Study On Production Process of Biodiesel from Rubber Seed (*Hevea Brasiliensis*) by In Situ Transesterification Method with Alkaline Catalyzed

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Abstract :

Biodiesel is methyl or ethyl fatty acids generated from vegetable oils (edible and non edible) or animal fats. Production of biodiesel from rubber seeds by in situ alkaline catalyzed method from non edible raw materials with a major goal for alternative fuels was studied. The objective of this research is to investigate the influence of reaction time, concentration of alkaline catalyst and ratio raw materials : methanol to the production of biodiesel. The first stage was carried out in order to get reaction time based on the density and viscosity of mixture. In this process, KOH 0.5% (w/v) was used as catalyst with the ratio rubber seed to methanol (1:2). Experiments followed by process with catalyst concentration variation in range 0.1-1% (w/v) and ratio rubber seed to methanol in range 1:1.5-1:3. Research method included, the preparation of samples, biodiesel production, biodiesel separation, and biodiesel characterization include density, viscosity, GC analysis, acid value and Iodine number. The results show that operation time for biodiesel production by using in situ method with alkaline catalyzed was 120 minutes and maximum yield of Fatty Acid Methyl Ester (FAME) was obtained at 52.86%.

Keywords: Biodiesel, rubber seed, in situ, (trans) esterification, Fatty Acid Methyl Ester (FAME).

1. Introduction

Recently, fossil fuel is the source of energy in Indonesia with the largest consumption among other energy sources. Fossil fuel consumption in Indonesia now has reached 363.52 million BOE (Barrels of Oil Equivalent) or approximately 36.41% of the total consumption of energy amounted to 998.53 million BOE. The magnitude of the oil consumption is reverse to the petroleum reserves in Indonesia which were reduced annually. In 2011 total remaining of fossil oil reserves is 7,73 billion barrels, decrease 0.3% from 2010 **[1]**. To reduce dependence on fossil oil and support the global environment safety program, the only way is to develop eco-friendly alternative fuels. One of the alternative energy is biodiesel.

Biodiesel is a methyl or ethyl esters of fatty acids generated from vegetable oils (edible and non edible) or animal fats. Biodiesel can be produced from various raw materials such as vegetable oils (e.g., soybean, cottonseed, coconut, nuts, canola/rapeseed, sunflower, safflower, coconut, castor), animal and used frying oil **[2]**. Meanwhile, Indonesia is a country with a largest rubber land area of the world's with vast acreage totalled 3.4 million hectares, with rubber production reached 2.6 million tons in 2009 **[3]**. On the other side rubber seeds are not much utilized, whereas oil levels contained are quite high 40-50% **[4]**. Therefore, utilization of rubber seeds as raw material for biodiesel production is very promising.

Currently, biodiesel is produced from Crude Oil Palm Oil (CPO) using methanol and base catalyst. CPO is edible so it can interfering the human needs. Alternative raw materials which not colliding is non edible oil such as canola/rapeseed, sunflower, rubber seed etc. In biodiesel production was occurs esterification or/and transesterification reaction. Esterification is reaction between alcohol with carboxylic acid (free fatty acid). Transesterification is reaction between triglyceride and alcohol with eliminate glycerol which presented in Figure 1. Biodiesel production process can be done by using a homogenous acid catalyst process **[5]**, supercritical process **[6]**, enzymatic process **[7]**, heterogeneous acid catalyst **[8]** and sonochemical **[9]**.

The biodiesel production from rubber seed oil was using two stage method of esterification-transesterification **[4,10]**. Biodiesel production process can save cost if use in situ (trans)esterification. In this process, costs for solvent extraction and purification of oil can be reduced, so biodiesel production are becoming more simple **[11]**.

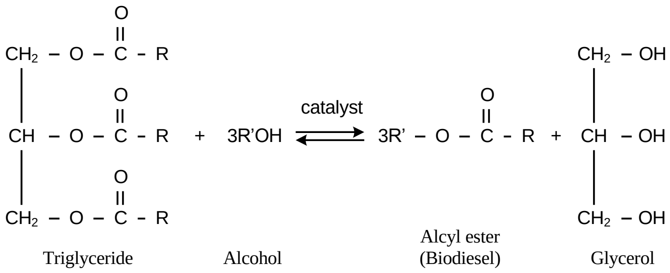

Fig. 1. Transesterification reaction of biodiesel production

In situ Esterification or transesterification is a method to produce biodiesel by contacting raw materials (seed) directly with alcohol/methanol assisted with acid/alkaline catalyst. In the process of in situ transesterification with either an acid or alkaline catalyst, molar ratio of methanol/oil is much higher than the value calculated based on the stoichiometry of the transesterification reaction, for instance, 532:1 **[12]**, 300:1 **[13]** and 543:1 **[14]**. Excess methanol will play the role of the extraction solvent **[12]**.

In situ transesterification was introduced by Harrington & Evans **[12]**. They use sunflower seeds as a raw material. Marinkovic., et.al **[13]** did experiments with the same process. Ozgul and Selma **[15,16]** used in situ esterification with rice bran as raw materials and ethanol and methanol as solvent and so Ginting., et.al **[17]** did in situ transesterification from castor seed *(Jatropha curcas)*. The objective of this research will produce biodiesel from rubber seeds with in situ process and study influence of reaction time, ratio rubber seed to methanol and alkaline catalyst concentration.

2. *Materials and methods*

2.1. Materials

The rubber seed was obtained from Perkebunan Karet Kendal Indonesia. Methanol that was used in the experiment is technical grade, while KOH as catalyst is analytical grade (Merck, Germany).

2.2. Experimental procedure

Rubber seeds samples were peeled. Seed contents was macerated, blended and dried in an oven at temperature of 55°C for 2 hours. One hundred grams samples were intake to bottle equipped with mixer (see Fig. 2). Methanol solution and KOH were added and then heated and mixed. The heating of solution in 60^{o}C temperature at atmospheric pressure. In situ processing (extraction reaction process) did until 120 minutes. The product was filtered and methanol was separated with distillation. Biodiesel product was analyzed for weight, viscosity, density and concentration. Concentration of methyl ester in biodiesel product was analyzed by GC.

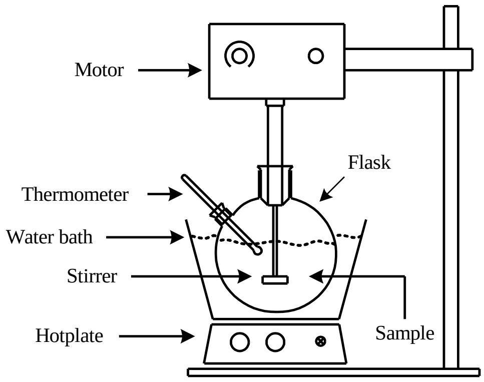

Fig. 2. Experiment tool sets

The experiment was divided into three stages. The first stage (preliminary study) was carried out to obtain reaction time for in situ processing. In this step, response variable was analyzed on density and viscosity. The experiment was done in condition of catalyst concentration of KOH 0.5% (w/v) and ratio of rubber seed to methanol (1:2) and every 15 minute was analyzed until constants condition. In second stage, experiment was investigated with catalyst concentration of KOH about 0.1; 0.25; 0.5; 0.75 and 1% (w/v). The experiments was done in variable ratio of rubber seed to methanol (1:2) and reaction time 120 minutes. In third stage, experiment conducted about effect of ratio rubber seed to methanol ie; 1:1.5; 1:1.75; 1:2; 1:2.5 and 1:3 (w:v).

Weight of product was used to calculated about biodiesel yield. Yield of FAME calculated using this equation **[17,18]**:

$$\text{Yield of FAME} = \frac{actual\,weight\,of\ biodiesel\,(g)}{theoretical\,weight\,of\ biodiesel\,(g)} x100\%$$

3. Results and discussion

3.1. Preliminary study

Figure 3 shows density and viscosity versus reaction time. Density and viscosity are physics properties that depend with composition in solution. (Trans)esterification reaction was produced methyl ester and glycerol. So, the in situ process can be obtained methyl ester, glycerol, and vegetable oil as products. Figure 3 shows that increasing time followed increasing the density and viscosity of product reaction. Product has constant density and viscosity at 120 minutes. It shows which biodiesel production and extraction of oil have been formed completely. Thus from this stage it was obtained 120 minutes as a maximum reaction time, which would be a reference time for the second and third stages.

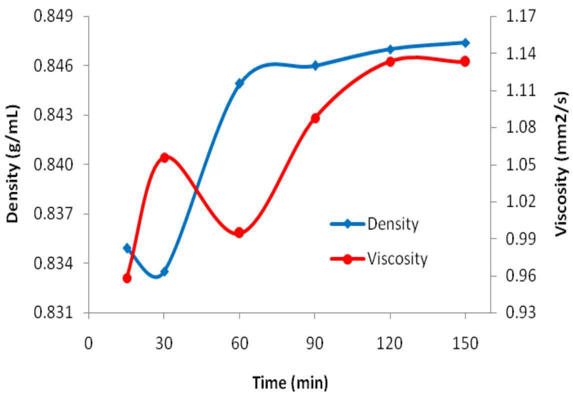

Fig. 3. Graph of time versus viscosity and density of biodiesel

3.2. Effect of catalyst concentration

In this stage, experiment was conducted to investigate the influence of catalyst concentration (KOH). Concentration of KOH was varied in range 0.1-1% (w/v). The results of these experiments are shown at Figure 4 & 5. Maximum yield of oil obtained at KOH concentration was 0.75% (w/v) with value 12.53% and the lowest on the concentration of KOH 0.5% (w/v) with 6.52%. According to Ramadhas et al., **[4]** and Ketaren, **[19]** the rubber seeds contain 40-50% of the oil. When it is compared with the results of this study, it was too small. This is because the low quality of rubber seeds and it was expected that the oil contained therein was small. Rubber seeds will quickly rots if its skin already peeled, but this can be avoid with dry it quickly and samples to be more durable and can be stored in a long time. As mentioned by Ramadhas., et al. **[4]** from physical appearance the higher catalyst concentration, the darker also biodiesel produced. Therefore the addition of a suitable catalyst concentration is important to the physical appearance of biodiesel.

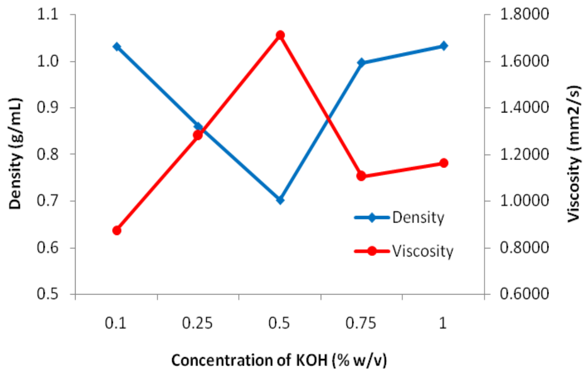

Fig. 4. Effect of catalyst concentration (%) on density & viscosity of biodiesel

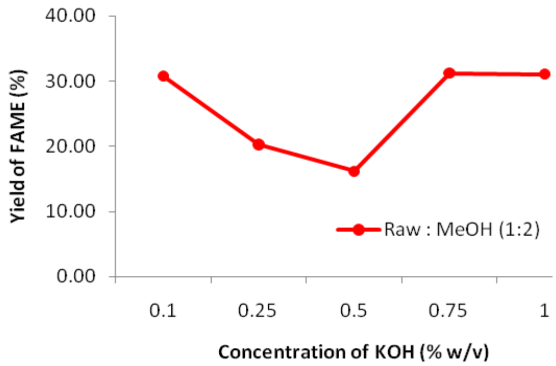

Fig. 5. Effect of catalyst concentration to yield of FAME

Figure 4 is a graph of the influence of catalyst concentration of KOH to biodiesel density and viscosity. Density of biodiesel was obtained the lowest value on KOH 0.5% (w/v) at 0.7014 g/mL, and the highest on KOH 1% (w/v) at 1.0323 g/mL. Density of biodiesel according SNI 04-7182-2006 is 0.85-0.90 g/mL. Density values obtained in this experiment is different from standard biodiesel. This is because the impurity still present in the product range. The product is the result of the extraction reaction, so in addition to biodiesel slightly even to the other products such as resin. Biodiesel product that obtained with catalyst concentration KOH 0.75% (w/v) is 0.9957 g/mL which slightly higher with biodiesel standard. The density of fuel has some effect on the break up of the fuel injected into the cylinder. In addition, more fuel is injected by mass as the fuel density increases **[20]**. The injected fuel amount, injection timing and injection spray pattern are directly affected by these parameters **[21]**. With increasing density, the diameter of the fuel droplets increases. Since the inertia of the big droplets is big, their penetrations in the combustion chamber will be higher, as well **[22].** As fuel with lower density and viscosity is injected, it will improved atomization and better mixture formation can be attained **[20]**.

The viscosity of an engine fuel is one of the most critical fuel features. It plays a dominant role in the fuel spray, mixture formation and combustion process. The high viscosity interferes with the injection process and leads to insufficient fuel atomization. Moreover, the mean diameter of the fuel droplets from the injector and their penetration increases with increasing fuel viscosity **[22]**. The inefficient mixing of fuel with air contributes to incomplete combustion in the engine. In addition to all these, high viscosity can cause early injection due to high line pressure, which moves the combustion of the fuel closer to top dead center, increasing the maximum pressure and temperature in the combustion chamber **[21, 22]**.

Viscosity of any fuel is related to its chemical structure. Viscosity increases with the increase in the chain length and decreases with the increase in the number of double bonds (unsaturation level) **[23, 24, 25]**. The viscosity increases with increasing concentrations of KOH up to 0.5% (w/v) (as shown in Figure 4) become the highest viscosity 1.7108 mm^2/s whereas the lowest viscosity 0.8729 mm^2/s at KOH 0.1% (w/v). Overall value of biodiesel viscosity (40^{o}C) is still under the standard value of the SNI 04-7182-2006 with range at 2.3-6.0 mm^2/s, it means more dilute than biodiesel standard and value its worth even closer with a solar standard viscosity 1.6-5.8 mm^2/s range at SNI so that this becomes no problem. In spite of, low viscosity causes rapid wear of engine parts such as injection pump and fuel injector as expressed by Chigier **[26]**. Viscosity of methyl ester from rubber seed oil is lower at higher temperatures and almost equal to the diesel fuel. This helps the combustion as air entrainment increases, as spray cone angle increases due to reduction in viscosity **[27]**.

Figure 5 shows that variation of catalyst concentration (KOH) effects on yield of FAME. The highest yield of FAME was obtained when in situ process did in KOH concentration 0.75% (w/v) with value of yield of FAME is 31.18%. Yield of FAME which was produced wasn't high because in this process used ratio of raw materials to methanol (1:2). Methanol used for solvent and reactant to small while compared with experiments that did by the other researcher **[12-14]**. Methanol used in situ process is very small in quantity, so the yield of oil and yield of FAME obtained also slightly small. It was supposed that less of methanol extraction and transesterification the oil into biodiesel. When the experiment was used ratio of raw materials to methanol (1:3), it was obtained maximum yield of FAME 52.86% as presented in Figure 7.

3.3. Effect of ratio rubber seed to methanol

The effect of ratio rubber seed to methanol was presented in Figure 6 and 7. Increasing ratio rubber seed to methanol can affect to amount of methanol that used to in situ processing. Methanol that used increase can cause density of biodiesel increase. Density of biodiesel was obtained the highest value 1.0034 g/mL on the ratio rubber seed to methanol (1:2.5) and the lowest value 0.9129 g/mL on the ratio rubber seed to methanol (1: 1.5). When compared with standard biodiesel SNI 04-7182-2006, density of biodiesel is 0.85-0.90 g/mL, then the overall value that near to the value of standard is at ratio of raw materials to methanol (1:1.5) until (1:2) and (1:3) Methanol in layers of esters can lower the flash point of biodiesel **[4]**.

Viscosity biodiesel has tends to constant in the ratio rubber seed to methanol (1:1,5) until (1:75) from 1.2049 mm^2/s to 1.2596 mm^2/s but at ratio of raw materials to methanol (1:2) decrease to 1.1048 mm^2/s which still lower if compared to solar standard with viscosity range at 1.6-5.8 mm^2/s on SNI 04-7182-2006. At ratio rubber seed to methanol (1:3), the viscosity was obtained at 1.1035 mm^2/s which is still lower than solar standard at SNI and this is not a problem because as in the previous discussion, when a fuel with lower density and viscosity is injected, improved atomization and better mixture formation can be attained **[20]**.

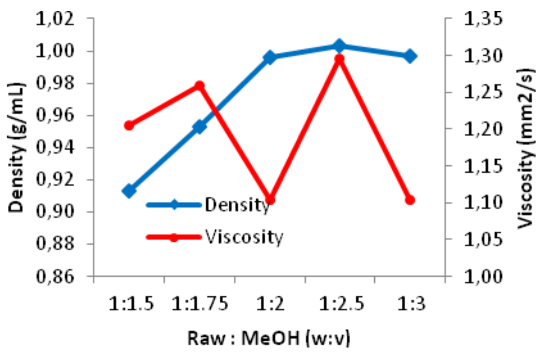

Fig. 6. Effect of raw materials to methanol on density & viscosity of biodiesel

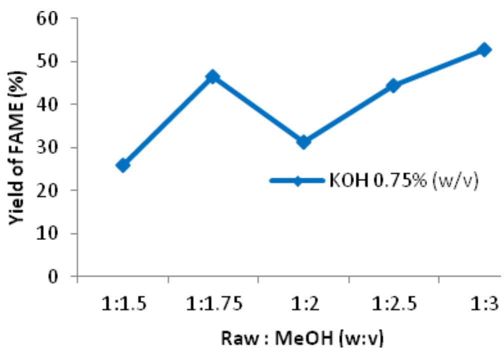

Fig. 7. Effect of raw materials to methanol on yield of FAME

As expressed by Özgül-Yücel and Türkay **[16]**, the role of methanol in the in situ process is very important because the methanol has a dual role: as a solvent for oil extraction as well as reactant, so the addition should be an excess. Figure 7 shows that yield of FAME increase significantly at the ratio rubber seed to methanol (1:2,5) and (1:3) by 44.55% and 52.86% respectively. The amount of methanol, however, should not be too exaggerated, as expressed by Ramadhas., et al [4], methanol on ester layers can lower the flash point of biodiesel. Therefore the purification process and removal of methanol with distillation or washing should be perfect. Distillation process should be concerned (±1 hour) because if it is too long causing a condensed biodiesel and hard to pour it at room temperature.

Acid number (acid value) is the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize one gram of chemical substance. The acid number is a measure of the amount of carboxylic acid groups in a chemical compound, such as a fatty acid, or in a mixture of compounds. Acid value on biodiesel product are still quite high with the lowest value 13.73 mg KOH/g biodiesel at concentrations of KOH 0.1% (w/v) and the highest value 71.46 mg KOH/g biodiesel at concentration of KOH 0.25% (w/v) like presented in Figure 8. Figure 8 shows that acid value decrease starting from concentration of KOH 0.25 until 1% (w/v) and also from ratio of raw materials to methanol (1:1.5) until (1:3) in Figure 9. This shows that there are still many free fatty acids that have not been converted into methyl ester. Free fatty acids obtained from the extraction process. Thus the extraction process is more dominant compared to the transesterification reaction. Figure 9 shows that with increasing methanol, then KOH will more and more causing decline in acid number. As for the reaction to form methyl ester have been low. High acid value not only will make deposits in the fuel system but also decrease the quality components in the fuel system **[28]**. So, to increasing quality of biodiesel or decreasing of acid number, product of in situ process must be followed by esterification processing.

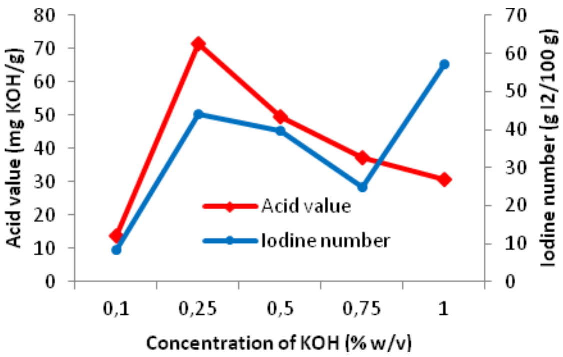

Fig. 8. Effect of catalyst concentration to acid number & Iodine number

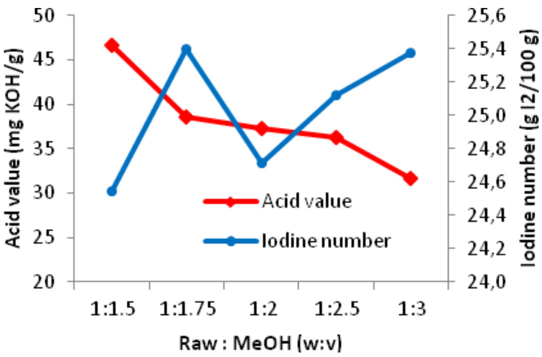

Fig. 9. Effect of ratio rubber seed to methanol on acid number & Iodine number

Iodine number is mass of iodine in grams that is consumed by 100 grams of a chemical substance. Iodine numbers are often used to determine the amount of unsaturation in fatty acids. This unsaturation is in the form of double bonds, which react with iodine compounds. The higher iodine number, the more C=C bonds are present in the fat [29]. Iodine number was relatively stable at ratio variations of raw materials to methanol as seen in Figure 9. In contrast to the Figure 8, Iodine number varies at different concentrations of catalyst. At the concentration of KOH 0.75% (w/v) had an Iodine number 24.72 g I_2/100 g biodiesel and at ratio of raw materials to methanol (1:3) had an Iodine number 25.38 g I_2/100 g biodiesel which means the unsaturation of biodiesel was relatively small and quite well and all of the Iodine numbers at all variations was still under the SNI 04-7182-2006 standard with a maximum value of 115 g I_2/100 g biodiesel.

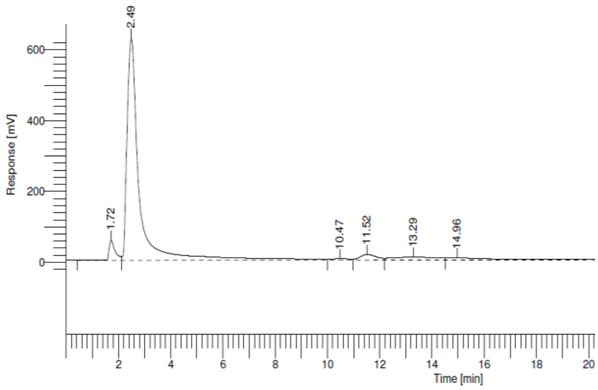

Fig. 10. GC chromatogram of biodiesel on the ratio raw materials to methanol (1:3) (w:v)

Chromatogram of Fatty Acid Methyl Ester (FAME) was detected at 10-14 retention time minutes and it was appropriate with the standard biodiesel chromatogram with FAME in minutes 6-14 retention time. When compared to standard, the expected results of biodiesel analysis with GC 10.47 minutes was methyl nonadecanoic ($C_{19:0}$), 11.52 minutes was methyl linolenic ($C_{18:3}$), 13.29 minutes was methyl eicosadienoic ($C_{20:2}$) and 14.96 minutes was methyl timnodonic ($C_{20:5}$). Although all of its peak wasn't obvious, but this shows that the FAME was indeed formed in biodiesel sample and the oil/triglyceride wasn't detected again.

4. Conclusion

In situ process that involve transesterification reaction of biodiesel production from rubber seeds with in situ method takes 120 minutes at 60^{o}C with concentration of KOH 0.75% (w/v) was obtained maximum yield of FAME 31.18% and at ratio of raw materials to methanol (1:3) was obtained maximum yield of FAME 52.86%. Based on the results, ratio of raw materials to methanol is quite important to increase yield of FAME significantly.

Acknowledgement

This research was supported by research grant of postgraduates from Directorate General of Higher Education, Ministry of National Education, Indonesia. Authors was thank to Department of Chemical Engineering Polytechnic Malang for Gas Chromatography analysis.

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