INTERNATIONAL JOURNAL OF INTEGRATED ENGINEERING
ISSN: 2229-838X e-ISSN: 2600-7916

IJIE

Vol. 16 No. 1 (2024) 161-177
https://publisher.uthm.edu.my/ojs/index.php/ijie

Physicochemical Study of Ethanol Ratio in the Transesterification Process for Biodiesel Synthesis from Kesambi (Schleichera Oleosa) Seed Oil

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DOI: https://doi.org/10.30880/ijie.2024.16.01.013

Article Info

Received: 13 October 2023
Accepted: 24 December 2023
Available online: 28 April 2024

Keywords

Biodiesel, ethanol ratio, kesambi (*Schleichera oleosa*) seed oil

Abstract

The demand for energy, particularly for fossil fuels, has been increasing in line with the growing number of transportation units. However, natural resource conditions such as fossil fuels are not always fulfilled. This is because fossil fuels are categorized as non-renewable resources. Moreover, all countries in the world are required to reduce the use of fossil resources and increase the use of green energy. Therefore, alternative green energy sources are needed to replace fossil fuels. Biodiesel is a green energy source that could be produced from renewable resources. Biodiesel could be obtained from non-food sources such as kesambi oil. In this research, the biodiesel production process was carried out by esterification and transesterification methods. The transesterification process was performed by varying the molar ratio between ethanol and kesambi oil. The molar ratio used in the transesterification process were 4:1, 6:1, 8:1, 10:1, and 12:1. The results showed that the molar ratio of 12:1 produced the lowest values of density, viscosity, and flash point, which were 0.839 g/ml, 3.98 CST, and 109.4°C, respectively, but the highest values of calorific value and yield, which were 9,040 cal/g and 91.30%, respectively.

1. Introduction

The increase in the number of vehicles over the last few decades has caused the demand for fossil fuels to increase [1]. Currently, fossil fuels, especially petroleum, are the main energy source for vehicles [2-3]. It is estimated that the decline in fossil fuel reserves will continue [4]. This prediction is based on the fact that fossil fuels come from the remains of living organisms that became extinct millions or billions of years ago, so they require a long process to produce energy. Therefore, efforts are needed to overcome the energy crisis that will occur in the future [5].

Transportation fuels are generally divided into two types, namely gasoline and diesel, depending on the type of engine. The types of vehicles in Indonesia vary, depending on the fuel used. Of the total number of vehicles, 1.965 million vehicles are buses and commercial vehicles. However, most buses and commercial vehicles use diesel fuel because they use diesel engines [6]. The growth of trucks and buses is expected to continue, increasing demand for diesel fuel. Apart from that, diesel engines are not only used in vehicles but also in industry and power plants [7]. To anticipate a surge in demand for diesel fuel, exploring renewable fuels is the right step, one of which is exploring biodiesel from vegetable materials.

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Biodiesel is a renewable fuel that can be obtained through a transesterification reaction between mono alkyl esters and alcohol [8].The biodiesel production process can use a base or acid catalyst to reduce the activation energy [9]. Without using a catalyst, biodiesel synthesis will take quite a long time [10]. The biodiesel production process can be carried out through in-situ processes, namely esterification and transesterification [11]. The purpose of esterification is to reduce the high levels of free fatty acids in oil. Transesterification aims to convert triglycerides resulting from the esterification process into methyl ester and glycerol [12]. One of the raw materials that can be used as biodiesel is oil from kesambi (*Schleichera oleosa*) seed oil [13]. Kesambi (*Schleichera oleosa*) seed oil can be converted into biodiesel through a transesterification process [14].

Previous research on the synthesis of biodiesel from kesambi seed oil using a ZnO-CuO catalyst supported by γ-Al_2O_3 has been carried out. The research method was carried out by deposition and impregnation based on the stöber gel method. The research results showed that the addition of the ZCA catalyst during the transesterification process affected the resulting yield. The highest yield was obtained in the three hour transesterification process, namely 80% [13]. Other biodiesel synthesis research has also been carried out by varying the use of alcohol in making biodiesel. The raw material used is sunflower seed oil. The research results show that the use of ethanol is bio-based and can affect the density and viscosity values of the biodiesel produce. This is because ethanol has lower toxicity compared to other alcohols such as methanol [15]. The research results show that the ratio of methanol to ethanol affects the yield and product, and can replace ordinary alcohol or methanol in the biodiesel synthesis process. Ethanol can affect the characteristics of the biodiesel produced, so further research is needed regarding the synthesis of biodiesel from kesambi oil [16].

This research aims to determine the physicochemical characteristics of kesambi biodiesel. Physicochemical characteristics include free fatty acid value, yield, flash point, heating value and density and viscosity of the biodiesel produced. The research was carried out by varying the composition of the mole ratio between raw materials and ethanol during the transesterification process. This is because much research has been carried out regarding the use of catalysts for biodiesel synthesis. Therefore, further research is needed regarding the effect of the mole ratio on the transesterification process of biodiesel synthesis from kesambi oil.

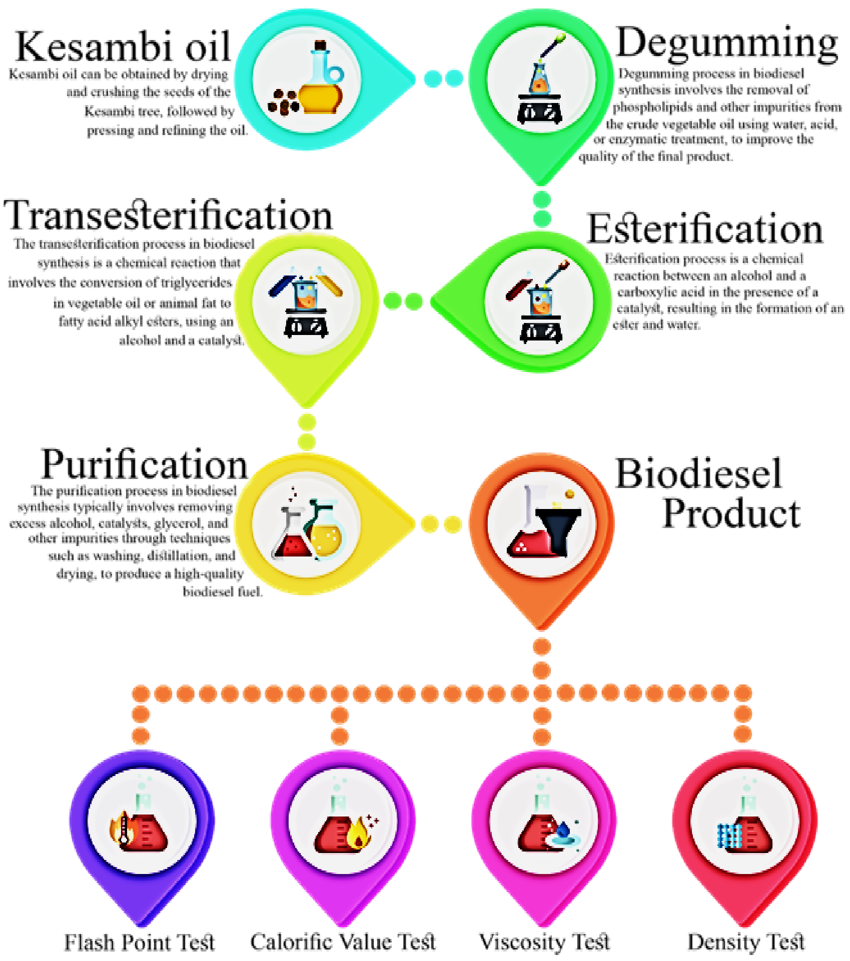

Fig. 1 *Research scheme*

2. Material and Method

The synthesis method of kesambi oil biodiesel as a renewable energy source was conducted through an experimental approach by analyzing the results of the kesambi biodiesel product. The treatment during the testing was carried out by varying the molar ratio at 4:1; 6:1; 8:1; 10:1; and 12:1. The testing results include yield data, calorific value, density, viscosity, and flash point. The stages of biodiesel synthesis begin with degumming, esterification, transesterification and purification. The scheme and explanation of the synthesis stages are shown in Figure 1 below, while the specifications of the materials used can be seen in Table 1 and the Indonesian National Standard (SNI) for biodiesel 7182: 2015 can be seen in Table 2. Images of samples of kesambi seeds and oil can be seen in Figure 2.

Table 1 *H_2SO_4, H_3PO_4, ethanol specifications*

H_2SO_4 specifications	
Specification	Information
Product name	Sulfuric acid
Formula	H_2SO_4
Molecular weight	98.08 g/mol
Physical condition	Clear, liquid
Color	Colorless
pH	1.2 at 5 g/l
Initial boiling point/boiling range	290°C - light up
H_3PO_4 specifications	
Specification	Information
Product name	Phosphoric acid
Formula	H_3PO_4
Molecular weight	98.00 g/mol
Physical condition	Clear, liquid
Color	Colorless
Density	1,685 g/mL at 25 °C - light up
Initial boiling point/boiling range	158°C - light up
Ethanol specifications	
Specification	Information
Product name	Ethanol
Formula	C_2H_6O
Molecular weight	46.07 g/mol
Physical condition	Liquid
Color	Colorless
Density	0.789 g/mL at 25 °C
Flash point	13 °C - closed cup
Autoignition temperature	363 °C

Table 2 *Indonesian national standard (SNI) for biodiesel 7182: 2015*

Specification	Units	Regulations
Density at 40 °C	gr/ml	0.850-0.890
Kinematic viscosity at 40 °C	CST	2.3 - 6
Flash point	°C	100

Calorific value	cal/gr	-

(a) **(b)**

Fig. 2 *(a) Kesambi seeds; (b) Kesambi oil*

2.1 Degumming

The degumming process is carried out to remove or separate the remaining gum or sap in kesambi oil. The gum in the oil could be phosphatide, protein, carbohydrate, residue, water, and resin. The degumming process is carried out by adding an H_3PO_4 solution to kesambi oil at 1% (mass). The H_3PO_4 solution and kesambi oil are stirred using a magnetic stirrer at a temperature of 60°C. The results of the degumming process are settled for 8 hours to separate the oil and gum.

2.2 Esterification

The esterification process aims to reduce free fatty acids. The esterification process is carried out by adding an acid solution, namely H_2SO_4, at 3% of the oil's mass. The amount of ethanol and oil is 21:1 with a mole ratio. The temperature used during the esterification process is 60°C. kesambi oil, H_2SO_4, and ethanol are mixed in a measuring glass and stirred for 90 minutes. The results of the esterification process are allowed to settle for 8 hours to precipitate. The precipitate results in two layers between oil and ethanol. The results of esterification are measured for their free fatty acid value. If it is less than 2%, the biodiesel production process could be continued to the transesterification stage. However, if the free fatty acid in kesambi oil is more than 2%, the esterification process is repeated twice with the same treatment.

2.3 Transesterification

The transesterification process is carried out to convert methyl ester into ethyl. The transesterification process is carried out by adding ethanol and a catalyst to the esterified oil. The catalyst used during the transesterification process is a basic catalyst with a 1% NaOH type of total oil mass. The amount of ethanol and oil during the transesterification process is 4:1; 6:1; 8:1; 10:1; and 12:1 using the mole ratio. Then, the temperature used during the transesterification process is 55°C and stirred using a magnetic stirrer for 120 minutes.

2.4 Purification

The purification process in biodiesel synthesis typically involves removing excess alcohol, catalysts, glycerol, and other impurities through techniques such as washing, distillation, and drying, to produce a high-quality biodiesel fuel. The washing process is carried out using distilled water with a 1:1 ratio between biodiesel and distilled water. The washing is repeated four times until the biodiesel is clear. After the biodiesel product is produced, the research continued to calculate the yield produced, then continued with calculating the density, viscosity, calorific value, and flash point. These parameters correspond to the research variation method, namely the mole ratio between ethanol and kesambi oil. Yield is the bioactive value of the extract of raw materials that are compared between the weight of the extract and the weight of the sample. The higher the yield produced, the more interested substances in the extracted content. To obtain the yield value, the following equation could be used (1).

$$\text{Yield} = \frac{\text{Biodiesel sample weight}}{\text{Raw material sample weight}} \tag{1}$$

2.5 Density

Density is the fluid density per unit volume. Density could be obtained by dividing the total mass of the fluid by the total volume of the fluid. The testing of the density of kesambi biodiesel is carried out using a hydrometer. The testing is done by pouring kesambi biodiesel into a measuring glass with a capacity of 100 ml. After the biodiesel is in the measuring glass, the hydrometer is inserted. There are two hydrometers used to measure the density of biodiesel. This is done because each hydrometer series has a different scale. The respective hydrometer series are 315H and 316H. Hydrometer specifications can be seen in Table 3 and 4. During the process of measuring the density, precision is necessary to ensure that the resulting value is under the sample density. The value of the density could be seen on the scale of the hydrometer. The value on the scale represents the relative density of the biodiesel sample.

Table 3 *Hydrometer 315H specifications*

Specification	Information
Amplitude range (kg/m^3)	800-850
Division (kg/m^3)	0.5
Length (mm)	330
Tolerancy accuray	± 0.5
Temperature range	0-85^{0}C

Table 4 *Hydrometer 316H specifications*

Specification	Information
Amplitude range (kg/m^3)	850-900
Division (kg/m^3)	0.5
Length (mm)	330
Tolerancy accuray	± 0.5
Temperature range	0-85^{0}C

2.6 Viscosity

Viscosity testing is used to measure the viscosity of kesambi biodiesel products. The viscosity testing equipment uses a Herzog Saybolt model ABR NL 90212 tester. The testing equipment uses a power of 5,000 watts. Before testing, water is prepared and poured into the heating tube at a temperature of 40°C. Water is used as a heating medium around the tube containing the sample to be tested. The testing is carried out by pouring biodiesel into the measuring tube. After the equipment is ready for use, the tube cap is opened and a ball is inserted into the sample. When the ball reaches the bottom of the tube, the time is calculated using a stopwatch. After completion, the time taken for the ball to reach the bottom is recorded. To obtain the viscosity value, equation (2) is used.

$$V = 0.0026 - \frac{1.175}{time\ (s)} \tag{2}$$

2.7 Calorific Value

Calorific value is a measure of the heat energy generated and contained in a fuel. The calorific value determines the quality of fuel when used. During testing, calorific value is measured using a bomb calorimeter system. The brand of the bomb calorimeter system used is PAAR, with model number PAAR 1241 EF. The voltage of the bomb calorimeter system used is 220 volts. The testing process begins by calibrating the equipment with benzoic acid before use. The working system of the bomb calorimeter is by burning the fuel adiabatically. Adiabatic combustion is carried out using an insulator. When the fuel is tested and the temperature rises, this temperature is used to calculate the calorific value of the tested fuel.

2.8 Flash Point

The flash point is the lowest temperature at which a fuel will ignite with the aid of an ignition source. If the flash point value is lower, then the substance is more easily combustible. The flash point testing of kesambi biodiesel is carried out using the Leybold brand of equipment, with a voltage of 220 volts and a power of 420 watts. The testing is done by pouring approximately 70 ml of kesambi biodiesel into a cup. The cup is inserted into the flash point tester and covered with the flash point cup cover. Next, the flash point stirrer is connected to the flash point cup cover, and a 3 mm flame is ignited. The power switch of the testing equipment is then turned on. At each one-degree Celsius increase, the ignition opener is turned to try to flash the biodiesel. The temperature is recorded when a small explosion occurs from the reaction of the flame with the fuel vapor.

3. Result and Discussion

Biodiesel synthesis is carried out in several stages so that the biodiesel product could meet the established SNI 7182:2015 standards. The stages of biodiesel production include degumming, esterification, transesterification, and washing. The results of the test are shown in Table 5 below. If viewed from the SNI 7182:2015 standard, the density, viscosity, heating value and flash point values meet the standards. The standard value of SNI 7182:2015 can be observed in Table 5. The formation of methyl ester occurs in the transesterification process involving free fatty acids with short-chain alcohols and acyl glycerides. The production process of kesambi oil into biodiesel is discussed in the following sub-section. After the degumming process, the total Free Fatty Acid (FFA) content in all samples was 23.2%. However, following the first esterification process, the FFA content decreased to a range of 11.9-13.1%. During this process, FFAs react with an alcohol in the presence of an acid catalyst, leading to the removal of water and the formation of an ester. Subsequently, a second esterification process was conducted, resulting in a similar reaction that further reduced the FFA content to 0.8-1.8%. Following this, through a transesterification process, the triglycerides within the ester and alcohol in the presence of a catalyst, were converted into FAME (Fatty Acid Methyl Ester or Biodiesel) and glycerol. Subsequent purification processes were carried out to remove residual glycerol and catalyst remnants from the product. Resulting in a biodiesel yield ranging from 77.6% to 91.3%.

Table 5 *Density, viscosity, calorific value, and flash point test results on biodiesel samples*

Mole Ratio (masss/mass)	Density gr/ml	Viscosity CST	Calorific Value cal/gr	Flash Point ºC
4:1	0.88	5.67	8,474	134.2
6:1	0.865	4.84	8,534	128.6
8:1	0.857	4.46	8,758	119.4
10:1	0.848	4.12	8,867	112.3
12:1	0.839	3.98	9,040	109.4

3.1 Degumming Analysis

The degumming process is a process for removing sap from the sample. kesambi oil during the degumming process amounted to 500 grams. The degumming process is carried out by adding phosphoric acid (H_3PO_4) to 1% of the total oil mass. kesambi oil and phosphoric acid that have been mixed are stirred using a magnetic stirrer for 45 minutes. The stirring process is added with a heat treatment using a temperature of 60°C. The results of the degumming process could be seen in Table 6 below.

Table 6 *Results of the degumming process*

Batch	Initial mass of kesambi oil (gram)	Final mass of kesambi oil (gram)	Yield (%)
1	500	429	85.8
2	500	431	86.2
3	500	434.5	86.9
4	500	431.5	86.3
5	500	423.5	84.7
	Average	429.9	85.98

The degumming process is carried out using five batches. The yield produced is calculated for each batch. The test results show that the yield value is not significantly different, shown in Figure 3. The highest yield value is 86.9% and the lowest is 84.7%. The average yield value is 85.98%. The quality of the biodiesel production results is also determined by the purity of the material. If the material still contains too much sap or gum, the resulting biodiesel yield will not be optimal [10]. This will affect the characteristics of biodiesel. In addition to sap or gum, free fatty acids also affect the quality of biodiesel. The higher the free fatty acid content, the more the biodiesel synthesis process must reduce free fatty acids by the esterification method. kesambi oil used in this study has a free fatty acid content of 23.2%, which is still far from the maximum limit of 2% for the biodiesel synthesis process.

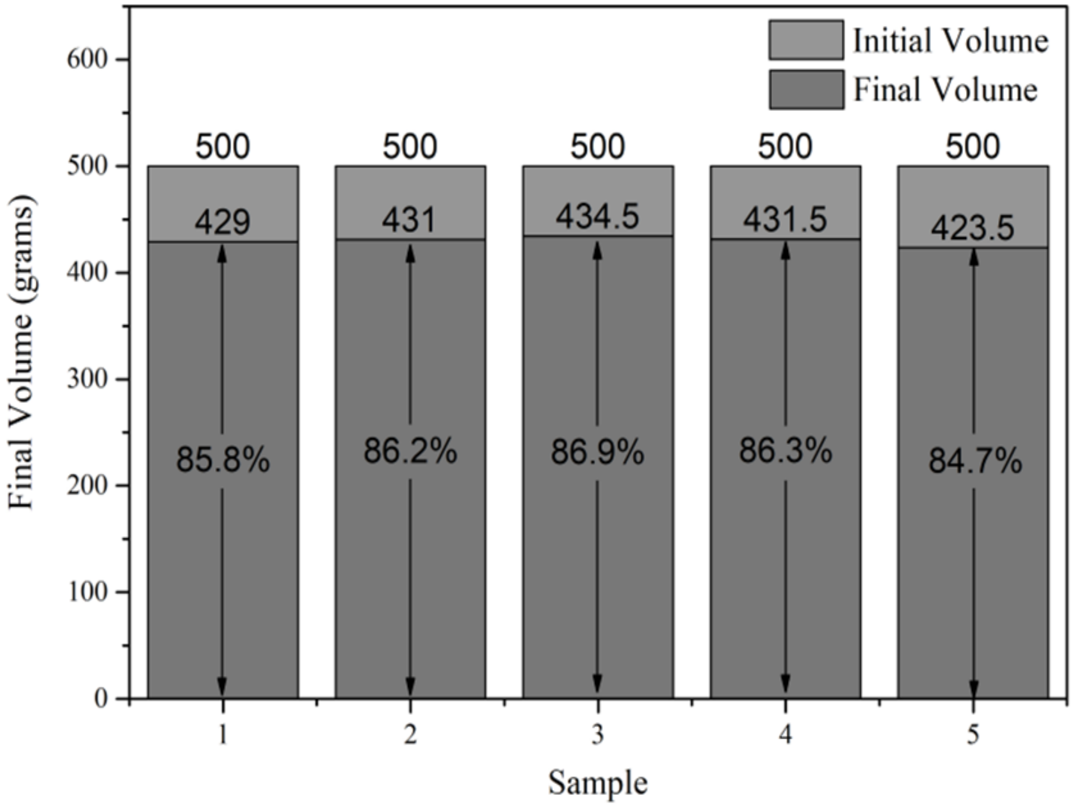

Fig. 3 *The yield results of the degumming process*

3.2 Esterification Analysis

The purpose of the esterification process is to reduce the free fatty acid content in kesambi oil. In this process, free fatty acids are converted into FAME (fatty acid methyl ester) through a methanolysis reaction, which requires a catalyst to accelerate the reaction process [17]. The free fatty acid content in kesambi oil in this study was found to be 23.2%, which renders it unsuitable for direct processing into biodiesel as it will result in the production of soap. Therefore, it is necessary to reduce the free fatty acid content through esterification. The esterification process was conducted according to the research method outlined in the study. A single esterification process couldnot reduce the free fatty acid content below 2%; hence, two esterification processes are necessary. The results of the esterification process are presented in Table 7.

Table 7 *Results of the esterification process*

Batch	FFA content before esterification (%)	FFA content in the first esterification (%)	FFA content in the second esterification (%)
1	23.2	12.2	1.1
2	23.2	12.5	1.3
3	23.2	13.1	1.7
4	23.2	12.8	1.8
5	23.2	11.9	0.8

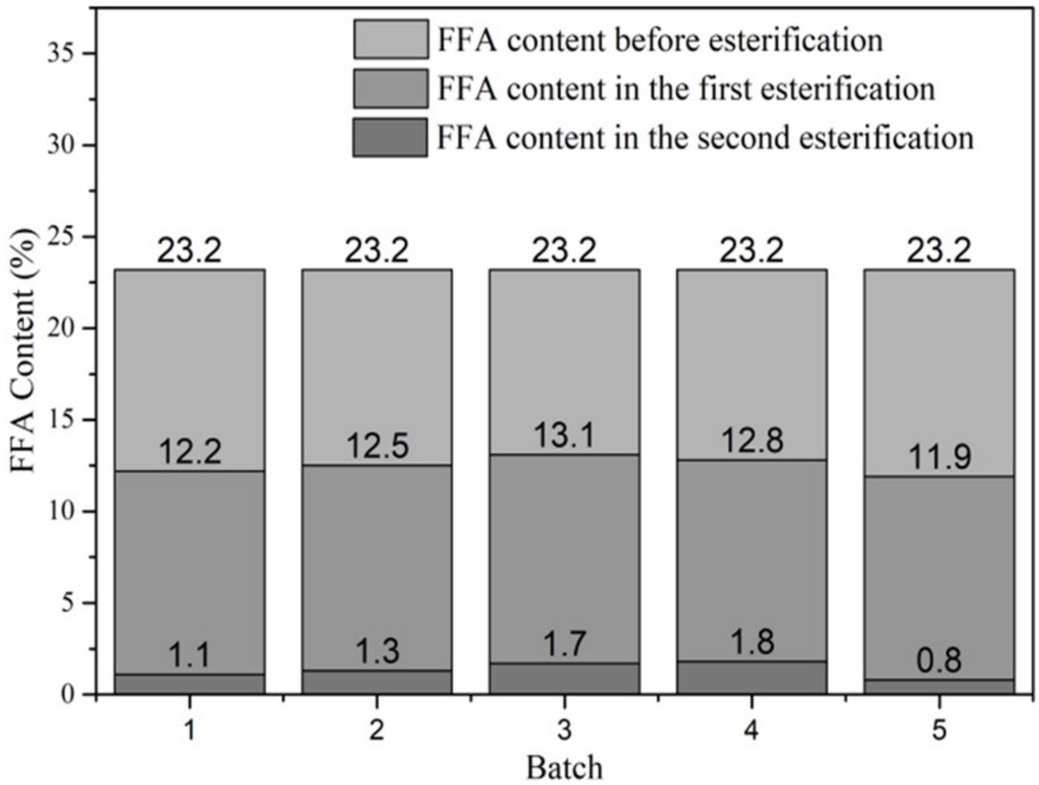

Fig. 4 *Results FFA content of the esterification process*

The esterification process was conducted using five batches, shown in Figure 4. In the first stage of the process, the highest free fatty acid content was 13.1%, while the lowest was 11.9%. The second stage of the esterification process resulted in the highest free fatty acid content of 1.8% and the lowest of 0.8%. There was no reduction in the free fatty acid content to below 2% in the first stage for each batch. The average decrease in free fatty acid content from the first to the fifth batch was 12.5% in the first stage and 1.34% in the second stage. The decrease in free fatty acid content in kesambi oil could be attributed to the role of ethanol and H_2SO_4 as catalysts. H_2SO_4 catalyst acts as a protonation reagent of the carbonyl oxygen of free fatty acid in triglycerides, while ethanol acts as a positive carbon binder, leading to the elimination and the formation of ethyl acetate and water [18]. The esterification equilibrium reaction could be observed in Figure 5.

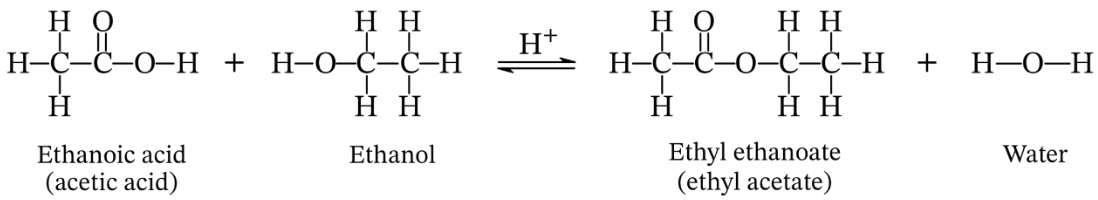

Fig. 5 *Equilibrium reaction of esterification into ester*

3.3 Transesterification Analysis

Figure 6 shows the results of the transesterification process in terms of biodiesel yield data. The transesterification testing was conducted by comparing the effect of the mole ratio between ethanol and kesambi oil produced from esterification. The mole ratio of 4:1; 6:1; 8:1; 10:1, and 12:1 varied during the transesterification process.

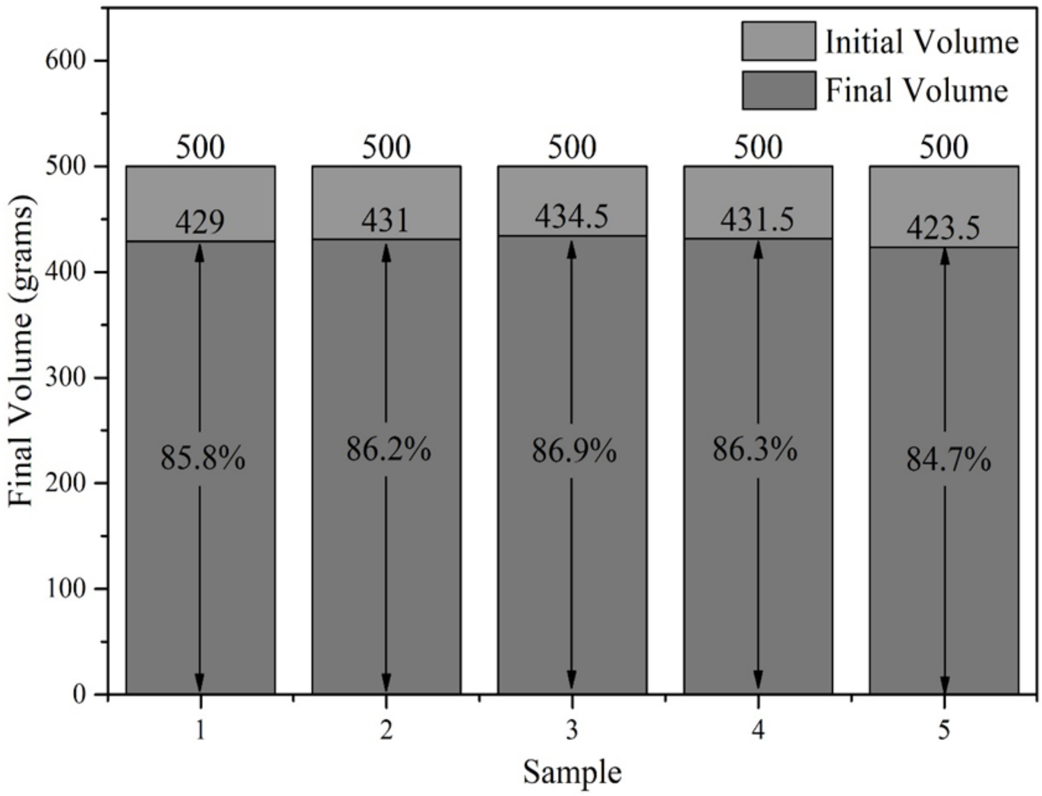

Fig. 6 *Biodiesel yield with mole ratio of the transesterification process*

The highest yield value was found at a mole ratio of 12:1, which was 91.30%, while the lowest yield value was 77.60% at a mole ratio of 4:1. Although the difference in yield value is not significant, there are differences in yield values for each mole ratio used. A mole ratio of 12:1 resulted in a higher yield value than other mole ratios. From the data obtained, it could be observed that the higher the mole ratio, the greater the biodiesel yield value. This is because there is more ethanol in the reaction mixture, resulting in more residuum being bound. The more residuum is bound, the higher the yield value of methyl esters in the biodiesel. However, not all NaOH residuum could be transformed into methyl esters during the transesterification process, which results in the formation of soap. Soap formation during the transesterification process reduces the yield value of biodiesel synthesized [19].

In Figure 6, upon closer examination, the difference in yield values is not very significant, although this study shows that a greater amount of ethanol produces a higher yield. In biodiesel synthesis, the amount of catalyst used during the transesterification reaction process should also be considered. The amount of catalyst determines the yield value produced. This is because the catalyst plays a role in lowering the activation energy during the reaction process between kesambi oil and ethanol. The reaction between kesambi oil and ethanol causes a transfer of molecular mass between different phases. The amount of catalyst was previously studied [13]. Biodiesel synthesis research was carried out using zinc oxide and alumina catalysts. The research results showed that using a catalyst of 1% of the total mass of oil produced a yield value of 70.12%. In the second test, the amount of catalyst was increased to 2% of the total mass of oil, resulting in a yield value of 81.40%, and then further increased to 3%, producing a yield value of 90.12%. This indicates that, in addition to the mole ratio, the amount of catalyst also plays a role in determining the yield value. The transesterification reaction could be observed in Figure 7.

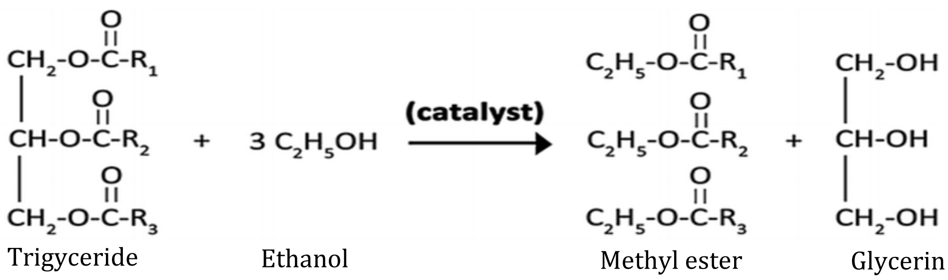

Fig. 7 *Transesterification reaction*

In addition to the yield value, testing was also conducted by measuring the density, viscosity, calorific value, and flash point values for each biodiesel product. The samples used for testing the density, viscosity, calorific value, and flash point were samples with a mole ratio during the transesterification process.

3.4 Density Analysis

In Figure 8, the relationship between density values and mole ratio could be observed. The characteristics of a fuel could be assessed, in part, by its density value. The density value of a fuel could affect the combustion reaction process inside the combustion chamber [20]. It was due to the fuel distribution process towards the combustion chamber using an injection system. When the density value is high, the fuel will be more difficult to distribute into the combustion chamber. Furthermore, high-density values will affect the fuel spray structure, resulting in suboptimal combustion and affecting engine performance and exhaust gas emissions. Density could be defined as the ratio of mass to volume at the same temperature.

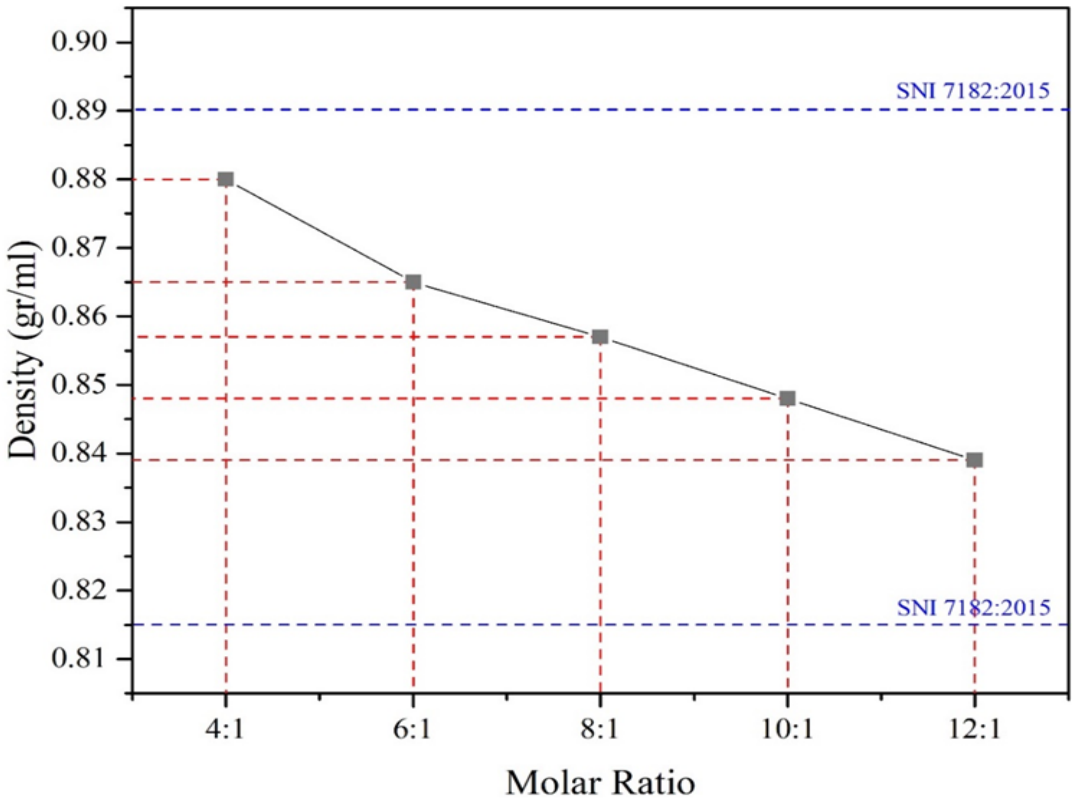

Fig. 8 *Relationship between density and mole ratio*

The average density value in the mole variation during the transesterification process is 0.858 g/mL, with the highest value of 0.880 g/mL and the lowest value of 0.839 g/mL. In Figure 8, the mole variation is observed to affect the density value of biodiesel synthesis. However, the difference in density values in each mole variation is not significant. In the transesterification stage, the mole variation shows varying density values. From Figure 8, it could be observed that the higher the mole ratio, the lower the density value. However, among all the mole ratios, the density value still meets the standard of SNI 7182:2015, which is set at 0.815 (g/ml) to 0.890 (g/ml).

In Figure 8, it is observed that the phenomenon of increasing the mole ratio between ethanol and kesambi oil produces lower density values. This is because the glycerol content decreases with a higher amount of ethanol. Glycerol and impurities will bind more with ethanol during the mixing process. This is what affects the density value of the biodiesel product. In addition, a larger volume of ethanol will bind more glycerol, resulting in lower polarity and mass in biodiesel. This research is also consistent with Jaya et al.'s (2022) research. The research was conducted by producing biodiesel from used cooking oil using a heterogeneous catalyst. The results of the research on the mole ratio of 1:12; 1:16; 1:20; 1:24, and 1:28 respectively produced density values of 0.8695; 0.8679; 0.8625; 0.8662, and 0.8537 g/ml. If the density values are observed, they decrease with an increasing mole ratio, although the decrease is not significant [21].

3.5 Viscosity Analysis

Viscosity is the value of the viscosity of fuel fluids. If the viscosity value is high, the fuel fluid rate will be lower. A low fuel fluid rate will affect the engine's performance. Currently, many vehicle engines use an injection system to distribute fuel into the combustion chamber. Therefore, the viscosity value must meet the established standards for optimal engine performance and perfect combustion. If the viscosity value is high, the injector will clog, and fuel distribution will be slow. If we look at the use of kesambi oil as fuel, then kesambi oil cannot be used directly in engines. This is because the viscosity of kesambi oil is very high, making it difficult to atomize. Therefore, a transesterification process is needed to reduce the viscosity of kesambi oil. The transesterification process is carried out using a catalyst and alcohol. However, the right composition is needed to produce optimal viscosity. One effort that can be done is to carry out research by varying the moles between alcohol (ethanol) and oil. The results of research on the viscosity of biodiesel from kesambi oil can be seen in Figure 9.

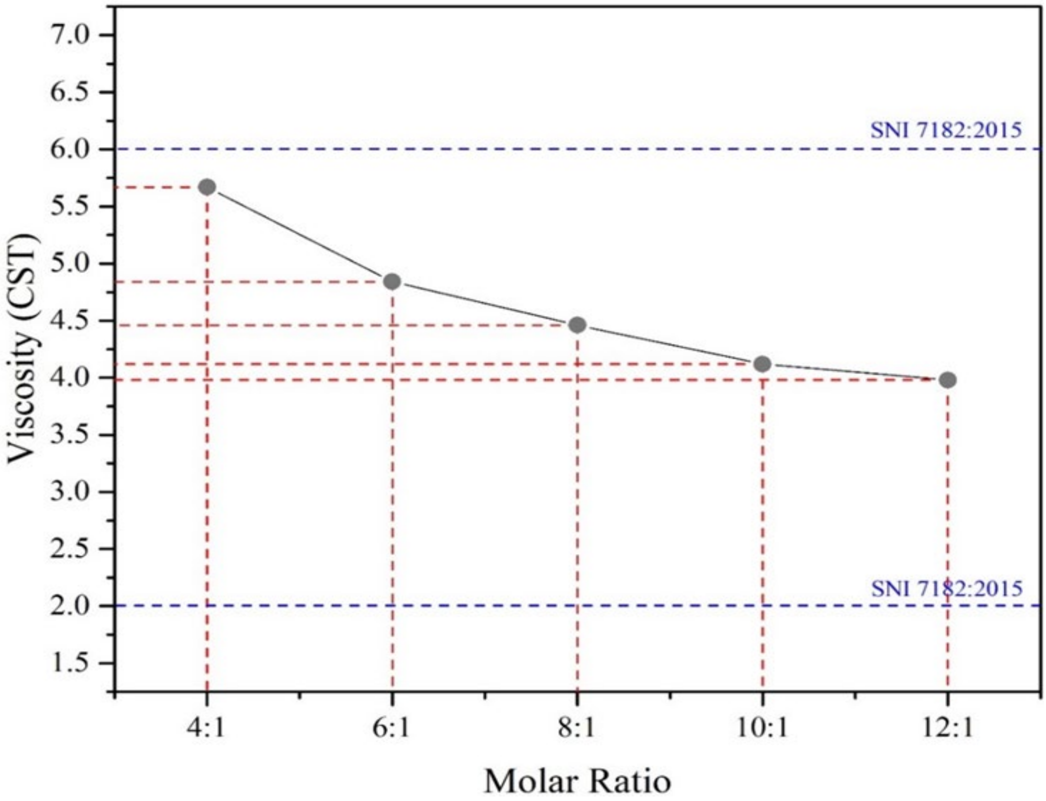

Fig. 9 *Relationship between viscosity and mole ratio*

The relationship between the molar ratio and the viscosity value of kesambi oil biodiesel can be seen in Figure 9. The viscosity values for the molar ratios of 4:1; 6:1; 8:1; 10:1, and 12:1 are 5.64, 4.84, 4.46, 4.12, and 3.98 CST, respectively. Viscosity values with varying molar ratios show mixed results. This can be observed in Figure 9, the higher the mole ratio between ethanol and oil, the lower the viscosity value. The viscosity value which decreases with increasing mole ratio during the transesterification process is caused by the free fatty acid content in kesambi oil. Free fatty acids with higher ratios bind more to ethanol. This causes the free fatty acids to turn into soap so that more residue is produced. Free fatty acid levels continue to decrease resulting in the molecular structure becoming looser. This results in lower viscosity values as the mole ratio between ethanol and oil increases during the transesterification process.

If viewed from the role of ethanol. Ethanol is a compound that can react with triglycerides in oil during the transesterification process. Ethanol and catalyst react with oil to produce ethyl ester. Ethyl ester is the main component of biodiesel. In this research, it appears that the mole ratio between ethanol and kesambi oil produces different viscosity values. Ethanol has a role as a solvent during the transesterification process, this causes the intermolecular forces to be lower. Lower intermolecular forces cause the viscosity of biodiesel to be lower. Low viscus causes the viscosity value to decrease as the ethanol mole ratio increases [22].

3.6 Calorific Value Analysis

The calorific value is the amount of heat energy contained in a fuel. In the study of kesambi oil biodiesel synthesis, the calorific value of each product produced was observed for each molar ratio during the transesterification process. The results of the study could be seen in Figure 10.

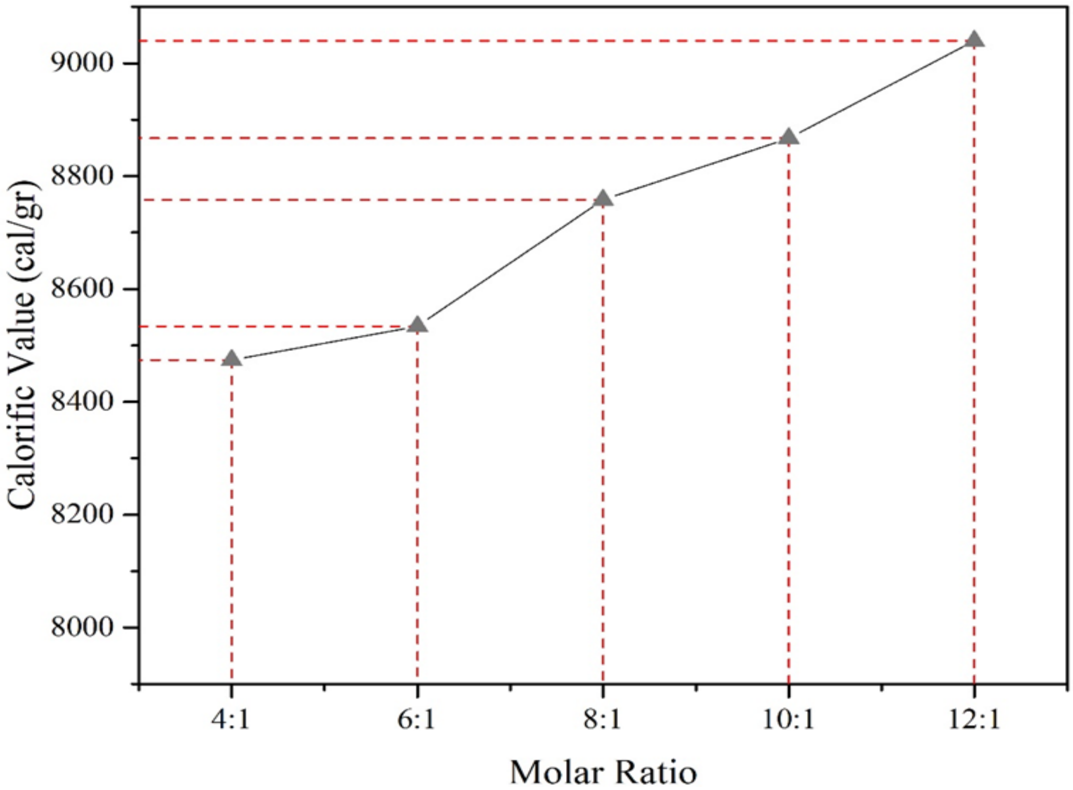

Fig. 10 *Relationship between calorific value and mole ratio*

The heating value of each molar ratio can be seen in Figure 10. The highest heating value was obtained at a 12:1 molar ratio of 9,040 cal/gr, while the lowest heating value was at a 4:1 ratio of 8,474 cal/gr. The average calorific value is 8,734 cal/gr. Figure 10 shows that there is a relationship between the molar ratio and the calorific value produced. However, there is no significant difference in heating value for each variation in molarity. This is shown by the difference in heating value for each molar variation used during the biodiesel transesterification process. However, the research results show that the molar ratio influences the calorific value of biodiesel. Calorific value is a parameter used to measure the heat or thermal energy produced by fuel per unit mass. Biodiesel contains saturated fatty acids and unsaturated fatty acids. Saturated fatty acids are single bonds between carbon atoms between carbon chains, while unsaturated fatty acids are double bonds between carbon atoms between carbon chains. During the transesterification process with a higher molar ratio it will cut the carbon chains in unsaturated fatty acids so that the composition will be dominated by saturated fatty acid chains. The more saturated fatty acid chain composition, the higher the calorific value contained in biodiesel.

Apart from that, density and viscosity values also need to be considered to analyze the heating value contained in biodiesel. The lowest calorific value in this study was located at a molar ratio of 4:1. If analyzed, this is caused by the viscosity and density values. Viscosity and density values are inversely proportional to heating value. The higher the viscosity and density values, the lower the calorific value of the biodiesel produced, as shown in Figure 12. Biodiesel has molecules arranged according to the composition contained therein. High viscosity and density values indicate that the molecular arrangement in biodiesel is tight. [23]. Molecules that are tightly packed together find it difficult to move and react during the combustion process. This causes the calorific value of biodiesel with a low molar ratio to be lower.

3.7 Flash Point Analysis

Flash Point is the lowest temperature value at which fuel ignites when exposed to an external flame source. The lower the flash point value of a fuel, the easier it is to burn. Flash point is an important parameter in determining the quality of biodiesel that has been produced. The flash point can affect the combustion reaction process in the combustion chamber. A good combustion process will produce optimal engine performance and produce lower exhaust emissions or pollutants. In research on kesambi biodiesel production, the flash point value can be seen in Figure 11.

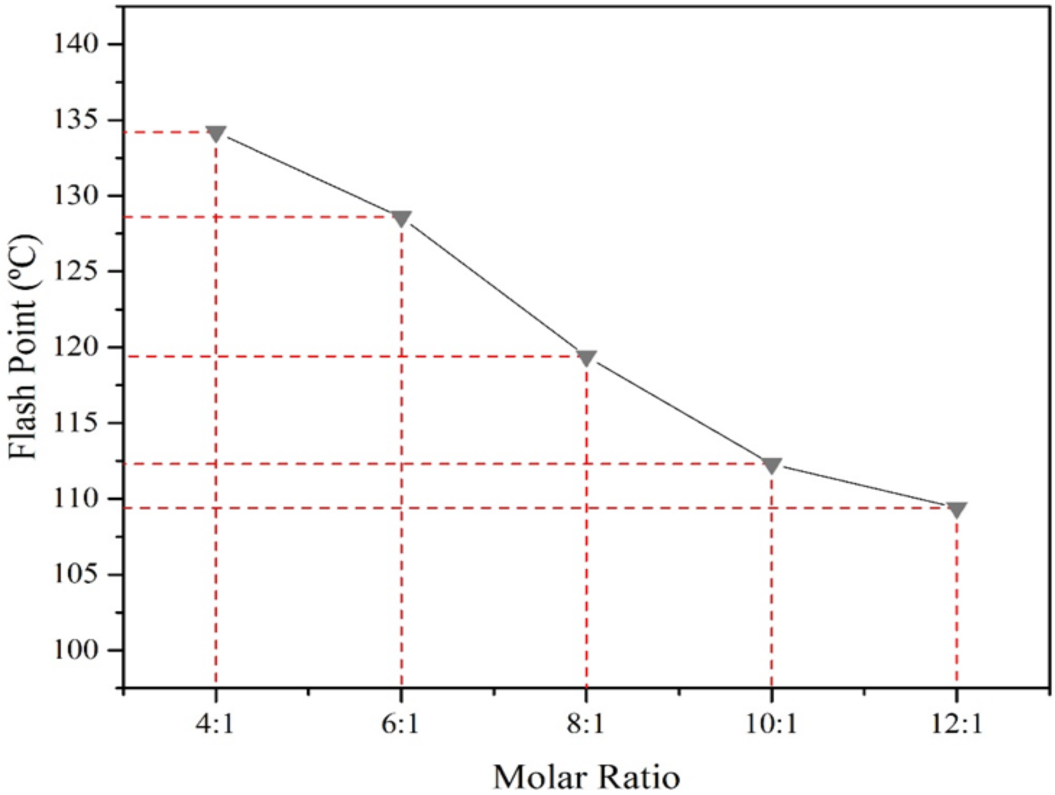

Fig. 11 *Relationship between flash point value and mole ratio*

Figure 11 shows the decrease in the flash point value as the molar ratio increases. The lowest flash point value was 109.4ºC with a molar ratio of 12:1, while the highest flash point value was 134.2ºC with a molar ratio of 4:1. In this case, the lowest flash point value is obtained by using a higher molar ratio. The flash point value is directly proportional to the density and viscosity values [17]. The greater the molar ratio in the transesterification process, the lower the resulting flash point value. In this research, it can be seen that variations in moles during the transesterification process produce varying flash point values. The flash point value increases with the higher the mole ratio between ethanol and kesambi oil. The flash point value increases because the amount of ester produced increases. The amount of ester produced is greater because there are more moles of ethanol in the transesterification process so that ester formation increases in the reaction process [24].

The transesterification process plays an important role in the biodiesel production process. This is because in the transesterification process the ester bonds in the oil are broken. The decomposition of esters in kesambi oil will change the ester groups into alkyl groups obtained from ethanol to form methyl esters and glycerol [25]. Apart from that, the decrease in flash point value is caused by the reduction in saturated fatty acids in biodiesel. The higher the ethanol molar ratio causes the reduction in saturated fatty acids. This reduction occurs due to molecular collisions between ethanol and saturated fatty acids. Saturated fatty acid molecules that collide with ethanol will bond to produce more fatty acid ethyl esters. Reducing fatty acid ethyl esters causes methyl esters to increase. Therefore, the flash point value becomes lower by using a higher mole ratio between ethanol and kesambi oil. The results of biodiesel synthesis research with variations in the number of moles between ethanol and kesambi oil produced parameters, such as density, viscosity, heating value and flash point which can be observed in Figure 12. In addition, the biodiesel synthesis from kesambi (*Schleichera oleosa*) oil from this research was compared with synthesis of biodiesel from other raw materials. The comparison results can be seen in Figure 13 and Table 8. Then the results of the transesterification process can be seen in Figure 14.

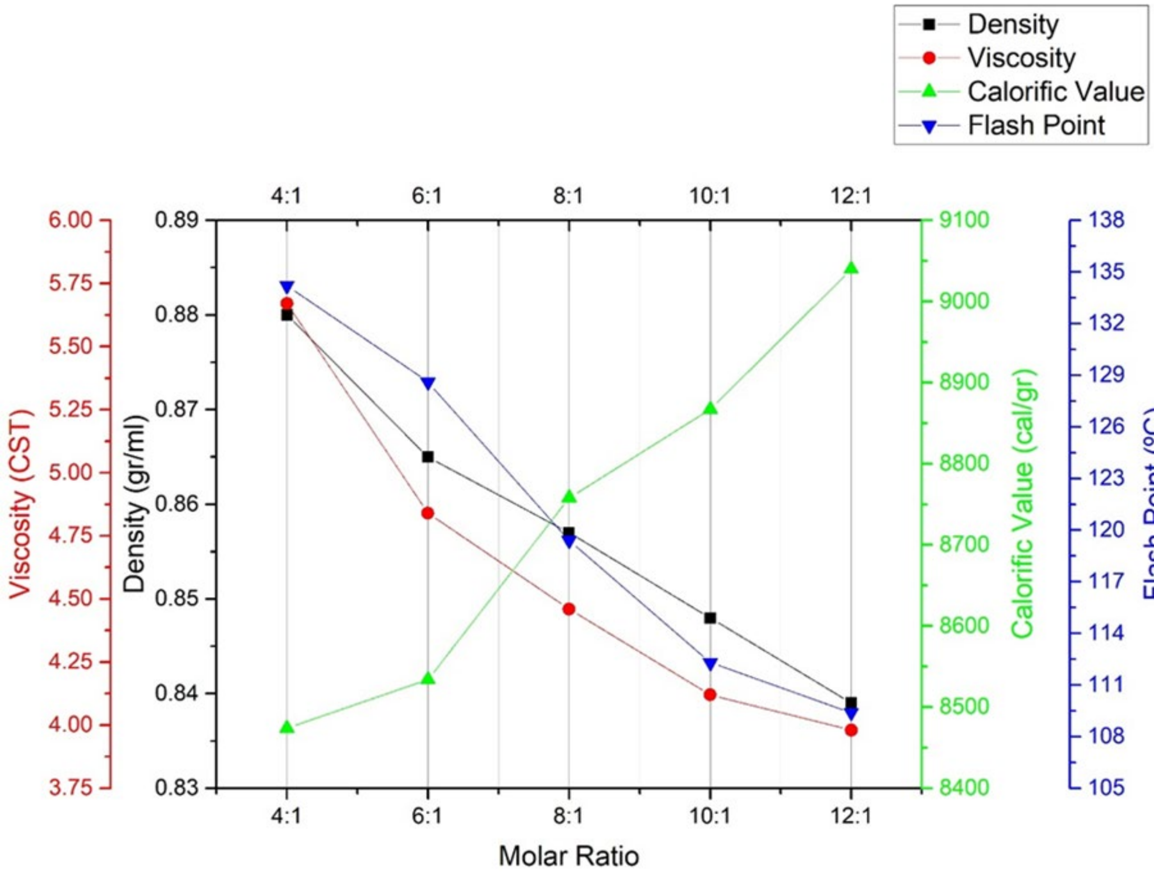

Fig. 12 *The comparation of density, viscosity, calorific value, and flash point test results on biodiesel samples*

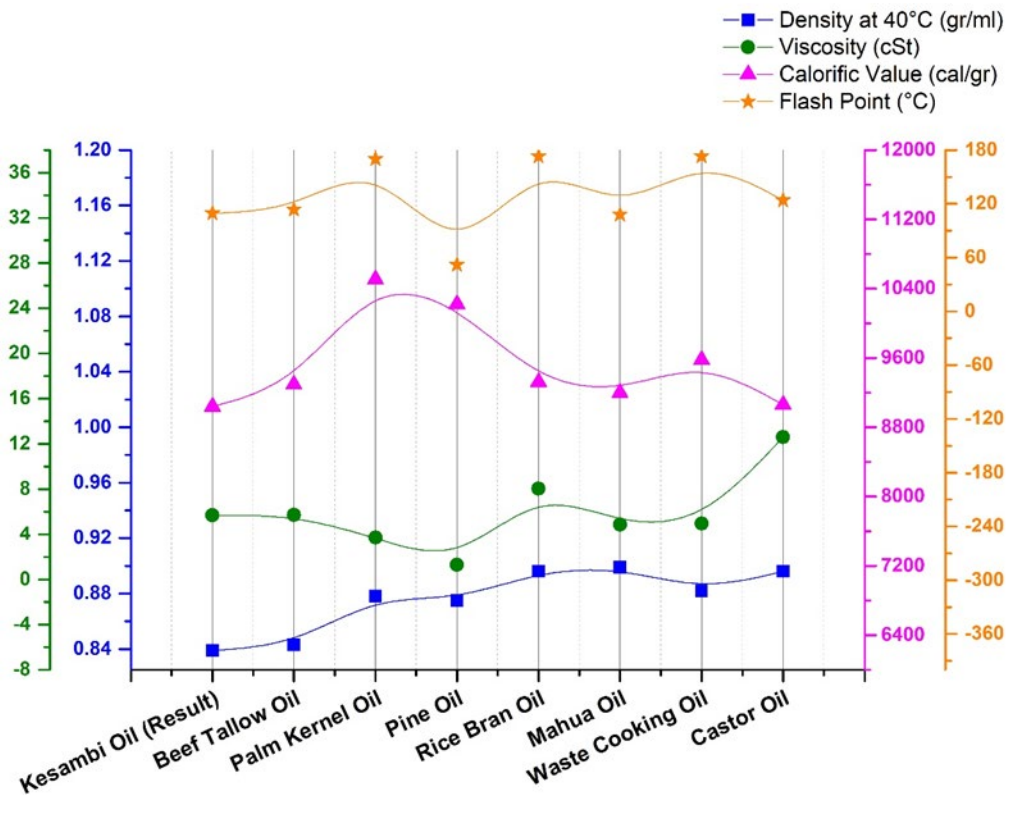

Fig. 13 *Comparison of kesambi biodiesel synthesis with biodiesel made from other raw materials*

Table 8 *Comparison of kesambi biodiesel synthesis with biodiesel made from other raw materials*

Raw material	Density at 40 °C (gr/ml)	Viscosity (CST)	Calorific Value (cal/gr)	Flash Point (°C)	Reff
Kesambi oil	0.839	3.98	8,474	109.4	result
Beef Tallow oil	0.843	5.7	9,296.9	113.5	[26]
Palm kernel oil	0.878	3.7	10,509	170	[27]
Pine Oil	0.875	1.3	10,222.6	52	[28]
Rice Bran Oil	0.896	8.05	9,322.1	173	[29]
Mahua oil	0.899	4.86	9,201	108	[30]
Waste Cooking oil	0.882	4.94	9,580.3	173	[31]
Castor Oil	0.896	12.59	9,059.6	124	[32]

4:1 **6:1** **8:1** **10:1** **12:1**

Fig. 14 *The results of the kesambi oil transesterification process*

4. Conclusions

The results of research regarding the influence of the molar ratio between ethanol and kesambi oil as a biodiesel product resulted in an average yield of 85.98% obtained from five samples of kesambi oil in the degumming process. The average reduction of free fatty acids was 12.5% in the first stage and 1.34% in the second stage during the esterification process. The highest yield of 91.30% was obtained with a molar ratio of 12:1, while the lowest yield of 77.60% was obtained with a molar ratio of 4:1. The highest density value of 0.880 gr/ml was obtained with a molar ratio of 4:1, while the lowest density value of 0.839 was obtained with a molar ratio of 12:1. The highest viscosity value of 5.67 CST was obtained with a molar ratio of 4:1, while the lowest viscosity value of 3.98 CST was obtained with a molar ratio of 12:1. The lowest calorific value of 8,474 cal/gr was obtained with a mole ratio of 4:1, while the highest calorific value of 9,040 cal/gr was obtained with a molar ratio of 12:1. The highest flash point value of 134.2ºC was obtained with a molar ratio of 4:1, while the lowest flash point value of 109.4ºC was obtained with a molar ratio of 12:1. The molar ratio influences the yield, density, viscosity, heating value, and flash point of kesambi oil biodiesel synthesis in this research.

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