Study on Different Capacity of Transesterification Process in Biodiesel Production from Kemiri Sunan (Reutalis trisperma)

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Abstract. Kemiri Sunan (Reutalis trisperma) is one of the plants that can be used as an alternative fuel because it contains triglyceride that can be converted into Fatty Acid Methyl Ester (FAME) or biodiesel by transesterification reaction. This study aimed to determine the effect of capacity increment of transesterification on yield and quality of biodiesel. The method used in this study was experimental method with descriptive analysis. The treatment performed in this study were five different capacity of transesterification i.e. 200, 400, 600, 800 and 1000 mL. Each treatment repeated three times. The parameters of biodiesel observed were yield, moisture content, density, acid number and FAME identification (GCMS). The results revealed that Kemiri Sunan biodiesel produced by transesterification process in 800 mL capacity fulfilled the SNI standard of Biodiesel SNI 7182:2015 with moisture content was 0.07%, acid number was 1.76 mg-KOH/g-oil and methyl palmitate, methyl linoleate, methyl oleate and methyl linolenate as the four major FAME in Kemiri Sunan biodiesel.

1. Introduction

Biodiesel is a renewable energy that can replace the use of fossil fuels, used as a substitute for diesel fuel for diesel engines. Biodiesel is an environmentally friendly fuel because it produces less emissions, exhaust fumes around 75% less than diesel, and higher cetane numbers (> 57) resulting in high burning efficiency [1]. Moreover, biodiesel produce low sulphur content as well as lubrication and cleaning machines which are better than diesel fuel [2] [3].

Indonesia have huge potential of biofuel production due to variety of plants that can be used as the raw material of biodiesel production such as palm, coconut, jatropha, and kemiri sunan. Kemiri sunan (Reutalis trisperma) is a potential plant used as raw material of biodiesel due to its high content of oil (> 50%) [4]. Moreover, utilization of kemiri sunan do not compete with food industry because kemiri
sunan oil contained α-oleostearic acid as a toxic component. Biodiesel from sunan pecan can be produced through the stages of esterification of sunan pecan oil, transesterification, washing and evaporation [5].

Biodiesel is defined as the mono alkyl esters, either methyl and ethyl ester of vegetable and animal oils fatty acid. It is produced by transesterification process of triglycerides in the form of Fatty Acid Methyl Ester (FAME) or Fatty Acid Ethyl Ester (FAEE). Triglycerides are converted into FAME or FAEE and glyceride by alcohol and a strong base catalyst [2] [6].

The main purpose of the transesterification process in the production of biodiesel is to reduce the viscosity of the material. According to biodiesel standard (SNI 7182 : 2015 ), biodiesel kinematic viscosity is 2.3 – 6 mm²/s, whereas vegetable oils from some plants more than 20 mm²/s. The studies by Aunillah & Pranowo (2012), showed that the transesterification process in kemiri sunan oil could reduce the kinematic viscosity from 99.012 to 4.4 mm²/s [7]. Viscosity is one of the important properties that determine the quality of biodiesel that determined the operation of fuel injection equipment. The high viscosity leads to poor atomization, resulted in uncomplete combustion. Research on the kemiri sunan biodiesel production process has been carried out by several researchers [5] [7], but the research is mostly still in a laboratory scale. To be applied on an industrial scale, it is necessary to scale up the laboratory scale. The conditions of the production process depend on the scale used, some materials will be different in behavior at the laboratory scale, pilot scale and industrial scale. Some differences that occur due to chemical changes, thermal changes and mechanical changes [8].These changes can be simulated in a model. To be able to create a simulation model, it is necessary to have data on the effect of different process scales on the quality parameters of the product. For this reason, it is necessary to do research on the effect of capacity increasement of transesterification process on the quality of kemiri sunan biodiesel produced. The study aimed to find out the effect of different capacity of transesterification on yield and quality of kemiri sunan biodiesel.

2. Research Methods

2.1. Material
Kemiri sunan (Reutealis trisperma) that obtained from Wanaraja, Garut region, West Java, methanol, H2SO4, KOH and aquadest.

2.2. Method
This study used descriptive analysis method with the correlation regression analysis. The transesterification process was carried out at 5 capacity level : 200, 400, 600, 800 and 1000 ml with 3 replications. The parameters studied were yield, moisture content, kinematic viscosity, density, acid number and biodiesel component by GCMS (Gas Chromatography-Mass Spectroscopy).

2.3. Procedure
• Biodiesel (FAME) Production : Oils from kemiri sunan were produced from dried kernel by mechanical pressure. Esterification reaction with methanol and H2SO4 was done prior to transesterification. After esterification process, the oils were mixed with methanol and KOH 1% (6:1). The transesterification process was conducted at a temperature of 60oC and stirred. After that, the mixture was settled down and the glycerol was separated with FAME.
• GCMS Analysis : The analysis of FAME was performed on Shimadzu QP 2010 Ultra with a ZB-5MS-fused silica capillary column (30m x 0.25mm x 0.25μm film thickness). The injector and detector temperature was 280 and 230oC, respectively. The carrier gas was hydrogen with a flow rate of 1.31 mL/min. The detector was operated in EI mode with a mass scan range from m/z 35 to 500 using a spray voltage of 0.7 kV. The components were identified using The National Institute of Standards and Technology (NIST 3.0) and WILEY 275 mass spectral libraries, and by comparison of the mass spectra with published data.
• FAME Characteristic : FAME of kemiri sunan was characterized using Indonesia National
Standard method for testing Biodiesel (SNI 7182-2015). The properties measured were kinematic viscosity, density, acid value and moisture content. Kinematic viscosity of the kemiri sunan FAME was measured by Ostwal viscometer. Relative density refers to the ratio of kemiri sunan FAME density to water density at the same temperature (25°C). Density was calculated using the following expression:

$$\text{Density (kg/m}^3\text{) = mass (kg)/volume (m}^3\text{)}$$

Acid value was measured by titrating of kemiri sunan FAME in neutral ethanol with 0.5 KOH. Acid value was calculated using the following expression:

$$\text{Acid value (mg KOH/g) = volume of titrant (ml)\times N\times 56.10/mass of the sample (mg)}$$

3. Result and Discussion

3.1 Characteristic of oil after esterification

Characterization of kemiri sunan oil after esterification and washing process was carried out prior to transesterification. The value of its kinematic viscosity, density, moisture content and acid number were showed in Table 1. This study showed that the kinematic viscosity and density of oil after esterification were higher than kinematic viscosity and density of SNI standard, whereas value of moisture content and acid number below the standard. Therefore, to decrease the kinematic viscosity it is needed transesterification process.

The kinematic viscosity of kemiri sunan oil after esterification is 23.82 mm²/s, higher than biodiesel standard (SNI). Kinematic viscosity is determined by component of the material, viscosity of triglycerides is much higher than of FAME, is also affected by carbon chain bonds in the fatty acid constituents of oil. The longer the carbon chain bond the higher the kinematic viscosity value. The density of kemiri sunan oil after esterification is 959.35 kg/m³. This density value is also influenced by the fatty acids of the oil. The transesterification process could reduce the density of kemiri sunan oil after esterification, if the biodiesel density does not decrease, then the possibility of transesterification reaction does not take place perfectly because triglycerides are not evenly converted. The moisture content of kemiri sunan oil after esterification is 0.21%, which is below the standard of moisture content of oil for transesterification. The presence of water in raw materials can cause saponification and reduce the amount of triglyceride conversion to FAME [9]. Acid numbers indicated the amount of free fatty acids contained in an oil. The acid value of kemiri sunan oil after esterification is 2.85 mg KOH / g of oil, which is fulfilling the requirements for the transesterification process in accordance with the opinion of Pranowo et al (2014) that acid value of material for the transesterification process should not be more than 5 mg KOH / g of oil.

| Criteria                        | Unit      | Value ± SD | SNI 7182 2015 |
|---------------------------------|-----------|------------|---------------|
| Kinematic viscosity (40°C)      | mm²/s     | 23.82 ± 0.21 | 2.3 – 6.0    |
| Density (25°C)                  | kg/m³     | 959.35 ± 1.03 | 850 - 890    |
| Moisture content                | %         | 0.21 ± 0.01  | Max. 7.00    |
| Acid value                      | mg KOH/g material | 2.85 ± 0.16 | Max. 5.00    |
3.2 Yield on different capacity

The yield is a comparison between the product to the raw material. The raw material is kemiri sunan oil which has been esterified while the product is the FAME resulted from transesterification process and after separation process of FAME with glycerol. The study showed that yield of biodiesel slightly increased along with increasing capacity at capacity of 400 – 1000 ml (Fig. 1). The lowest yield is at capacity of 200 ml, it may due to the occurrence of vortex or basin when stirring in the transesterification process so that most of the triglycerides are not converted into FAME/biodiesel but mixed in glycerol as the by product. At capacity of 1000 ml produced the highest yield of biodiesel. This shows that the stirring speed affects the condition of the transesterification process. 100 rpm of stirring speed is effective for transesterification process at capacity of 400 – 1000 ml but not for capacity of 200 ml.

![Figure 1. Yield of kemiri sunan biodiesel on different capacity](image)

3.3 Kinematic viscosity

The relationship between capacity increasement and its kinematic viscosity in transesterification process is presented in Fig. 2. The study showed that kinematic viscosity decreased along with capacity increasement, the higher capacity, the lower its kinematic viscosity. Indicators of the success of the transesterification process can be seen when the viscosity of the raw material has decreased after becoming biodiesel. The transesterification process causes shorter carbon chain shrinkage. The smaller the carbon chain bond in an oil compound, the kinematic viscosity value will also decrease [3]. The smaller the kinematic viscosity value the better the quality of biodiesel because it will accelerate the process of material flow in the combustion system, as well as reduce the risk of deposits on the engine. The results showed that the esterification process can reduce the kinematic viscosity and kinematic viscosity values of all treatments meet the requirements in the SNI standard for kinematic viscosity of biodiesel (2.3 - 6 mm²/s).

![Figure 2. Kinematic viscosity of kemiri sunan biodiesel on different capacity](image)
3.4 Density
The value of biodiesel density in the standard set by SNI 7182: 2015 is 850-890 kg / m$^3$. The transesterification process is carried out to reduce the value of raw material density and is expected to meet the requirements of standard that has been determined. The relationship between increasing the capacity of making biodiesel and the density value is shown in the graph in Fig. 3. The capacity increase did not affect the number of its density. The amount of the oil density is influenced by the compounds contained in the oil. The transesterification process makes saturated oil compounds such as triglycerides break down into methyl esters which have a short double bond chain which causes the density to be lower than that of raw materials.

The biodiesel produced by transesterification for all treatments still has a density value that has not met the maximum limit of biodiesel. This is strongly suspected because the biodiesel produced by the transesterification has not been purified. Biodiesel that has not been purified still contains a mixture of impurities in the form of water molecules, glycerol, and the remaining methanol. The impurity mixture present in biodiesel can increase the biodiesel density value [5]. Therefore, it is needed to wash the FAME produced by transesterification to get the pure FAME without any impurity materials.

![Figure 3. Density of kemiri sunan biodiesel on different capacity](image)

3.5 Moisture content
Moisture content is an indicator of biodiesel quality, excessive water in biodiesel can cause various potential problems. Moisture presence in biodiesel causes microbial growth that lead to rancidity as well as accelerate corrosion or rusting on the engine [9]. The relationship between increasing the capacity of making biodiesel and the moisture content is shown in the graph in Fig. 4.

Moisture content of the biodiesel tends to increase along the increasing of transesterification capacity. The 200 mL capacity treatment has a moisture content below the moisture content value of the raw material. This occurs because the heating process at the transesterification stage cause some of the water evaporates. At capacity of 400 mL, the moisture content tends to level off, this may occur because KOH as a catalyst in the transesterification process reacts with triglycerides and binds to water molecules. In the treatment of 600, 800, and 1000 mL, the amount of moisture content increased with the increase of capacity. This can occur because of the presence of free fatty acids. KOH as a catalyst does not only react with triglycerides, but KOH may react with free fatty acids too, so that a neutralization reaction occurs and produces water molecules. The neutralization reaction is thought to increase the water content of biodiesel. The moisture content of all of the sample are higher than its standard, therefore it is needed an evaporation process after separation and washing of FAME.
3.6 Acid value
Acid value indicates the amount of free fatty acids contained in biodiesel. Acid value is the amount of KOH in the unit of volume needed to neutralize one gram of oil. This value indicates the purity of biodiesel, the pure biodiesel is only presence of Fatty Acid Methyl Ester. The acid value may increase during storage time due to oxidation reaction that affected by environmental factors such as oxygen and light. The relationship between increasing the capacity of making biodiesel and the moisture content is shown in the graph in Fig. 5. The study showed that capacity increasement do not affect acid value in all transesterification capacity, but it proved that transesterification process could decrease the acid value.

There was a decrease in acid value which was initially 2.85 mg KOH / g Oil, it due to the free fatty acids contained in the raw material had been converted to methyl esters in the transesterification process. However, the acid value for all of these treatments have not been matched with SNI 7182: 2015 where the maximum acid value for biodiesel is 0.5 mg KOH / g Oil. This high acid value may due to the presence of acid in biodiesel, so the biodiesel need to be washed after transesterification process to remove its acid. High acid value make it easier for the engine to get rusting. Therefore, the smaller the acid value in biodiesel, the better it is in use as a fuel for diesel fuel engines [10].

3.7 Biodiesel composition by GCMS
Chromatogram of FAME by Gas Chromatography-Mass Spectroscopy (Shimadzu QP 2010 Ultra) were shown at Fig. 6. All samples contained methyl myristate, methyl palmitate, methyl palmitoleate, methyl stearate, methyl oleate, methyl linoleate, methyl linolenate, methyl arachate, and methyl arachidonate. Methyl linolenate is the highest content in all sample followed by methyl linoleate, methyl oleate and methyl palmitate (Table 2). This finding is different from the study by Djenar & Lintang (2012), which is the highest content of FAME is methyl oleate followed by methyl palmitate and methyl linoleate [11].
This difference may due to the differences in the origin of kemiri sunan that lead to the difference in its fatty acid.

The results showed that increasing capacity did not affect the type of FAME produced (Fig. 7 and Table 3). This can be seen from the R² value of all equations that are less than 0.95. Therefore, it can be concluded that the composition of FAME in kemiri sunan biodiesel is not affected by the capacity of the transesterification process.

Figure 6 Chromatogram of FAME from transesterification at (a) 200 ml; (b) 400 ml; (c) 600 ml; (d) 800 ml; (e) 1000 ml; and (f) glycerol
### Table 2. FAME and residue compound from transesterification process

| FAME          | Molecular formula | Molecular weight | 200 ml | 400 ml | 600 ml | 800 ml | 1000 ml | Residue/glycerol |
|---------------|-------------------|------------------|--------|--------|--------|--------|---------|-----------------|
| Glycerol      | C₃H₈O₃            | 92               | 1.38   | 23.81  |        |        |         |                 |
| Methyl myristate | C₁₅H₃₀O₂      | 242              | 0.16   | 0.15   | 0.19   | 0.20   | 0.16    | 0.00           |
| Methyl palmitate | C₁₇H₃₄O₂    | 270              | 13.58  | 14.23  | 13.12  | 12.80  | 13.31   | 11.55          |
| Methyl palmitoleate | C₁₇H₃₂O₂  | 268              | 0.12   | 0.21   | 0.23   | 0.24   | 0.53    | 0.00           |
| Methyl stearate | C₁₉H₃₈O₂      | 298              | 5.98   | 6.07   | 5.62   | 6.47   | 6.27    | 4.28           |
| Methyl oleate  | C₁₉H₃₆O₂        | 296              | 17.47  | 17.82  | 15.35  | 16.82  | 17.77   | 13.92          |
| Methyl linoleate | C₁₉H₃₄O₂      | 294              | 17.76  | 17.84  | 17.87  | 16.91  | 16.87   | 13.78          |
| Methyl linolenate | C₁₉H₃₂O₂      | 292              | 44.45  | 43.42  | 40.04  | 44.55  | 44.92   | 32.65          |
| Methyl arachate | C₂₁H₴₂O₂      | 326              | 0.00   | 0.00   | 0.00   | 0.00   | 0.16    | 0.64           |
| Methyl arachidonate | C₂₁H₴₄O₂ | 318              | 0.29   | 0.27   | 0.44   | 2.95   | 0.00    | 0.00           |

**Figure 7.** FAME component on different capacity of transesterification process
Table 3. Regression analysis of FAME after transesterification process

| Compound          | Equation                      | R²     |
|-------------------|-------------------------------|--------|
| Methyl myristate  | y = -0.0064x² + 0.0436x + 0.112 | R² = 0.4407 |
| Methyl palmitate  | y = -0.197x + 13.999          | R² = 0.3324 |
| Methyl palmitoleate | y = 0.085x + 0.011         | R² = 0.7517 |
| Methyl stearate   | y = 0.0514x² - 0.2106x + 6.148  | R² = 0.3247 |
| Methyl oleate     | y = 0.3671x² - 2.2429x + 19.736 | R² = 0.4499 |
| Methyl linoleate  | y = -0.271x + 18.263          | R² = 0.6977 |
| Methyl linolenate | y = 0.7636x² - 4.3744x + 48.2 | R² = 0.5371 |
| Methyl arachate   | y = 0.0229x² - 0.1051x + 0.096 | R² = 0.8571 |
| Methyl arachidonate | y = -0.2514x² + 1.7186x - 1.6 | R² = 0.2235 |

4 Conclusion

It can be concluded that the transesterification process can reduce kinematic viscosity (3.91 - 4.74 mm²/s) in all tested capacities (200, 400, 600, 800 and 1000 ml) so that it meets SNI standards for kinematic viscosity (2.3 - 6 mm²/s), but increasing capacity do not affect this value.

Transesterification was able to decrease acid value (from 2.8 to 0.95 – 1.88 mg KOH/g FAME), however increasing capacity did not affect the acid value.

Increasing capacity affects the moisture content of biodiesel. The greater the capacity, the higher the moisture content.

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