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Biodiesel Production from Rubber Seed Oil by Supercritical Methanol Method

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***Abstract*—The purpose of this research is to investigate the effect of reaction temperature, reaction time and molar ratio between methanol and oil on the yield of biodiesel product. Rubber seeds with 45.63 wt% oil content and contained 17 wt% Free Fatty Acid was used as the main feedstock. Supercritical treatment with the methanol temperature of around 350°C and pressure of about 43MPa was used as the reaction method. It was found that yield of biodiesel product increased with the increase of reaction temperature until the temperature of about 350oC, reaction time, until the time of 9 min and molar ratio of methanol to oil until the ratio of 42:1. The highest yield of biodiesel produced was achieved under the reaction temperature of 350°C, reaction time of 9 minutes and 42:1 methanol to oil ratio.**

Keywords—**rubber seed oil, biodiesel, supercritical methanol method**

I. Introduction

Until now, the Diesel auto-vehicles, agriculture equipments, commercial and industrial machines in Indonesia are still heavily utilizing the fuels derived from the fossil crude oil as the source of their energy. Due to positive trends of the auto-vehicles sales and machinery utilization in the various aspects over the years and the non-renewable natures of crude oil, the crude oil reserves will be diminished within the short time. The new type of energy sources have been intensively investigated during the last 10 years, and biodiesel has been considered as the promising substitute for the conventional diesel. Biodiesel or methyl ester becomes more attractively nowadays because of renewable, environmental-friendly, can be produced from various animal fats and vegetable oils, and can be used in any diesel machine without modification. Biodiesel consists of methyl-esters of fatty acids, and obtained via transesterification reaction of triglycerides of fats and oils with methanol [1].

Rubber seed is the waste material from rubber plantation, and its transformation into a material or substance with a higher economical value than that of its raw form is rarely known. On the other hand, previous study has already mentioned that the rubber seed contains relatively high amount of vegetable oil [2] as shown in Table 1.

With the oil content of about 46%, rubber seed has a great potential to be utilized as the main feedstock of biodiesel production, even the water content is high (3.71 %). The water presence in the conventional base-catalyzed transesterification reaction of biodiesel causes the formation of free fatty acids, and subsequently reacts with the base catalyst and forms the saponification materials in the final products, which is usually avoided or limited. Saponification materials emulsify the biodiesel product and the other materials after the transesterification reaction takes place and the separation between them become very difficult. On the other hand, the water presence in the oil shows no significant effect on the yield biodiesel, when the non-catalyzed supercritical methanol treatment is used.

Supercritical methanol treatment is the one of non-catalyzed methods in biodiesel production. By use this treatment, the transesterification of feedstock oil with the methanol is carried out under the temperature and pressure which exceeding the critical properties of methanol. The reactor temperature is above 240 °C and its pressure is above 7.75 MPa, as shown in Fig. 1. In this study, the transesterification of rubber seed oil was carried out under the temperature range of 300 to 350°C and pressure of 43 MPa, as suggested by Hawash and El Diwani (2009) [3].

The advantages of this method compared to the conventional one are:

1. Requires no catalyst
2. Has very fast reaction time
3. Is not affected by the presence of water in oil
4. Has higher yield of biodiesel
5. Does not generate soap and other significant wastes
6. Can be used in any raw materials
7. Converts the unsaturated fatty acids into fatty acid methyl esters.

On the other hand, this method is conducted under higher pressure and temperature, and much larger amount of methanol is required, compared to that of the conventional method [1].

Table 2 shows the amount of free fatty acid in the rubber seed oil [2]. Free fatty acid content in the unrefined rubber seed oil is about 17%. The FFA of rubber seed oil has high amount of the unsaturated fatty acid, then it is expected that by use of the supercritical methanol treatment, the time of reaction completion is shorter, compared to that of the oil with the high saturated oil its FFA content, since the unsaturated fatty acids are esterified faster than saturated fatty acids by use of supercritical methanol treatment.

II. Materials and Method

A. *Materials*

The rubber seed oil, provided by PTPN XII in Jember, East Java was used as the feedstock. Methanol with “*Pure Analysis*” grade was purchased from Merck KGaA.

B. *Pre-treatment of Materials and Biodiesel Production*

At first, the water content in the rubber seed kernel was reduced by use of natural evaporation under the direct sunlight for the time of 90 min, then, the extraction of

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rubber seed oil from the kernel was carried out via mechanical pressing by use of a screw press machine.

TABLE 1.
COMPOSITION OF RUBBER SEED

Composition	Content (%)
Oil	45.63
Ash	2.71
Water	3.71
Protein	22.17
Carbohydrate	24.21

After the extracted rubber seed oil was obtained, Phosphic acid (H_3PO_4) was added into the oil, while the mixture was heated until 70^{o}C, in order to separate the oil and gums (phospholipid, carotenoid, and pigment). The separation of oil and gums was carried out by use of a decantation process.

After the oils and gums were segregated, the purified oil was ready to be trans esterified. Trans esterification reaction with supercritical methanol treatment was carried out in a batch-type tube reactor. The reactor was designed in order to work safely under high temperature and pressure, which is needed for supercritical treatment. The experimental setup of the trans esterification reaction with supercritical treatment is described in Fig. 2.

Initially, rubber seed oil and a fixed amount of methanol were mixed and put together in the batch reactor. The reactor was heated under a fixed temperature in a 1000W heater. After the trans esterification reaction was taking place under a fixed reaction time, the reactor tube was quickly moved into a 5^{o}C cooled water bath in order to stop the reaction and prevent the thermal degradation of the methyl ester which is esterified from the FFA in the oil. After the temperature of reactor achieved the room temperature, the biodiesel product was collected and decanted in order to separate the biodiesel product and excess methanol.

The experiment was carried out two times for each variable point in order to confirm the resulted data. The sample of products from the reaction were collected and analyzed by use of gas chromatography (HP19091N-133) with a HP-INNOWax (30m x 0.32mm x 0.2μm, cross-linked PEG) and a flame ionization detector (FID).

C. Method of Analysis

Gas chromatography analysis was carried out in order to determine the amount of produced biodiesel. Helium was used as the carrier gas under the initial oven temperature of 150^{o}C and time of 1 min. Then the temperature was increased to 225^{o}C with the increment temperature of 15^{o}C/min. The temperatures of the injector and detector were set at 220^{o}C and 275^{o}C, respectively. In each run, 1$\mu\ell$ of sample was injected into the column. The methyl chloride solution was used as the internal standard.

III. RESULTS AND DISCUSSION

A. Effect of Molar Ratio of Methanol to Rubber Seed Oil on Yield of Biodiesel

In this study, the effect of molar ratios of methanol to rubber seed oil of 12:1 and 42:1 on the yield of produced biodiesel was investigated. As shown in Fig. 4, for the reaction temperature of 350^{o}C and reaction time equal to 9 min, the yield of produced biodiesel was 89.36% under the molar ratio 12:1 and achieved a value of about 90.86% under the molar ratio of 42:1.

TABLE 2.
FREE FATTY ACID IN RUBBER SEED OIL

Free Fatty Acid	Content (%)
Saturated Fatty Acid	
$C_{16:0}$ Palmitic Acid	10.2
$C_{18:0}$ Stearic Acid	18.7
Unsaturated Fatty Acid	
$C_{18:1}$ Oleic Acid	24.6
$C_{18:2}$ LinoleicAcid	39.6
$C_{18:3}$ Linolenic Acid	16.3

From the reaction stoichiometry, the trans esterification of triglycerides in rubber seed oil needs three moles of methanol for A mol of triglyceride, as described in Fig. 4. Since the trans esterification is an equilibrium reaction, the higher amount of methanol reactant is required in order to shift the reaction to the product side, i.e the produced biodiesel.

Furthermore, methanol can resolve little amount of oil in normal condition. When the methanol is in its supercritical state, the solubility of non-polar material (oil) in it increases, because of the dielectric constant, and subsequently the polarity of methanol decreases. Increase of methanol to oil ratio cause the amount of oil which dissolves in the methanol increase, and reduces the mass transfer restraints between the reactants. Consequently, the rate of reaction increases. When the molar ratio of methanol to oil is very high, *i.e*., 42:1, the oil dissolves in the methanol completely, then the phase of methanol-triglycerides mixture changes from heterogeneous to homogenous, and subsequently the mass transfer resistance between the two reactants is completely disappears. As the results, the reaction rate increases greatly and could reach a high yield in very short reaction time [4].

The previous study of biodiesel production from rapeseed oil shows the same trend of results. Under the molar ratio of methanol to oil of 21:1 and 42:1, the yield of biodiesel produced from rapeseed oil was 80 and 90 %, respectively [5].

Increase the molar ratio of methanol to oil exceeding the value of 42:1 is not recommended. When the mixture of reactants exists in the homogenous phase, the yield of biodiesel is not increasing by further addition of supercritical methanol, because of the restrictions of equilibrium reactions. This action is only leading to the cost increasing for recycling and storing the excess methanol [6].

Based on our experiment it can be concluded that the yield of biodiesel increases as the increase of molar ratio of methanol to oil until the ratio of 42:1.

B. Effect of Reaction Temperature on Yield of Biodiesel

In order to investigate the effect of reaction temperature, the trans esterification reaction was carried out in the batch tube reactor under the reaction temperature of 300 and 350^{o}C, respectively. Fig. 5 shows the effect of reaction temperature on the yield of biodiesel produced under the fixed molar ratio of methanol to oil. The yield of biodiesel under the temperature of 350^{o}C and reaction time of 9 min achieved the value of 90.86%, while the yield was lower (about 89.87%), when the experiment was carried out under the temperature of

300^{o}C. Based on the Arrhenius' law, the rate of many common chemical reactions is increasing by the increase of reaction temperature, including the trans esterification reaction of triglycerides. Ma (2009) [7] reported that the solubility of triglycerides increased at the rate of 2~3% per 10^{o}C of temperature increase. Increasing the reaction temperature causes the degradation of hydrogen bonding of methanol, and reduces its polarity. Similar to that of the increase of molar ratio of methanol to oil, the amount of oil which dissolves in the methanol increases, as the temperature increases, and lead to a higher rate of trans esterification reaction.

The same trend is also found in the previous study of biodiesel production from the palm oil. In the case of trans esterification reaction of palm oil with the supercritical methanol, it is found that the yield of biodiesel was 11.6% under the temperature of 250^{o}C, and the yield was 60.30% under 300^{o}C [8]. Under the same time of reaction, the yield of biodiesel produced from rubber seed oil is higher compared to that of the palm oil. Since the FFA in the palm oil contains high amount of saturated fatty acids, the esterification of those saturated fatty acids is slower than that of the unsaturated fatty acids which is the dominant compounds in the FFA of rubber seed oil. Then the reaction time of producing biodiesel by supercritical treatment from rubber seed oil is shorter than that of the palm oil [6].

Several previous studies concluded that the yield of biodiesel decreases when the reaction was carried out under the excessive temperature reaction (above 350^{o}C). The side reactions, including the thermal decomposition of unsaturated fatty acid (UFA) methyl esters took place by applying a very high reaction temperature [9,10]. Decomposition of UFA methyl esters causes the reduces of biodiesel yield, and since the rubber seed oil as the main feedstock contains high amount of UFA in its FFA contents, it is expected that when the reaction temperature is raised above 350^{o}C, the yield of biodiesel is lower compared to that of under the temperature of 350^{o}C.

C. Effect of Reaction Time on the Yield of Biodiesel

The times of 3 to 9 minutes were investigated in order to obtain the effect of reaction time on the yield of biodiesel. The experiment was carried out under the fixed temperature of 350^{o}C and the molar ratio of methanol to oil of 42:1. Fig. 6 shows the effect of the reaction time on the yield of biodiesel. The yield rate of biodiesel shows large value for the time interval of 3 to 7 minute, as indicated by a high slope of the line in that figure under those time interval. The yield rate gradually decreased from the time interval of 7 to 9 minute. And at the time of 9 minute, the yield of biodiesel was found to be about 90.86%.

At the interval time of 3 to 7 minute, the linoleic acid, the highest compound in the free fatty acid of rubber seed oil which has three double bonding's, undergo the esterification and forms the methyl linoleate, resulting in the high rate of biodiesel produced.

After 7 minute, the esterification reaction of methyl linoleate is completed, the reaction of the saturated fatty acid and other minor compound is still taking place, results in a lower reaction rate [9]. It is expected that the yield rate would decrease for the time longer than 9 minute, and the yield biodiesel achieves a maximum value after a certain time.

Sawangkeaw et al.,(2010) observes that the conversion efficiency of fatty acid methyl esters by use of supercritical methanol treatment follows the general rate law, for instance, the yield of biodiesel increases gradually with the reaction time and then levels off when the maximum yield of biodiesel or the optimum point is achieved [10]. Then it is also expected that the yield of biodiesel decreases, when the reaction time is longer than the time at which the yield of biodiesel achieves the maximum value.

Based on our experimental results, the highest yield of biodiesel produced from the rubber oil is 90.86%, and it was achieved under the 42:1molar ratio of methanol to oil, temperature of 350^{o}C and reaction time of 9 minute conditions.

IV. CONCLUSION

It can be concluded that the yield of biodiesel increases with the increase of molar ratio of methanol to oil until the ratio of 42:1. The yield of biodiesel also increases with the increase of reaction temperature for the maximum temperature of 350^{o}C. The yield of biodiesel increases with the increase of reaction time for the reaction time shorter than 9 minute. The highest biodiesel yield achieved was 90.86%, which is obtained under the molar ratio of methanol to oil of 42:1, the reaction time of 9 minute and the temperature of 350^{o}C.

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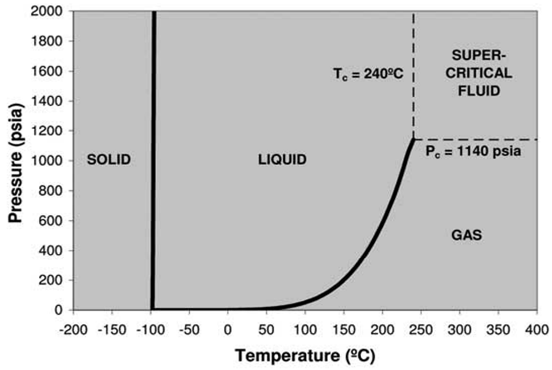

Fig. 1. Phase diagram of methanol

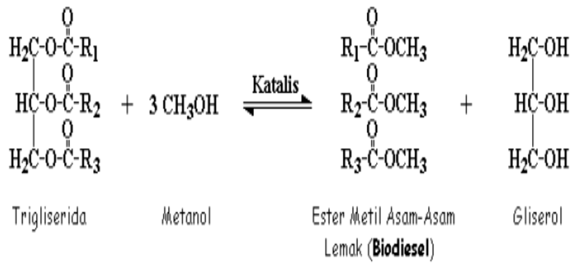

Fig. 4. Trans esterification reaction of tryglycerides

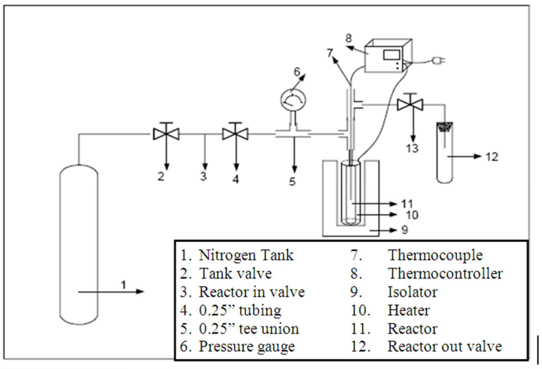

Fig. 2. Experimental setup

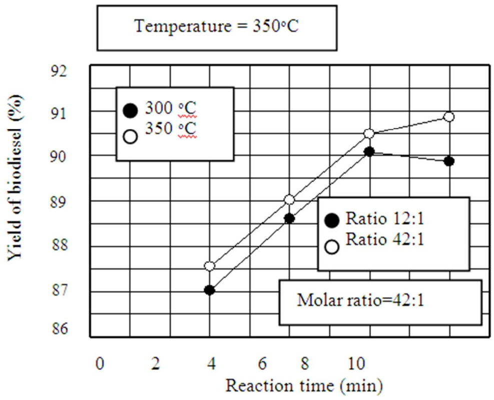

Fig. 5. Effect of molar ratio of methanol to oil on yield of biodiesel

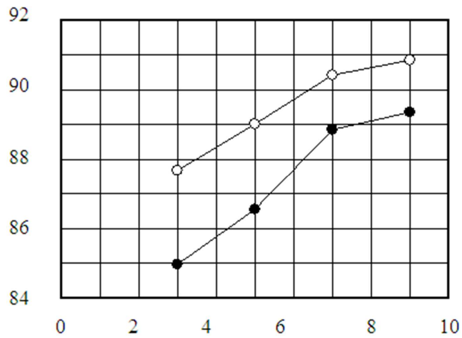

Fig. 3. Effect of molar ratio of methanol to oil on yield of biodiesel

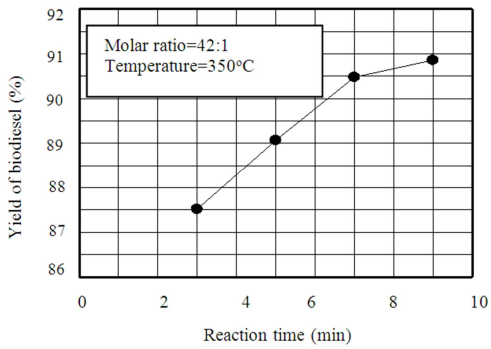

Fig. 6. Effect of reaction time of methanol to oil on yield of biodiesel