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Effect of CaO/Fe_2O_3 Mass Ratio and Oil/Methanol Molar Ratio on Biodiesel Production from Waste Cooking Oil

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Abstract

Biodiesel is a renewable liquid fuel that can be produced through transesterification reaction of triglycerides containing oils and fats. The objective of this research was to examine the effect of composition ratio of CaO and Fe_2O_3 on CaO/Fe_2O_3 catalysts derived from eggshells and Fe_2O_3 in the production of biodiesel from waste cooking oil (WCO). In addition, the effect of the ratio of oil and methanol on the yield and characteristics of the biodiesel produced was also studied. Catalysts were prepared through impregnation. The esterification-transesterification process was carried out with the conditions WCO:methanol molar ratio of 1:3, 1:6, 1:9, 1:12 and 1:15, catalyst (3%wt oil), at 65°C for 3 hours with a stirring speed of 1200 rpm. The results showed that the biodiesel production using CaO: Fe_2O_3 catalyst with the ratio of CaO: Fe_2O_3 70:30 and WCO:methanol molar ratio of 1:9 obtained a higher yield (84.5%) compared to others. The best operating condition for transesterification of WCO obtained in this research is the $CaO:Fe_2O_3$ catalyst ratio of 70:30 and the WCO:methanol molar ratio of 1:9 with a biodiesel yield of 84.50% with a methyl ester content of 99.63% and a FAME yield of 84.14%. The biodiesel produced has met the requirements of the Indonesian National Standard (SNI) in terms of density and viscosity.

Keywords: CaO; Fe_2O_3; biodiesel; catalyst

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INTRODUCTION

The energy issue that is related to the increasing demand of fossil fuels as a result of growing population and rapid industrialization has been one of important global concern. However, the reserve of petroleum as the main global energy source will continue to deplete along with its high demand. To overcome this problem, other alternative energy as a substitute to fuel oil is required. Biodiesel has been widely approved for application as the alternate fuel to petroleum diesel oil. Biodiesel is a renewable liquid fuel that can be produced through transesterification reactions derived from biomass, such as vegetable and animal oils or fats, or waste cooking oil (Akram et al., 2022).

Waste cooking oil (WCO) contains triglycerides that are composed of glycerol and esters from fatty acids so that it has the potential to be converted to biodiesel. Unfortunately, the use of waste cooking oil as a raw material for biodiesel has been limited by its high free fatty acid (FFA) content, which is normally above 1% and could retard the transesterification process. So, it requires a pretreatment process to reduce FFA content to an allowable level prior to its conversion to biodiesel by the transesterification method (Suzihaque et al., 2022).

Because a catalyst is required to speed up the transesterification of WCO, sustainable and affordable raw materials should be carefully selected to prepare the catalyst. For the case of base catalyst, CaO, Fe_2O_3 and their combination can be good candidates. The catalytic activity of pure CaO can be enhanced by the addition of supports of alkaline, organic compounds and mixing with metal oxides (Mazaheri et al., 2021). CaO can be used as a catalyst base that can be developed in the production of biodiesel. Ezzah-Mahmudah et al. (2016) explained that the addition of Fe_2O_3 as a catalyst support could increase the number of strong acid sites and had been proven to be suitable for the esterification of FFA compounds. Fe_2O_3 also has adsorption ability for carboxylic groups, including fatty acid components. Otherwise, the addition of metal oxide supports (Fe_2O_3) to CaO obtained high catalyst stability due to the substitution of Fe^{3+} ions with Ca^{2+} ions in the calcium grid, which causes defects to occur, thereby changing the characteristics of the catalyst surface. As a result, the stability of the catalyst increases without reducing the catalytic activity. Research on the use of catalysts in the production of biodiesel has been widely performed. Some important variables that affect the conversion and characteristics of the biodiesel produced are the ratio of the catalyst and the ratio of the raw materials used.

This study aims to examine the effect of CaO and Fe_2O_3 composition ratio on CaO/Fe_2O_3 catalysts from eggshells and Fe_2O_3 in the production of biodiesel from waste cooking oil. In addition, it was also studied the effect of the molar ratio of oil and methanol on the yield and characteristics of the resulting biodiesel.

MATERIALS AND METHODS

Preparation of Catalyst

Chicken eggshells were washed and then oven dried at 100°C for 24 hours. The dried chicken eggshells were ground into powder and sieved using a 100-mesh sieve to obtain a uniform particle size. After that, the eggshell powder was calcined at 900°C for 4 hours using a furnace (Risso et al., 2018).

Mass of CaO and Fe_2O_3 were determined according to the ratio of catalyst mass 90:10, 80:20, 70:30, 60:40, and 50:50. The CaO was dissolved in 250 ml of distilled water in a beaker and stirred until homogeneous to form a $Ca(OH)_2$ solution. The Fe_2O_3 powder was then added and the stirring was continued using a hot plate magnetic stirrer. Operating conditions were performed at a temperature of 70°C for 4 hours with a stirring speed of 700 rpm. The resulting slurry was oven dried at 105°C for 24 hours to remove any residual H_2O. The dried slurry was then calcined in the furnace at 850°C for 2 hours (Hafiz et al., 2017).

Preparation of Waste Cooking Oil

The was cooking oil was heated, and then fatty acids to solution was added until the mixture reached the desired FFA level. Furthermore, the oil was filtered using filter cloth to remove any solid residues and heated to a temperature of 100°C to remove the water content.

The content of free fatty acid was determined using the acid-base titration method. Five grams of oil was introduced into 100 ml of Erlenmeyer and then 15 ml of ethanol was added. Two drops of phenolphthalein (PP) indicator were added to the solution and then titrated using 0.05 N NaOH solution until pink color is established and does not disappear when the solution was shaken. The %FFA was then calculated using the equation (Buchori et al., 2018):

$$FFA(\%) = \frac{V_{titrant} \times N_{NaOH} \times MW_{fatty\ acid}}{1000 \times m_{sample}} \quad (1)$$

Production of Biodiesel

Firstly, waste cooking oil and methanol with molar ratios of 1:3, 1:6, 1:9, 1:12 and 1:15 was introduced into a three-neck flask. Then, CaO/Fe_2O_3 catalyst with a catalyst concentration of 3%-wt oil was added to the WCO-methanol mixture. The mixture was heated to a temperature of 65°C for 3 hours at a stirring scale of 1200 rpm using a magnetic stirrer. As soon as the reaction time was reached, the product was separated by a split funnel by leaving it for ± 12 hours until two layers consisting of biodiesel and glycerol products were formed. Then, the products were centrifuged at 2500 rpm for 15 minutes to separated biodiesel products and catalyst.

Characterization of Biodiesel

The resulting biodiesel product was analyzed for its chemical composition using gas chromatography mass spectroscopy (~~a~~ GC-MS). After that, the yield of biodiesel and the yield of FAME is calculated using the equation:

$$Yield_{Biodiesel}(\%) = \frac{weight\ of\ biodiesel\ (g)}{weight\ of\ WCO\ (g)} \times 100\% \quad (2)$$

$$Yield_{FAME}(\%) = \frac{\%_{Area\ GC\ FAME} \times weight\ of\ biodiesel\ (g)}{weight\ of\ WCO\ (g)} \times 100 \quad (3)$$

Additionally, the biodiesel obtained was also analyzed for density and kinematic viscosity.

RESULTS AND DISCUSSION

X-Ray Diffraction (XRD) Analysis

The crystal structure of the dispersed catalyst particles was analyzed by XRD. Figure 1 shows the XRD pattern of the synthesized CaO/Fe_2O_3 powder before and after calcination treatment at 850°C for 2 hours. The XRD pattern shows the confirmation of CaO/Fe_2O_3. As seen in Figure 1, the unique XRD diffraction patterns of CaO crystals before calcination are shown at peaks of 33.53°, 36.23°, 51.5° and 64.49°.

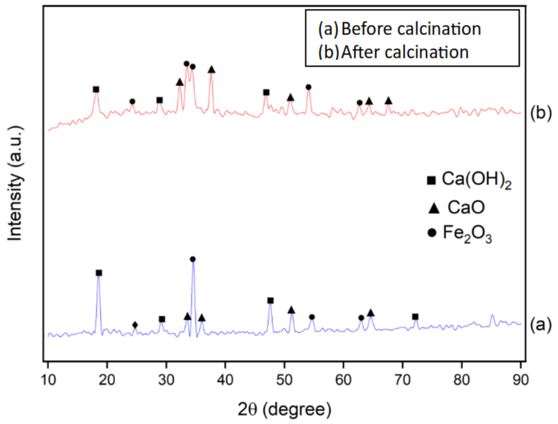

Figure 1. XRD pattern of the synthesized CaO/Fe_2O_3 before and after calcined.

The XRD patterns of CaO crystals after calcination at 850°C for 2 hours are shown at the peak points of 32.28^o, 37.63^o, 53.82^o, 64.48^o and 67.64^o. Meanwhile, the Fe_2O_3 XRD diffraction pattern before calcination are shown at the peak points of 24.64^o, 34.52^o, 54.66^o and 63.32^o. XRD patterns of Fe_2O_3 after calcination at 850°C for 2 hours were shown at peaks of 24.3^o, 33.56^o, 34.46^o, 43.68^o, 54.30^o, and 62.56^o. In addition to CaO and Fe_2O_3, there are $Ca(OH)_2$ compounds that appear in the XRD diffraction pattern before calcination which is shown at the peak of 2θ namely 18.52^o, 29.2^o, 47.54^o, 72.26^o and after calcination at 850°C for 2 hours is shown at the peak of 18.24^o, 29.03^o, 47.04^o.

The $Ca(OH)_2$ peak that appears in the XRD diffraction pattern is due to the interaction between CaO and water vapor after drying and after the sample has decomposed. As a result, many of the pores in the CaO sample are opened, which induces the reaction of CaO with water vapor to occur in each particle and water vapor circulates easily in the pores. This affects the total conversion of CaO to $Ca(OH)_2$ (Lesbani et al., 2013).

In the XRD analysis results, there were differences in the diffraction pattern between the catalyst before and after calcination at 850°C for 2 hours. This is related to the crystal size of the material where an increase in temperature causes an increase in the crystallization of a layer of a material (Elhendaw et al., 2014). In addition, an increase in temperature also causes defects in atomic crystals to decrease due to the supply of sufficient energy to the atoms so that they can adjust or restore the shape and structure of the lattice (Mishjil et al., 2015).

Effect of Oil to Methanol Ratio on Biodiesel Yield

The results of the FFA analysis show that the FFA content in waste cooking oil was 5.076%. However, the reaction that occurs in the production of biodiesel is a simultaneous esterification-transesterification reaction. The simultaneous esterification and transesterification reactions which are illustrated in Figure 2.

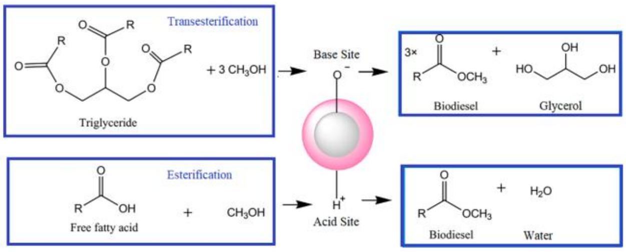

Figure 2. Simultaneous esterification and transesterification reactions (Mulyatun et al., 2021)

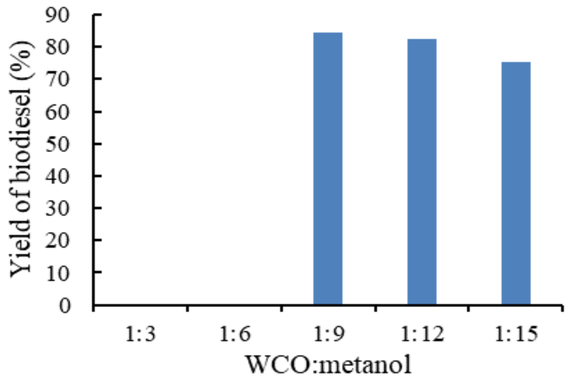

Figure 3. Effect of oil to methanol ratio on biodiesel yield

This reaction is influenced by several factors, one of which is the molar ratio of oil and methanol (Salaheldeen et al., 2021). Figure 3 depicts the relationship between the molar ratio of oil:methanol to the yield of biodiesel.

Figure 3 confirms that oil to methanol molar ratio directly affects biodiesel yield. The biodiesel yield was found to decrease with an increase of WCO:methanol ratio from 1:9 to 1:15. The decline of biodiesel yield at the oil:methanol molar ratio of 1:9 to 1:15 can be associated to the high methanol to oil ratio which interferes with the separation of glycerol due to the increased solubility of glycerol in excess methanol. When glycerin remains present in solution, it promotes the equilibrium reaction reverses back to the left direction, lowering the ester yield and pushing the equilibrium backward towards the formation of mono, di, and triglycerides thereby reducing ester products. When methanol quantity was beyond the optimum value, it will deactivate the catalyst and therefore favor the backward reaction of the transesterification process (Erchamo et al., 2021). Separation of methyl esters and glycerol in the reaction is difficult due to the polar hydroxyl group in methanol, which acts as an emulsifier (Gonzaga et al., 2021).

Figure 3 also shows that the yield results on WCO:methanol ratio 1:3 and 1:6 was not converted to biodiesel products. Stoichiometrically, the alcohol to oil ratio is 3:1 and the reaction is a reversible reaction.

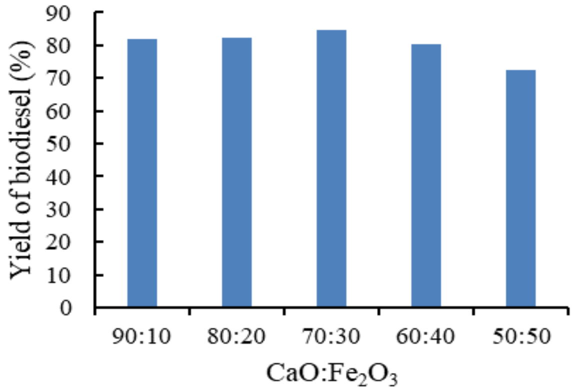

Figure 4. Effect of mass ratio $CaO:Fe_2O_3$ on biodiesel yield

However, to increase miscibility and contact between alcohol molecule and triglyceride, a higher molar ratio is needed. In addition, a molar ratio value higher than the stoichiometric ratio is also required to shift the reaction towards the product (Musa, 2016). In this research, this poor ratio effectiveness could be the result of the high viscosity of mixture, which reduces the intensity of physical contact between the catalyst sites and the mixture molecules (Jume et al., 2022). In this study, the optimum molar ratio of oil to methanol was found to be 1:9 for a maximum biodiesel yield of 84.5%.

Effect of Mass Ratio of CaO/Fe_2O_3 Catalyst on Biodiesel

Catalysts play an important role in chemical reaction, especially to accelerate reaction and to selectively govern the reaction to generate specified products (Spencer, 1988). In this study, a CaO catalyst supported by Fe_2O_3 was used with various $CaO:Fe_2O_3$ mass ratios of 90:10, 80:20, 70:30, 60:40 and 50:50. Figure 4 presents a graph of the relationship between the mass ratio of $CaO:Fe_2O_3$ and the yield of biodiesel. Figure 4 shows that the catalyst ratio has a significant impact on biodiesel yield. In the mass ratio variable CaO:Fe2O3 at 70:30 the results with the highest yield were obtained. The addition of CaO to the CaO: Fe_2O_3 catalyst mass ratio variable at 80:20 and 90:10 resulted in lower biodiesel yields. This can occur as a result of the accumulation of excess CaO so that it can disrupt the surface of the catalyst and the active site for contact with the reactants (Liu et al., 2010). In the variable with a mass ratio of CaO, which is lower than the variable 70:30, namely the mass ratio variable at 60:40 and 50:50 also experienced a significant decrease in biodiesel yield. This is due to the lack of CaO levels needed to form the active oxide and base active sites on the catalyst. The reduced active oxide and base active sites formed on the catalyst resulted in low biodiesel yields (Liu et al., 2010).

Biodiesel Product Characteristics

Table 1. Characteristics of biodiesel products at a WCO:methanol molar ratio of 1:9

$CaO:Fe_2O_3$ mass ratio	Parameter		
	Density (gr/ml)	Viscosity (cSt)	Yield of biodiesel (%)
90:10	0.88	4.65	81.97
80:20	0.87	3.42	73.90
70:30	0.87	2.78	84.50
60:40	0.87	2.58	80.23
50:50	0.87	2.49	72.24

Table 2. Characteristics of biodiesel products at a $CaO:Fe_2O_3$ mass ratio of 70:30

WCO:methanol molar ratio	Parameter		
	Density (gr/ml)	Viscosity (cSt)	Yield of biodiesel (%)
1:3	0	0	0
1:6	0	0	0
1:9	0.87	2.78	84.50
1:12	0.86	2.59	82.57
1:15	0.87	2.56	75.26

The characteristics of biodiesel in this study were analyzed through two important parameters, namely the density and viscosity. The measurement of the density and viscosity of the biodiesel products is used as a reference for product eligible with the Indonesian National Standard (SNI) of biodiesel. The results of measuring the density and viscosity of biodiesel products are presented in Tables 1 and 2.

Density is defined as mass per unit volume. The higher the density of the fuel, the more mass it contains so that it will produce higher emissions after combustion (Tüccar et al., 2018). Viscosity is one of the important fuel parameters that affect the formation of NO_x. A low viscosity value will result in lower NOx emissions so that it can reduce the greenhouse effect (Tüccar et al., 2018).

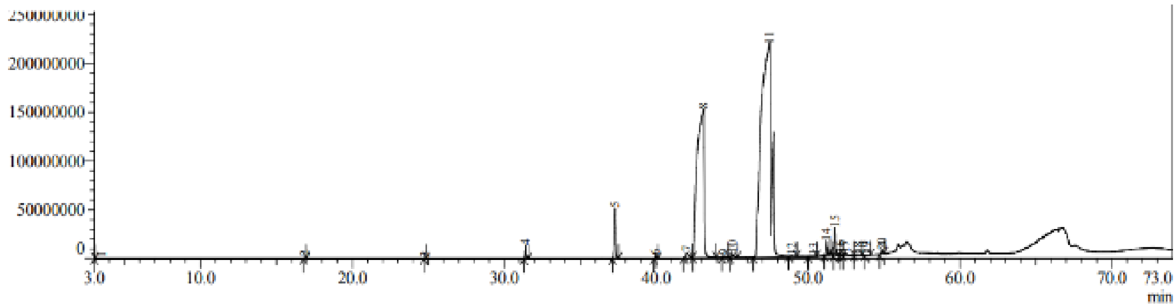

Figure 5. GC-MS result of biodiesel using CaO/Fe_2O_3 catalyst

Table 3. Composition of fatty acid methyl esters (FAME) in biodiesel product

Retention time (min)	Area (%)	Component
16.857	0.03	Octanoic acid, methyl ester
24.773	0.03	Decanoic acid, methyl ester
31.404	0.40	Dodecanoic acid, methyl ester
37.290	1.83	Tetradecanoic acid, methyl ester
39.939	0.09	Pentadecanoic acid, methyl ester
42.007	0.45	9-Hexadecenoic acid, methyl ester
43.118	30.65	Hexadecanoic acid, methyl ester
45.015	0.22	Heptadecanoic acid, methyl ester
47.457	64.08	9-Octadecenoic acid, methyl ester
48.915	0.04	9,12-Octadecadienoic acid, methyl ester
50.365	0.02	6,9,12-Octadecatrienoic acid, methyl ester
51.199	0.47	11-Eicosenoic acid, methyl ester
51.765	1.09	Eicosanoic acid, methyl ester
52.404	0.21	Oxiraneoctanoic acid, 3-octyl-, methyl ester
53.815	0.02	Pentacosanoic acid, methyl ester

Therefore, the density and viscosity of the biodiesel produced should meet the quality standards set by the government for emission control.

A good characteristic of biodiesel according to SNI 7182-2015 is biodiesel with a density and viscosity values of 0.85-0.89 g/mL and 2.3-6 cSt, respectively. Tables 1 and 2 show that the density and viscosity of the biodiesel obtained in this study has met the biodiesel standards of SNI 7182-2015.

Results of GC-MS Analysis of Biodiesel Products

The biodiesel product obtained was analyzed using gas chromatography-mass spectrometry (GCMS) to determine the composition of FAME in the biodiesel. The results are shown in Figure 5 and summarized in Table 3.

The results of the GC-MS analysis showed that the highest area percentage was obtained for 9-Octadecenoic acid which was 64.08% with a retention time of 47.457 minutes and hexadecanoic acid was 30.65% with a retention time of 43.118 minutes. The total content of methyl esters contained in the biodiesel product is 99.63%. The methyl ester content meets the SNI 7182-2015 standard where the minimum methyl ester content in biodiesel is 96.5%.

The methyl ester content in the biodiesel product was then used to calculate the yield of fatty acid methyl ester (FAME). In this study, the yield of FAME on biodiesel products was 84.14%.

CONCLUSION

The best reaction conditions for producing biodiesel from waste cooking oil using a CaO/Fe_2O_3 catalyst obtained in this study were a WCO:methanol molar ratio of 9:1, a mass ratio of catalyst CaO/Fe_2O_3 70:30 with a reaction temperature of 65°C and a reaction time of 3 hours. The biodiesel yield obtained was 84.50% with a methyl ester content of 99.63% and a FAME yield of 84.14%. The density and viscosity of the biodiesel obtained in this study comply the SNI 7182-2015 for biodiesel standards.

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