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Biodiesel production with DES (deep eutectic solvent) catalyst using used cooking oil feedstock through two-stage transesterification process

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Abstract

Most of biodiesel in Indonesia is still produced by costly processed utilizing pricey catalysts and high grade fatty acid methyl esther (FAME). Low cost catalysts need to be invented in order to make biodiesel more affordable, while raw material also need to be obtained from low cost alternatives. such as broadly available waste cooking oil.This research used waste cooking oil as raw material in biodiesel transesterification process, utilizing DES (Deep Eutectic Solvent) K_2CO_3-gliserol, as alternative catalyst. The output was biodiesel with near SNI 7182:2015 criteria. Optimum biodiesel production was achieved in low 65 ^oC temperature while utilizing two step transesterification process using DES K2CO3-gliserol 5.5 % and 35 % methanol, whereas glycerol total was 0.32 % and methyl esther contain was 96.89 %.

Keywords: biodiesel, catalyst, deep eutectic solvent, transesterification, waste cooking oil

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1. INTRODUCTION

Indonesia is a country rich in energy sources, including fossil fuels, as one of the main source of national energy. Petroleum usage is increasing in line with the growing population and demand for energy. However, it is important to note that Indonesia still heavily relies on fossil fuels to meet its energy needs. According to data from Central Statistics Agency (BPS) in 2020, each province distributed an average of 390,233 kiloliters of premium fuel, 999,153 kiloliters of biosolar, and 1,645 kiloliters of kerosene (https://www.bps.go.id/id/statistics-table/2/OTIjMg==/produksi-bahan-bakar-minyak.html). This represents a 28.8 % increase from 2019, which predicts future fuel scarcity. Hence, fossil fuels usage as primary energy source needs to be reduced and alternative energy sources need to be intensified. Biofuel is one of the solutions to this problem, given their abundant availability in Indonesia.

Biodiesel or bioenergy can be derived from materials with long alkyl ester groups, such as vegetable oils, animal fats, and waste oil. Used cooking oil, also known as waste cooking oil, is a common environmental pollutant due to improper disposal.

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Continuous use of this oil can have negative effects on human health. Therefore, it is important to handle it sustainability to minimize its waste. One of the sustainable solution is to use it as a basic material for biodiesel production.

Biodiesel is produced from vegetable oil through a transesterification process, which replaces the alcohol group of an ester with another alcohol. This process resembles hydrolysis, but instead of using water, it prefers use alcohol. Homogeneous catalysts such as KOH, NaOH, or H_2SO_4 are commonly used to assist in the production of biodiesel. The transesterification reaction is an equilibrium reaction that must be driven to the right to produce methyl esters (biodiesel) with an excess of alcohol (Syahrul, 2021). Biodiesel is a methyl ester compound produced by the esterification reaction of fatty acids with short-chain alcohols. This reaction is relatively slow and requires assistance to speed it up. To enhance the reaction rate and yield, effective stirring, excess reactants, and catalysts can be employed to lower the activation energy (Kapuji, 2021). The catalyst should be selected based on its ease of use, separation from the product, and the quality and quantity of biodiesel produced.

Homogeneous catalysts have several weaknesses, including corrosion problems, susceptibility to soap formation, catalyst recovery, water production, and the production of glycerol as a byproduct (Zaki et al., 2019). On the other hand, heterogeneous catalysts have more advantages for use in biodiesel production. This is because the heterogeneous catalyst nature supports clean (green) and environmentally friendly technologies. It is easy to separate from the reaction mixture, can be used multiple times, and is also low in toxicity (Husin et al., 2018). Heterogeneous catalysts are often implemented for the conversion of vegetable oil biodiesel, such as CaO, SrO, and TiO_2-based catalysts.

Deep Eutectic Solvents (DES) is a type of catalyst used in biodiesel production can also be used to separate biodiesel from Free Fatty Acids (FFA), Unsaponifiable Matter, and Unreacted Oil (Dzakiroh et al., 2021). DES is a two-component solvent consisting of quaternary ammonium salt and hydrogen bond donor, which are mixed together in the appropriate ratio to achieve eutectic point. DES can be made from various types of alkali-based compounds which are abundant in Indonesia (Manurung et al., 2016; Hayyan et al., 2013) and as green solvent thats inexpensive, biodegradable, and recyclable catalyst (Khandelwal, 2016). DES can be applied as a catalyst and co-solvent in the transesterification process because it has many advantages such as reducing the saponification reaction, and simplifying the separation and purification process. Several types of DES are also considered efficient for separating glycerol and base catalyst residues in biodiesel products (Troter et al., 2016). This research investigates potential use of DES as alternative affordable solvent in catalytic biodiesel production, as well as non-toxic and biodegradable properties of this solution as catalyst.

2. MATERIALS AND METHODS

This research is conducted in Energy Engineering and waste management engineering laboratory, Department of Chemical Engineering, Faculty of Engineering, Sriwijaya University. The raw materials used were household waste cooking oil, DES catalyst produced by in-home lab, technical methanol, and pro grade chemicals for analysis.

Pretreatment

Used cooking oil was filtered three times using monyl paper to remove impurities. Additionally, bentonite was utilized to adsorb the oil, separating dyes, reducing free

fatty acid levels, and removing other impurities. K_2CO_3-glycerol DES catalyst prepared following Naser (2013) procedures with K_2CO_3-glycerol mol ratio 1 : 3.5.

Esterification

Esterification process was conducted in batches using a three-neck flask connected to a condenser. The process employed used cooking oil, which was heated to 65 °C in the flask. The ratio of oil to methanol was 1 : 10. Methanol was heated separately in another container until it reached 40 °C. At this point, a catalyst (H_2SO_4) was added in a percentage of 1 % by weight of oil and stirred until homogeneous. After the oil temperature reached 65 °C, a mixture of methanol and H_2SO_4 was added to the oil while temperature of the mixture was kept at 65 °C. Reaction started after the addition of methanol and ran for 4 hours.

Esterification product then separated for 45-60 minutes in a 500 ml funnel. Biodiesel and glycerol were separated to ensure that there was no biodiesel in glycerol. The glycerol was evaporated at 90 °C in stirrer for 1 hour, cooled, weighted, and stored in a closed container. Biodiesel obtained from the process then washed with distilled water at 40-50 °C. Water was slowly poured over the entire surface of the biodiesel during washing process, which was continued until the water has clear apprearance. Remained water was evaporated by heating the biodiesel in a stirred glass jar for approximately 1 hour at 100 °C. The obtained biodiesel product was weighed and stored in a clean, dry glass bottle with a tight lid for analysis.

First Stage Transesterification

Stage 1 transesterification process was conducted in a 500 ml three-neck flask connected to a condenser. The process utilizes 100 grams of esterified oil, which is heated to 65 °C. Methanol, comprising 10 % of the oil's weight, is heated in a separate container to 40 °C. Once the temperature reaches 40 °C, K_2CO_3-glycerol DES catalyst, comprising 1 % of the oil's weight, is added to the methanol and stirred until homogeneous. The mixture was divided into two parts, with 85 % of it heated to 60 °C and the remaining 15 % kept in a tightly closed container. Once the oil was heated to 65 °C, the 85 % mixture of methanol and DES catalyst was added, and the temperature was maintained at 65 °C. The reaction began when the methanol-DES K_2CO_3-glycerol mixture was added, and it rested for 2 hours.

The resulting mixture of biodiesel and glycerol was then left to stand for 45-60 minutes in a separating funnel. The biodiesel and glycerol were separated to ensure that no biodiesel was included in the glycerol. The resulting glycerol was collected in a closed container. The biodiesel was weighed and placed into a washed and dried flask to continue with the second stage transesterification process.

Second StageTransesterification

During second stage transesterfication of the transesterification process, the biodiesel produced in stage 1 is heated in a 500 ml three-neck flask until it reaches a temperature of 65 °C. The remaining 15 % mixture of methanol and catalyst is also heated to 60 °C. Once the oil temperature reaches 65 °C, the remaining mixture and methanol are added, and the temperature is maintained at 65 °C throughout the reaction. The reaction begins upon the addition of methanol and lasts for 2 hours. The reaction product, a mixture of biodiesel and glycerol, was left to stand for 45-60 minutes in a separating funnel.

The resulting biodiesel and glycerol were then separated.The glycerol obtained from transesterification stages 1 and 2 was combined in one container, evaporated at 90 °C while stirring for 1 hour, weighed, and stored in a closed container. The biodiesel was washed with distilled water at 40-50 °C. Distilled water was used to wash the biodiesel until the water ran clear. Then biodiesel was heated in a 250 ml glass jar while stirring for less than an hour at 100 °C to evaporate any remaining water. After weighing the biodiesel, it was stored in clean, dry, and tightly sealed glass bottles for analysis of its quality.

Analytical Procedures

The characteristics of biodiesel were analyzed through viscosity, density, acid number, methyl ester content, total glycerol content, and monoglyceride content analysis. Viscosity was measured using the Ostwald Viscometer at 40 °C, following the ASTM D445 standard test method. Density analysis was conducted using a pycnometer and following the standard method of SNI 06-4085-1996 test at 40 °C. Additionally, acid number analysis was performed using the titrimetric method which adhere FBI A01-03 test method standard. The total glycerol content was analyzed using the periodic acid idiometric method which referring standard pattern of the FBI A01-03 test method. Calculation of methyl ester content was based on analysis of acid number, saponification number, and total glycerol, using the following formula:

$$\text{Methyl Ester Content (\%)} = Sv - Av - (18.29 \times TG) \times 100Sv$$

Av = Acid Value
Sv = Saponification Value
TG = total glycerol

3. RESULTS AND DISCUSSION

Free Fatty Acid of Biodiesel

Acid numbers of the product meet the requirements of Indonesian National Standard (SNI 7182-2015), which specify a maximum of 0.5 Mg-KOH/gram, except when using a 35 % methanol ratio and 3.5 % or 4 % catalyst. Figure 1 illustrates that increasing amount of catalyst results in a smaller acid number, except for 30 % methanol ratio. This finding is consistent with Wicakso's statement (2011) that a larger amount of catalyst leads to a smaller acid number. This is because the alkaline catalyst will neutralize the free fatty acids in the waste cooking oil. The DES K_2CO_3-glycerol catalyst used is alkaline. This catalyst can neutralize free fatty acids within the oil. Therefore, a higher catalyst content results in a lower free fatty acid content, as indicated by the acid number.

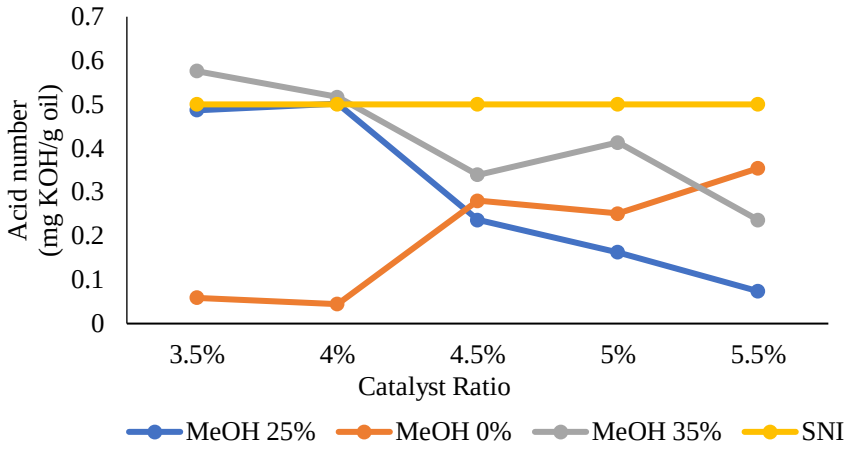

Figure 1. The effect of the amount of catalyst and methanol on the biodiesel acid number

Density of Biodiesel

Biodiesel ideal density range in SNI 7182-2015 (40 °C) is between 0.85 g/cm^3 and 0.89 g/cm^3. Figure 2 exhibits the effect of catalyst quantity and methanol on biodiesel density. Highest density value (0.8875 g/cm^3) was presented when using 3.5 % DES catalyst and 25 % methanol ratio. The lowest density (0.8679 g/cm^3) was produced with the use of 5.5 % DES catalyst and 35 % methanol ratio. The densities of the biodiesel products in this study range from 0.8679 to 0.8875 g/cm^3, meets the requirements of SNI 7182-2015.

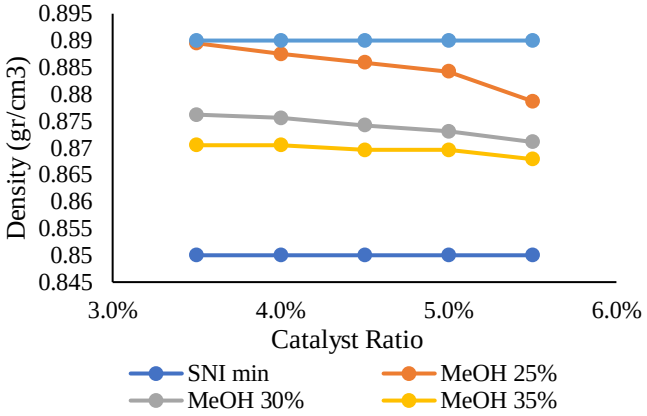

Figure 2. The effect of the amount of catalyst and methanol on biodiesel density

Viscosity of Biodiesel

Viscosity is a measure of the collisions that occur between adjoining layers in the fluid (Sukria, 2022). According to SNI 7182-2015, the viscosity of biodiesel should fall within the range of 2.3-6.0 cSt. Figure 3 shows the viscosity of the produced biodiesel. As seen in Figure 3, the viscosity value decreases with each addition of catalyst. The greater the amount of catalyst used, the more triglycerides will react. Viscosity of

FAME is smaller than triglycerides, as a result the viscosity of the biodiesel produced will decrease along with increasing the amount of catalyst used. The highest viscosity value of 5.3239 cSt was observed when 3.5 % DES catalyst with 30 % methanol ratio was used, while viscosity value was 5.5 % cSt when 5.5 % DES catalyst with 35 % methanol ratio was used.

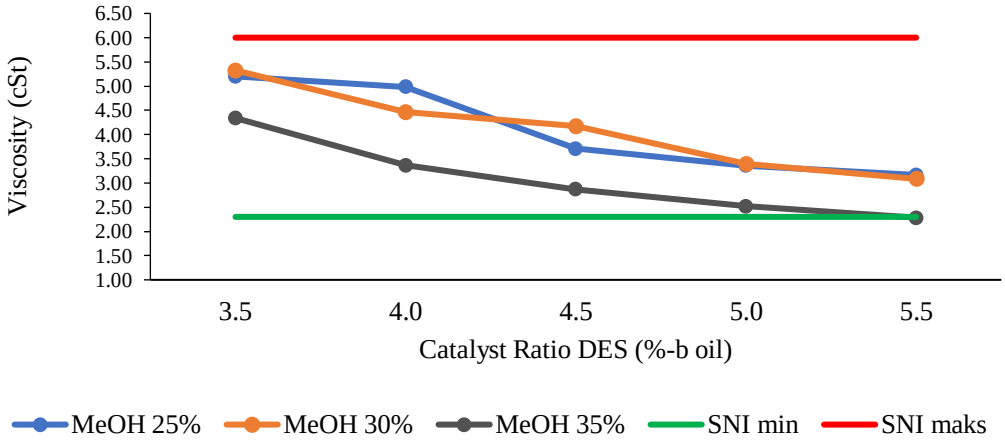

Figure 3. The effect of the amount of catalyst and methanol on the viscosity of biodiesel

According to Figure 3, viscosity value decreases progressively with each addition of the catalyst. The highest viscosity value (5.3239 cSt) was obtained when using 3.5 % DES catalyst with a 30 % methanol ratio. Conversely, the smallest viscosity value (2.2848 cSt), was obtained when using 5.5 % DES catalyst with a 35 % methanol ratio. This study found that the viscosity of biodiesel was affected by the concentration of catalysts. Specifically, as the percentage of catalyst increased, the viscosity decreased due to the faster breakdown of triglycerides into three fatty acid esters (Wiyata, 2021).

All biodiesel produced met SNI 7182-2015 standards, except for biodiesel generated using a 5.5 % catalyst ratio and 35 % methanol. Increasing the amount of catalyst can decrease the viscosity of biodiesel (Busyairi, 2020), This is because the viscosity of FAME is lower than the viscosity of wates cooking oil. The viscosity number determines the thickness of the biodiesel solution, with lower numbers indicating a more liquid solution and higher numbers indicating a thicker solution. It is important to avoid using biodiesel with low viscosity as it may cause leakage when used to fuel devices such as injection pumps. On the other hand, a high viscosity value can cause losses due to high friction in the pump, as the fluid is difficult to flow and leads slow movement (Regina, 2018).

Total Glycerol of Biodiesel

Biodiesel's important parameter is total glycerol content, which is closely linked to its ester content. Both are determined by the amount of residual monoglycerides, diglycerides, and triglycerides that remain unconverted. According to SNI 7182:2015, maximum quality standard for total glycerol in biodiesel is 0.24 %. Figure 4 illustrates that total glycerol content of biodiesel generally decreases with the addition of a catalyst. Thoai et al. (2017) found that increasing the amount of catalyst leads to a decrease in total glycerol production, indicating higher conversion rates in the two

stage transesterification reaction. A low total glycerol content suggests that the transesterification reaction is maximized (Jatyaraga et al., 2016).

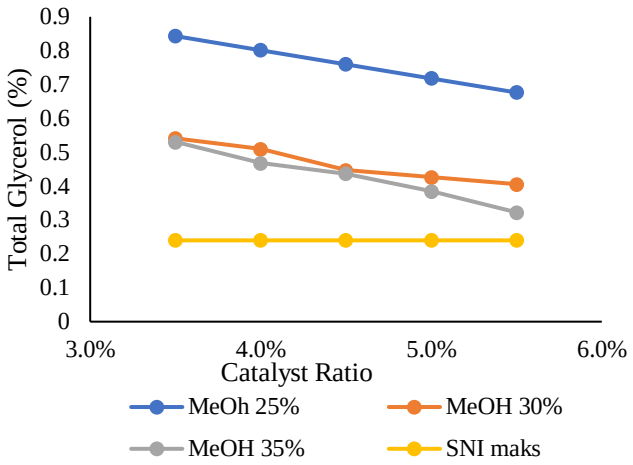

Figure 4. The effect of the amount of catalyst and methanol on the total glycerol of biodiesel.

Total glycerol decreased as the ratio of methanol used increased due to the increased reactions between triglycerides and methanol to form methyl esters. However, all the product still has a total glycerol content above 0.24 %, which does not meet the SNI 7182:2015 standard. The addition of a catalyst and methanol is expected to provide a total glycerol value that meets the Indonesian National Standard (SNI 7182:2015). The low total glycerol value proves that DES K_2CO_3-glycerol , which is a glycerolate compound, has potential as a transesterification catalyst. Dikjstra (2005, 2008) suggests that the true catalyst for methanolysis and interesterification is not the methoxide/methylate ion, but the glyceroxide (or glycerolate) ion and the enolate ion. The Dijkstra mechanism has encouraged the development of glycerolate of alkaline earth metals as a solid (heterogeneous) catalyst for biodiesel production (Da Silva Lisboa et al., 2014, Esipovich et al., 2014, and Esipovich et al., 2018).

Methyl Ester Content

The methyl ester content is a measure of the quality of biodiesel and ~~can~~ illustrate the effectiveness of the transesterification process used to make it (Laila and Oktavia, 2017). The SNI 7182:2015 standard for biodiesel methyl ester content is at least 96.5 %, which is presented in Figure 5. Figure 5 shows the levels of methyl esters resulting from the two-stage transesterification process with varying amounts of DES catalyst and methanol (25 % by volume). The highest yield, at 93.71 %, was achieved with a catalyst ratio of 5.5 % by volume, while the lowest yield, at 91.97 %, was achieved with a catalyst ratio of 3.5 % by volume. When using 30 % methanol (by volume), the highest yield of methyl ester content was achieved with a catalyst ratio of 5.5 % by volume, at 96.07 %, while the lowest yield was achieved with a catalyst ratio of 3.5 % by volume, at 94.97 %.

The highest methyl ester content of the DES catalyst and methanol 35 % mixture was achieved at a catalyst ratio of 5.5 %, with a value of 96.90 %. Conversely, the lowest methyl ester content was obtained at a catalyst ratio of 3.5 %, with a value of 94.80 %. These results indicate that the methyl ester content increases as the amount of DES catalyst increases. The analysis results align with Ningtyas et al.'s

(2013) statement that increasing the amount of catalyst in the biodiesel production process leads to higher methyl ester content. The 3.5 %-b and 5.5 %-b catalysts at 65 °C and employing a two-stage transesterification process with 30 %-b methanol produced methyl ester levels that meet SNI 7182:2015 standards.

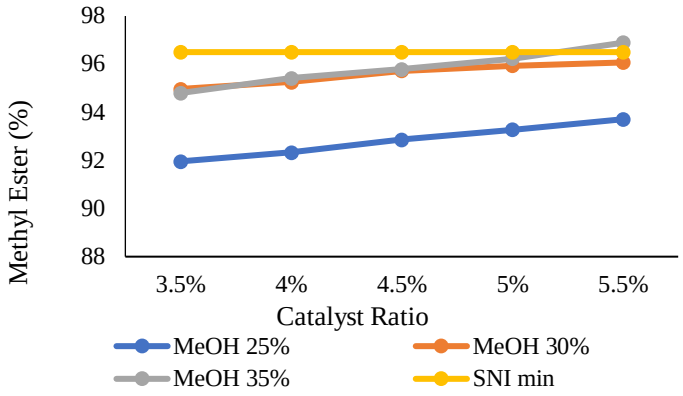

Figure 5. The Effect of catalyst and methanol amounts on biodiesel's methyl ester content

Methyl ester content is an indicator of the amount of methyl esters obtained from used cooking oil during the two-stage transesterification reaction process. Product with 25 % methanol form fewer methyl esters than those produced using 30 % and 35 % methanol ratios. Excessive methanol usage in the transesterification reaction results in high levels of methyl esters (Elma et al., 2016). Excessive amounts of methanol allow more transesterification reactions to occur. The reaction between used cooking oil and methanol is optimized by using a reflux system with a condenser and a low temperature of 65 °C. This is performed in order to minimize of methanol evaporation, leading to a more optimal condensation process. The reaction between used cooking oil and methanol was optimized by using a reflux system with a condenser and a low temperature of 65 °C. It can be concluded that a higher mol ratio of used cooking oil and methanol leads to better conversion dan methyl ester content.

4. CONCLUSION

This research exhibits that acid number was decreased along with density, methyl ester content, and viscosity with an increase in the ratio of used cooking oil and methanol. Additionally, the total glycerol was also decrease. Optimal conditions for producing biodiesel that meets the requirements of SNI 7182:2015 involve using a 35 % methanol ratio and a 5.5 % DES catalyst ratio, with density 0.87 g/cm^3, viscosity 2.28 cSt, acid value 0,2805 mg KOH/g oil, glycerol total 0.32 % and methyl esther contain 96.89 %.

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