesel Sebagai Energi Alternatif Masa Depan. Yogyakarta: Press UGM
7. Demirbas, A. 2007. Biodiesel Fuel from Vegetable Oil Via Catalytic and non Catalytic Supercritical Alcohol Transesterifications and Other Method: *Energi Conversion and Management* 44 2093-2109.
8. Lutfi. 2008. *Pembuatan Margarin dari Minyak Biji Karet*. Bandung: Prima Tani.