PRODUCTION OF BIODIESEL FROM NYAMPLUNG OIL (*Calophyllum inophyllum*) USING IMMOBILIZED LIPASE ENZYME CATALYST WITH VARIATION OF TEMPERATURE AND NUMBER OF CYCLES IN A PACKED BED REACTOR

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Abstract: Biodiesel, Minyak Nyamplung, Enzim Lipase Amobil, Packed Bed Biodiesel is a type of fuel made from a mixture of mono-alkyl esters of long-chain fatty acids. It is used as an alternative to diesel fuel and is produced from renewable sources such as vegetable oil or animal fat. The biodiesel production process involves transesterification reactions between Nyamplung oil (*Calophyllum inophyllum*) and methanol using immobilized enzyme lipase as a catalyst with activated charcoal in a Packed Bed Reactor. This research aims to investigate the influence of variations in the molar ratio of Nyamplung oil and methanol (1:8 and 1:10) as well as the number of cycles (1-5) on biodiesel products. It also aims to identify the quality differences in biodiesel produced from these variations. The analyses conducted in this research include density analysis, viscosity analysis, iodine number analysis, saponification analysis, cetane number analysis, %Yield, and gas chromatography analysis. The best %Yield of biodiesel product obtained was 88.2%, achieved with a Nyamplung oil to methanol molar ratio of 1:10 in the first cycle, with a Methyl Ester yield of 97.12%.

Keywords: Biodiesel, Nyamplung Oil, Immobilized Lipase, Packed Bed Reactor.

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1 Introduction

The growth of the population and the continuous economic development are two factors leading to an increase in energy demand. Most of the energy currently used comes from resources such as petroleum, natural gas, and coal. The increasing energy consumption can deplete the stocks of these fossil fuels, which are non-renewable natural resources. In Indonesia, in particular, there has been significant importation of petroleum fuels, especially diesel. Therefore, it is necessary to explore alternative fuels, especially from renewable sources. One of the alternative options is biodiesel, which can replace the use of diesel [1].

Belonging to the *Clusiaceae* family, the Nyamplung plant (*Calophyllum Inophyllum*) can thrive in areas with annual rainfall ranging from 1000 to 5000 mm, at elevations from 0 to 200 meters above sea level. This plant holds great potential as a raw material for biodiesel production due to its high oil content in its seeds (between 40 to 73% (w/w)). With an oil production yield of up to 4,680 kg/ha, Nyamplung oil, which is classified as non-edible oil, is highly advantageous as it does not compete with food requirements. The extraction process of Nyamplung oil is carried out using press machines, with two types of press machines being applicable: manual hydraulic presses and extruder presses (screw system). The oil produced by the press machines has a dark color due to impurities from the skin and chemical compounds such as alkaloids, phosphatides, carotenoids, chlorophyll, and others [2].

Biodiesel is produced through a process called transesterification, where vegetable oil reacts with short-chain alcohols such as methanol or ethanol, producing glycerol as a byproduct. The alcohol in commercial biodiesel production is methanol. Lipase enzymes are acyl hydrolases that play a role in digesting and processing fats. Lipase has to break down various types of fats and oils. Each unit per mL of lipase activity can release 1µmol of free fatty acid in one minute. Lipase activity reaches its peak under optimal temperature and pH conditions, which can be measured by observing changes in enzymatic activity at various temperature and pH variations [2].

In Aznury et al.'s research in 2022 [3] , the best %yield obtained from Nyamplung oil as a raw material was 87.67%, with a molar ratio of oil to methanol at 1:5 and a constant temperature of 37°C. A Packed Bed Reactor was used for the transesterification process with Nyamplung oil mixed with methanol, and the catalyst used was NaOH [4] with a concentration of 0.5%. The best %yield achieved in this study was 40.91%, with a reaction temperature of 60°C. Based on this background, a research project was conducted titled "Production of Biodiesel from Nyamplung Oil (*Calophyllum inophyllum*) Using Immobilized Lipase Enzyme Catalyst in a Packed Bed Reactor." The Packed Bed Reactor was designed to react Nyamplung oil (*Calophyllum inophyllum*) and methanol with the assistance of an enzyme lipase catalyst previously activated with activated charcoal.

2. Material And Methods

The materials used in this research are Nyamplung oil, methanol, lipase enzyme, activated charcoal, and distilled water. The equipment used is a Packed Bed Reactor. 500 grams of Nyamplung oil is placed in the feed tank with a oil-methanol molar ratio of 1:8 and 1:10. Then, immobilized lipase enzyme prepared with activated charcoal is placed into the packed bed reactor column. The mixture of oil and methanol is heated at a constant temperature of 35°C and stirred at a speed of 650 rpm until the mixture becomes homogeneous. The mixture is then flowed into the column containing the lipase enzyme at a flow rate of 1 ml/s. From this reaction, 100 grams of biodiesel product is obtained and ready for analysis. The remaining product will undergo 5 cycles of recycling as a variation in this research.

The analysis conducted includes density analysis, viscosity analysis, iodine number analysis, saponification number analysis, cetane number analysis based on the Indonesian National Standard (SNI) 7182:2015[5] for biodiesel standards. The %Yield is determined by dividing the mass of the obtained product by the total mass of oil multiplied by 100%, following the research by Rachmadona et al., 2017 [6]. Lastly, to determine the methyl ester content in the product, Gas Chromatography Mass Spectrometry (GC-MS) analysis is performed.

3. Results And Discussions

The Influence of the Number of Cycles and the Ratio of Raw Materials of Nyamplung Oil and Methanol (1:8 and 1:10) on Biodiesel Density

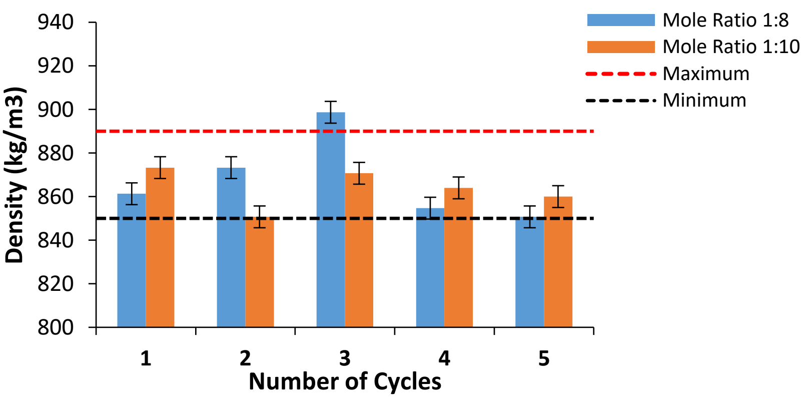

Fig. 1. Graph of the Influence of the Number of Cycles and the Ratio of Nyamplung Oil Raw Material to Methanol on the Density of Biodiesel

According to the Indonesian National Standard (SNI) 7182:2015 [5], the standard density range for biodiesel is between 850 - 890 kg/m3. In Figure 1, it can be observed that the obtained biodiesel densities range from 870-898. This means that only one sample does not meet the standard, which is the biodiesel sample with a 1:8 Nyamplung oil to methanol ratio in the third cycle. The biodiesel density exceeds the standard, it should not be used in diesel engines as it may increase engine fatigue [7].

The Influence of the Number of Cycles and the Ratio of Raw Materials of Nyamplung Oil and Methanol (1:8 and 1:10) on Biodiesel Viscosity

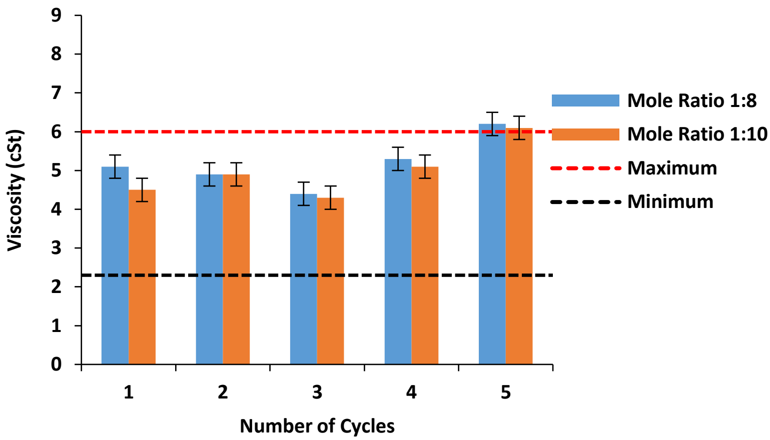

Fig. 2. Graph of the Influence of the Number of Cycles and the Ratio of Nyamplung Oil Raw Material to Methanol on the Viscosity of Biodiesel

Based on Figure 2, the viscosity of biodiesel ranges from 440 to 620 kg/m^3. The highest viscosity, exceeding the standard, is observed at a 1:8 ratio in the fifth cycle. This is because a smaller methanol ratio can reduce the triglyceride-breaking capability of methanol, leading to a decrease in biodiesel viscosity. This aligns with the findings of [4], where biodiesel viscosity with 65 ml of added methanol was higher compared to biodiesel with 95 ml of added methanol. However, in the current study, a 1:10 ratio in the fifth cycle also exhibits high viscosity. This is due to the prolonged reaction time, which increases the carbon bond activity in the oil, causing a decrease in the biodiesel boiling point during the methanolysis process and resulting in higher viscosity [4]. According to fuel atomization, the fuel can be injected too quickly.

The Influence of the Number of Cycles and the Ratio of Raw Materials of Nyamplung Oil and Methanol (1:8 and 1:10) on Biodiesel Saponification.

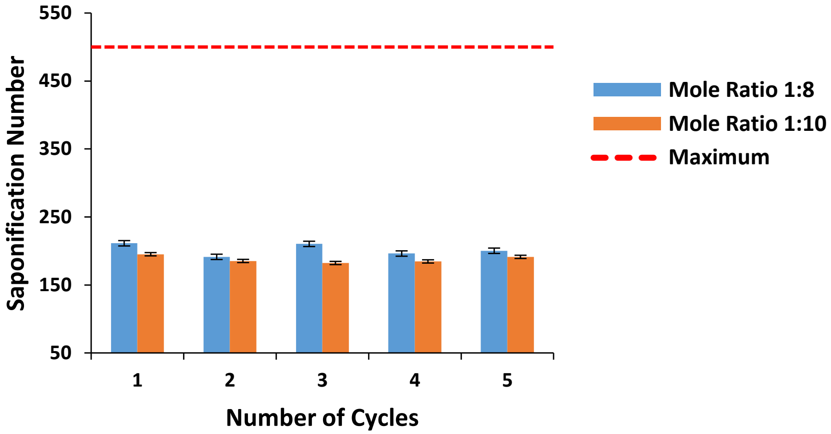

Fig. 3. Graph of the Influence of the Number of Cycles and the Ratio of Nyamplung Oil Raw Material to Methanol on the Saponification Number of Biodiesel

In Figure 3, it can be observed that the highest saponification number is found in the product with a 1:8 ratio in the fifth cycle, which is 200.3, and the lowest is 182.3, which corresponds to the product with a 1:10 ratio in the third cycle. In a previous study conducted by Kurniati, et. al. 2021[8] , biodiesel production using raw material from Nyamplung oil through transesterification with KOH catalyst yielded a saponification number of 172.09 mg KOH/g. This result indicates that the saponification value in biodiesel production meets the SNI 7182-2015[5] standard, which is 168.02 mg KOH/g.

The Influence of the Number of Cycles and the Ratio of Raw Materials of Nyamplung Oil and Methanol (1:8 and 1:10) on Biodiesel Iodine Number

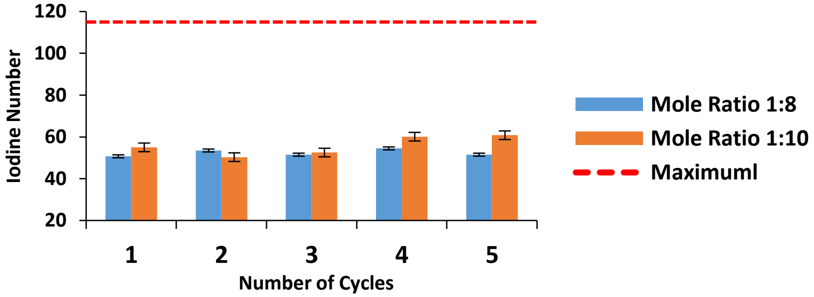

Fig. 4. Graph of the Influence of the Number of Cycles and the Ratio of Nyamplung Oil Raw Material to Methanol on the Iodine Number of Biodiesel

The highest iodine number can be seen in Figure 4 is found in the fifth cycle with a methanol-to-oil ratio of 1:8, while the lowest iodine number is found in the fifth cycle with a methanol-to-oil ratio of 1:8. In the iodine titration process, heating is performed on 100 ml of distilled water, which causes the bonds in the fatty acids that make up biodiesel to degrade due to the temperature, resulting in a low iodine number in biodiesel. Conversely, an increase in the iodine number occurs with the increasing concentration of catalyst because the fatty acid bonds are not completely degraded during the heating process, which causes the iodine number to rise [9].

The Influence of the Number of Cycles and the Ratio of Raw Materials of Nyamplung Oil and Methanol (1:8 and 1:10) on Biodiesel Cetane Number

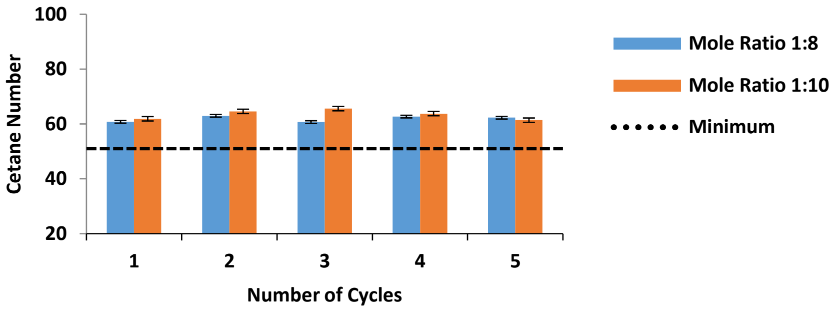

Fig. 5. Graph of the Influence of the Number of Cycles and the Ratio of Nyamplung Oil Raw Material to Methanol on the Cetane Number of Biodiesel

From Figure 5 above, it can be seen that the highest octane number is found at a methanol-to-oil ratio of 1:8 in the third cycle. The figure also indicates that the octane number characteristics of the biodiesel from the experiment meet the Quality Standard for biodiesel (SNI) and the diesel fuel from petroleum (SNI biodiesel), which is a minimum of 51. The octane number of biodiesel is related to the composition of fatty acids contained in the biodiesel; biodiesel containing saturated fatty acids with long carbon chains has a high octane number.

The Influence of the Number of Cycles and the Ratio of Raw Materials of Nyamplung Oil and Methanol (1:8 and 1:10) on Biodiesel %Yield

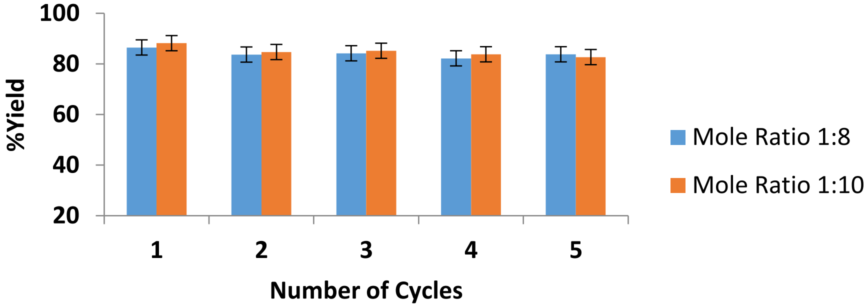

Fig. 6. Graph of the Influence of the Number of Cycles and the Ratio of Nyamplung Oil Raw Material to Methanol on the %yield of Biodiesel

In Figure 6, it can be seen that the highest %Yield is found at a raw material ratio of 1:10 in the first cycle, which is 88.2%, while the lowest %Yield is at a raw material ratio of 1:8 in the fourth cycle, which is 82.2%. This indicates that the decrease in catalyst activity is caused by the washing or blockage of active catalyst sites by the products formed during the transesterification process [10]. Furthermore, the influence of the oil and methanol ratio is that the larger the molar ratio of reactants, the higher the %yield of biodiesel produced. By using an excess of methanol, the reaction is shifted to the right (towards product formation) to achieve maximum conversion [3].

Result of Gas Chromatography GC-MS

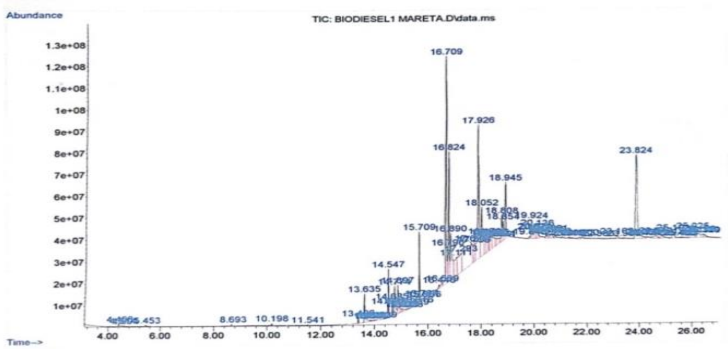

Fig 7. Result of Gas Chromatography GC-MS Analysis

Based on Figure 7, the results of biodiesel synthesis were qualitatively identified using Gas Chromatography to determine the composition of methyl esters in biodiesel and Free Fatty Acids (FFA). In the analysis, it was found that biodiesel consists of methyl esters. The obtained methyl ester content was 97.12%, which is in accordance with the Indonesian National Standard (SNI) of 96.50%. Gas Chromatography-Mass Spectrometry (GC-MS) analysis results showed that the product is indeed a biodiesel compound, namely methyl ester. The main composition found in the product can be seen in the table above, which includes Hexadecanoic Acid Methyl Ester, Pentadecanoic Acid Methyl Ester, and Hexadecanoic Acid, 15-Methyl Ester.

4. Conclusions

From the results of the conducted research, it can be concluded that the ratio of raw materials and the number of cycles affect several factors, including density, viscosity, saponification number, iodine number, cetane number, and %Yield. The %Yield of biodiesel produced increases with an increase in the ratio of raw materials but decreases with an increase in the number of cycles. The highest %Yield was obtained in the biodiesel product with a 1:10 raw material ratio in the first cycle, which amounted to 88.2%. Meanwhile, the lowest %Yield was achieved at 82.7% in the fifth cycle of biodiesel production with a 1:10 raw material ratio. The quality of biodiesel produced from variations in the raw material ratio (1:8 and 1:10) and the number of cycles (1 to 5) is not significantly different. The analysis results indicate that the biodiesel products obtained already meet the standards according to SNI 04-7182-2015 [5].

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