Edelweiss Applied Science and Technology
ISSN: 2576-8484
Vol. 9, No. 1, 779-791
2025
Publisher: Learning Gate
DOI: 10.55214/25768484.v9i1.4248

Biodiesel production using simultaneous esterification-transesterification method from waste cooking oil with CaO/Fe_2O_3 bifunctional catalyst

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Abstract: Biodiesel is one of the products resulting from the initiation of energy diversification which can overcome the energy crisis both in Indonesia and in the world. Biodiesel can reduce combustion emissions. The purpose of this study was to produce biodiesel from waste cooking oil (WCO). The study was conducted using the simultaneous esterification-transesterification method with the help of a catalyst. The catalyst used was a bifunctional catalyst, namely CaO/Fe_2O_3. Waste cooking oil raw materials and biodiesel products were analyzed by GC-MS, while the catalyst was analyzed by SEM-EDX and XRD. The catalyst calcination temperature was varied at 750-950°C and the esterification-transesterification reaction time was varied at 1-5 hours. The results of the study showed that the highest biodiesel yield was obtained at 82% at a catalyst calcination temperature of 800°C and a reaction time of 4 hours. The methyl ester composition formed was 97.61%. The research results show that the biodiesel products produced comply with SNI 7182-2015 standards. This finding proves that waste cooking oil can be used as a raw material for biodiesel so that it will reduce the impact of environmental pollution.

Keywords: *Bifunctional, Biodiesel, Catalyst, Simultaneous, Waste cooking oil.*

1. Introduction

National energy needs are still dominated by the use of fuel oil. But in reality, oil production worldwide has decreased due to the depletion of the availability of fossil energy raw materials. To overcome the current crisis, there has been an initiative to diversify energy by developing new renewable energy sources as alternative energy.

Indonesia is considered capable of developing biodiesel production because it has the title of being the second largest palm oil producing country in the world. In addition, the level of consumption of palm oil in Indonesia is quite high, reaching more than 2.5 million tonnes per year [1]. To support the continuity of raw materials and avoid competition for use with food ingredients, the use of waste cooking oil (WCO) as non-edible oil is preferred. Sharma, et al. [2] explained that waste cooking oil contains accumulated fatty acids containing triglycerides, so it has the potential to be processed as biodiesel.

The biodiesel production process from waste cooking oil as a raw material with high levels of free fatty acids (FFA) requires two catalytic process stages, namely the esterification reaction followed by the transesterification reaction. However, if both stages of the process are carried out conventionally, it can produce large amounts of wastewater and cause pollution to the environment. For this reason, it is necessary to develop a biodiesel production process from WCO with a bifunctional heterogeneous catalyst using a simultaneous esterification-transesterification method [3].

The bifunctional heterogeneous catalyst used in this study was the CaO/Fe_2O_3 catalyst. One source of raw materials used to meet CaO needs is chicken eggshells. Meanwhile, Fe_2O_3 will act as catalyst support. Calcium oxide (CaO) can be formed from the decomposition reaction of the main constituent of chicken eggshells, namely calcium carbonate (CaCO3), by calcination at high temperatures to produce calcium oxide (CaO) and carbon dioxide (CO_2) [4].

History: Received: 10 December 2024; Revised: 4 January 2025; Accepted: 10 January 2025; Published: 14 January 2025
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Research on biodiesel production from used cooking oil (WCO) with various concentrations has been carried out by several researchers. Ezzah-Mahmudah, et al. [5] have used CaO/Fe_2O_3 bifunctional heterogeneous catalysts in the production of biodiesel made from waste cooking oil (WCO). However, there is no study regarding the effect of catalyst calcination temperature on the biodiesel produced. Hidayati, et al. [6] conducted a study to determine the effect of using a CaO catalyst in the formation of biodiesel from waste cooking oil (WCO). However, this study also did not explain the effect of CaO calcination on the performance of the catalyst in the biodiesel formation process. Erchamo, et al. [7] investigated the effect of a CaO nano catalyst derived from a mixture of methanol-ethanol and eggshells to increase biodiesel production from waste cooking oil (WCO). However, it does not explain the influence of reaction time parameters in analyzing the effect of the catalyst on the biodiesel produced.

Meanwhile, Mulyatun, et al. [3] in their research highlighted bifunctional heterogeneous catalyst technology which is capable of processing raw materials with high FFA levels and the development of these catalysts in biodiesel production. Mulyatun, et al. [3] also recommend modification efforts and technology for developing bifunctional heterogeneous catalysts in biodiesel production that is economically better and more sustainable.

In order to answer the global challenge of providing energy diversification by developing potential new renewable energy sources, research related to biodiesel production from waste cooking oil (WCO) needs to be carried out. The focus of this research is the effect of calcination temperature on the CaO/Fe_2O_3 bifunctional heterogeneous catalyst and the length of reaction time in biodiesel production using the simultaneous esterification - transesterification method on the resulting biodiesel yield.

2. Materials and Methods

2.1. Materials

Used cooking oil and eggshells were obtained from restaurants around Tembalang, Semarang, Indonesia. The chemicals used such as Fe_2O_3, methanol, ethanol, NaOH, PP indicators were obtained from Merck, Germany.

2.2. Variables

The fixed variables used include the $CaO:Fe_2O_3$ ratio, which is 4:1 with a mass basis of 20 grams (14 grams of CaO and 6 grams of Fe_2O_3); the ratio of used cooking oil:methanol is 1:12 with a base volume of 300 mL (202 mL of waste cooking oil and 98 mL of methanol); CaO calcination temperature 900°C for 4 hours; Fe_2O_3 calcination temperature 700°C for 2 hours; CaO/Fe_2O_3 catalyst calcination time for 2 hours; esterification-transesterification reaction temperature of 65°C; and the catalyst concentration used was 3%.

The independent variables determined are the calcination temperature of the CaO/Fe_2O_3 catalyst with temperature variations of 750, 800, 850, 900, and 950°C and the esterification-transesterification reaction time with reaction time variations of 1, 2, 3, 4, and 5 hours.

2.3. Preparation of CaO/Fe_2O_3 Catalyst

Eggshells were washed and dried at 100°C for 24 hours in the oven. Then, the eggshells were ground using a grinder and sieved with a 100-mesh sieve. Next, the eggshell powder was calcined at a temperature of 900°C for 4 hours using a furnace [8] to obtain the CaO content from the decomposition reaction of the $CaCO_3$ content in chicken eggshells [9]. After that, Fe_2O_3 impregnation was carried out. CaO and Fe_2O_3 are weighed with a weight ratio of $CaO:Fe_2O_3$ of 4:1. Before the two are mixed, CaO is dissolved in 250 mL distilled water and stirred to form a homogeneous $Ca(OH)_2$ solution. Then, Fe_2O_3 powder was added to the solution and stirred at a stirring speed of 700 rpm at a temperature of 70°C for 4 hours. The resulting slurry is then dried in an oven at 105°C for 24 hours to remove the water content (H_2O). After drying, the solid was calcined at varying temperatures of 750, 800, 850, 900, and 950°C for 2 hours. After calcination was complete, 5 samples of CaO/Fe_2O_3 catalyst powder were obtained from various variations in calcination temperature.

2.4. Characterization of Catalyst

The catalyst was characterized using X-Ray Diffraction (XRD) and Scanning Electron Microscope – Energy Dispersive X-Ray (SEM-EDX) analysis. Characterization was carried out at the Integrated Laboratory UPT, Diponegoro University.

XRD analysis aims to determine the composition of the catalyst using the SHIMADZU XRD-7000 XRD tool and produces a 2θ value in the range 10°C – 90°. This analysis was carried out on the CaO/Fe_2O_3 mixture before calcination, all CaO/Fe_2O_3 catalysts from various calcination temperatures of 750 – 950°C, as well as the catalyst that was used which produced the highest biodiesel yield.

SEM-EDX analysis aims to determine the morphology and microstructure on the catalyst surface using the JEOL JSM-6510LA SEM-EDX tool. This analysis was carried out on the CaO/Fe_2O_3 catalyst from the calcination temperature which produces the best biodiesel yield, before and after being used for the biodiesel formation reaction.

2.5. Biodiesel Synthesis

Waste cooking oil (WCO) is filtered and then heated at 100°C to remove the water content. Next, waste cooking oil was analyzed using GC-MS to determine its content and free fatty acid levels were analyzed using acid-base titration. A total of 5 grams of oil was taken and 15 mL of methanol was added in an erlenmeyer flask. Two drops of phenolphthalein (PP) indicator were added to the solution and titrated using 0.05 N NaOH until a pink color was formed. Free fatty acid (FFA) levels were calculated using Equation 1 [10]:

$$\%\,\text{FFA} = \frac{\text{Vol. NaOH (mL)} \times \text{N NaOH} \times \text{MW FFA}}{\text{Sample Mass} \times 1000} \tag{1}$$

Biodiesel production is carried out through simultaneous esterification-transterification reactions. The reaction was carried out in a 250 mL three-neck flask equipped with a water-cooled condenser and thermometer. The CaO/Fe_2O_3 catalyst was activated at 40°C by mixing it with methanol and constant stirring for 40 minutes. Waste cooking oil (WCO) that has been heated at 100°C for 1 hour is added to the reactor with an oil:methanol ratio of 1:12. Biodiesel synthesis was carried out at 65°C.

The reaction was carried out for 3 hours using catalysts of different calcination temperatures, namely 750 – 950°C. After the reaction is complete, the mixture is transferred to a separating funnel and left for 24 hours for the phase separation process and 3 layers are formed (residual methanol, glycerol, and catalyst). The remaining mixture is centrifuged to obtain complete biodiesel and then heated at 65°C to evaporate the remaining methanol and obtain pure biodiesel [11]. This process produces a catalyst with a calcination temperature that produces the highest biodiesel yield. The same process is carried out to produce the highest biodiesel yield in the esterification-transesterification reaction time variable. Finally, we will know the best reaction time and calcination temperature that produces biodiesel with the highest yield.

Biodiesel and FAME yields are calculated using the Equations 2 and 3 [10]:

$$\text{Yield}_{\text{biodiesel}}\,(\%) = \frac{\text{weight of biodiesel (g)}}{\text{weight of WCO (g)}} \times 100\% \tag{2}$$

$$\text{Yield}_{\text{FAME}}\,(\%) = \frac{\%_{\text{GC area FAME}} \times \text{weight of biodiesel (g)}}{\text{weight of WCO (g)}} \times 100\% \tag{3}$$

3. Results and Discussion

3.1. Catalyst Characterization

3.1.1. Catalyst Characterization Using XRD

The CaO/Fe_2O_3 catalyst was characterized by XRD using SHIMADZU XRD-7000. In this research, XRD analysis was carried out on the CaO/Fe_2O_3 catalyst at various catalyst manufacturing conditions, namely under catalyst conditions without calcination, calcination at temperatures of 750, 800, 850, 900, and 950°C. Apart from that, XRD analysis was also carried out on the CaO/Fe_2O_3 catalyst which was used in the biodiesel formation reaction for 4 hours with a calcination temperature of

800°C. X-Ray Diffraction (XRD) analysis is a non-destructive analysis technique used to identify the phase of crystalline materials. The characterization results using XRD are presented in Figure 1.

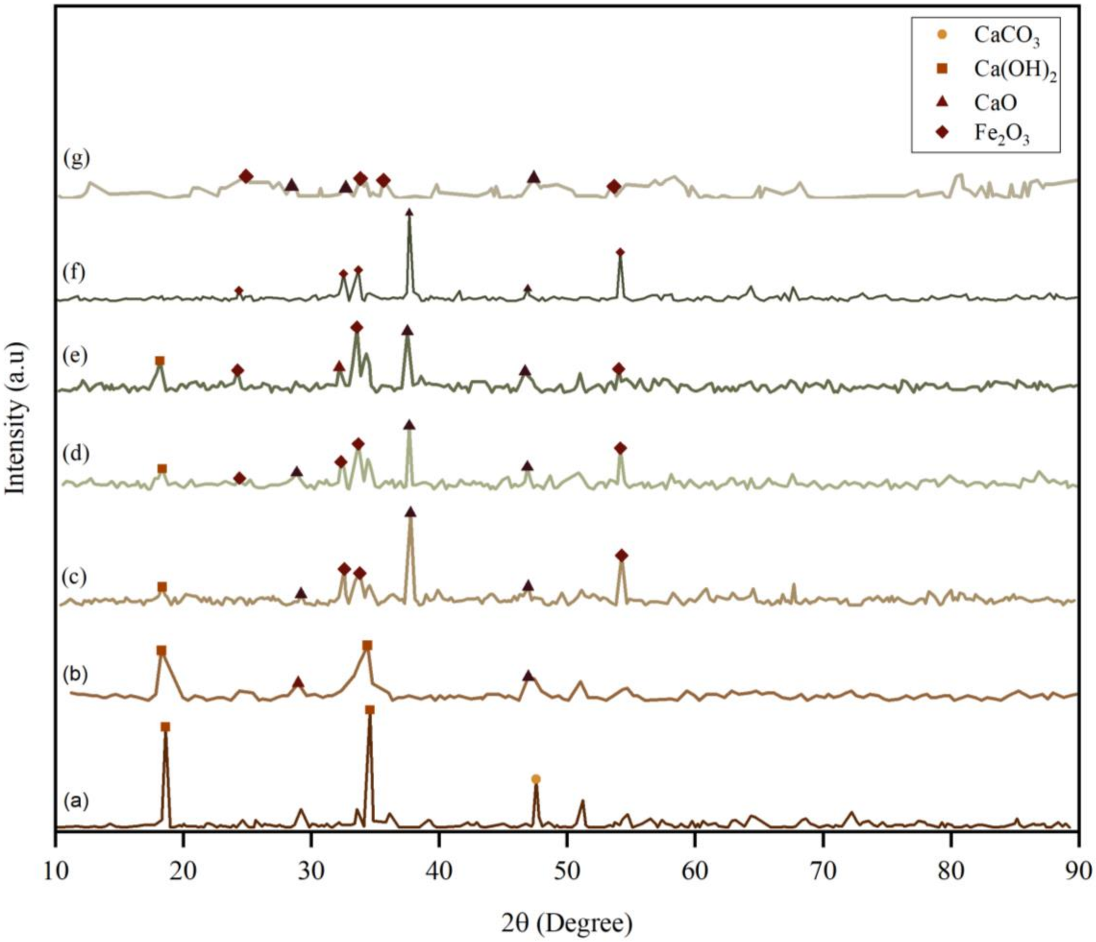

Figure 1.
Results of XRD analysis: (a) without calcination, (b) calcination at 750°C, (c) calcination at 800°C, (d) calcination at 850°C, (e) calcination at 900°C, (f) calcination at 950°C, and (g) after 4 hours of reaction with calcination at 800°C

Figure 1 shows various peaks of $CaCO_3$, $Ca(OH)_2$, CaO, and Fe_2O_3 compounds on the CaO/Fe_2O_3 catalyst used for the production of biodiesel from waste cooking oil. The $CaCO_3$ compound was found at peak $2\theta = 47.6°$ (JCPDS 00-001-0837). The $Ca(OH)_2$ compound was found at peaks $2\theta = 18.3°$ and 34.3° (JCPDS 00-004-0733). Meanwhile, CaO compounds were found at peaks $2\theta = 32.2°$ and 37.4° [12] (JCPDS 00-003-0425). The Fe_2O_3 compound was found at peaks $2\theta = 33.15°$ and 54.08° [13] (JCPD 33-0664; JCPD 39-1346).

Chicken eggshells as a raw material for the CaO/Fe_2O_3 catalyst contain the main constituent compound in the form of calcium carbonate ($CaCO_3$). In the CaO/Fe_2O_3 catalyst used in this research, the $CaCO_3$ compound was only found in conditions where the catalyst had not been calcined. In catalysts that have been calcined at various temperatures, no $CaCO_3$ compounds are found due to oxidation which causes the formation of calcium oxide (CaO) compounds [4]. The oxidation reaction that occurs during calcination of eggshells and produces CaO is as follows:

$$CaCO_3 \xrightarrow{High\ temperature} CaO + CO_2$$

The presence of $Ca(OH)_2$ compounds in catalysts that have not been calcined cannot be separated from one of the series of processes for forming the CaO/Fe_2O_3 catalyst, namely the hydration process immediately before impregnation of CaO with Fe_2O_3. After calcination, a CaO/Fe_2O_3 catalyst will be formed [14]. Apart from that, the finding of $Ca(OH)_2$ compounds in calcined CaO/Fe_2O_3 catalysts occurred due to contact with air containing water vapor [15]. The reaction is as follows:

$CaO + H_2O \rightarrow Ca(OH)_2 + H_2O$

According to Helwani, et al. [14] the use of the CaO catalyst in the production of biodiesel from unedible oil using the transesterification reaction is actually very popular because it can be used directly. In this reaction, oxygen ions on the surface of the CaO catalyst will form hydrogen bonds between methanol and glycerine which causes the viscosity of glycerine to be high, thus forming a CaO suspension. In fact, CaO and glycerine are very difficult to separate from the final product, namely biodiesel. To overcome this problem, CaO should be impregnated with a catalyst support or other metal oxide and form a bifunctional catalyst. One metal oxide that has the potential to be used is iron (III) oxide (Fe_2O_3). The catalyst used in this research, namely Fe_2O_3, was successfully impregnated with CaO and detected at catalyst calcination temperature conditions of 800, 850, 900, 950°C, and was still contained in the catalyst that had been used in the biodiesel formation reaction for 4 hours. This high temperature is suitable for forming the Fe_2O_3 structure so that it can be impregnated with CaO to form a bifunctional catalyst.

The results of XRD analysis of the CaO/Fe_2O_3 bifunctional catalyst show the number of diffraction peaks shown in Figure 1. The diffraction peak values correlate with the crystallinity index of the catalyst, that is, the higher the diffraction peak, the higher the crystallinity index value. In this research, the CaO/Fe_2O_3 catalyst calcined at 800°C had the highest crystallinity index value of 91.028%. This shows that the catalyst produced has a fairly stable structure [16]. The crystallinity index values for the CaO/Fe_2O_3 catalyst at various calcination conditions are shown in Table 1.

Table 1.
Crystallinity index values for CaO/Fe_2O_3 catalysts

No	Catalyst treatment	Crystallinity (%)
1	Without calcination	45.145
2	Calcination at 750°C	71.162
3	Calcination at 800°C	91.028
4	Calcination at 850°C	68.874
5	Calcination at 900°C	68.698
6	Calcination at 950°C	26.776
7	Calcination after 4 h reaction at 800°C	72.043

3.1.2. Catalyst Characterization Using SEM

SEM-EDX analysis was carried out with the aim of knowing the morphology and surface microstructure of the catalyst used. In this research, SEM-EDX analysis was carried out twice, namely on catalyst conditions before and after being used in the reaction to make biodiesel. The surface morphology of the catalyst was tested using SEM (scanning electron microscope) with a magnification of 5000x. The results of the SEM catalyst observations can be seen in Figure 2.

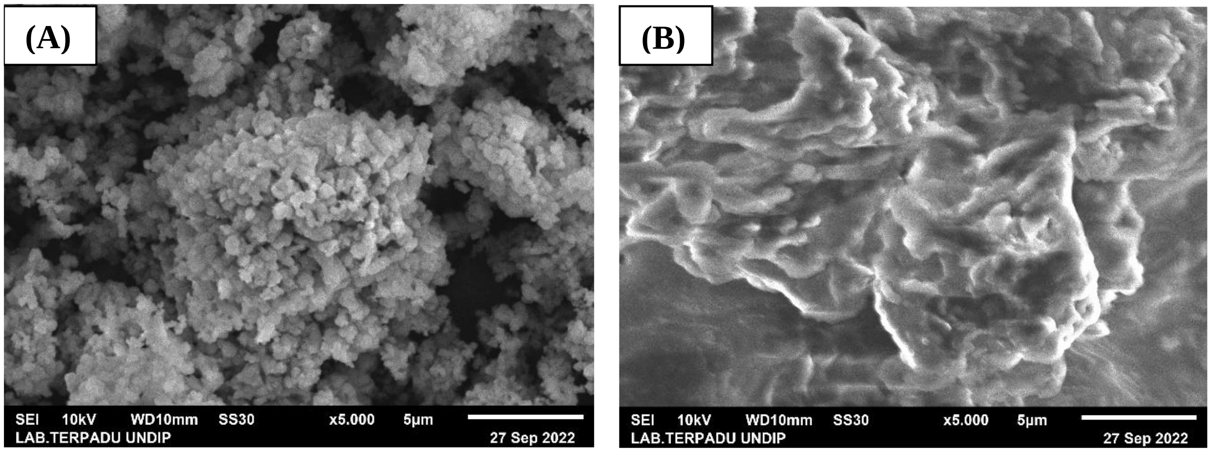

Figure 2.
Analysis results of SEM-EDX from CaO/Fe_2O_3 catalyst: (A) before reaction (B) after reaction

Figure 2(A) shows an image of the catalyst surface in the form of a collection of granular solid particles distributed unevenly on the catalyst surface. This indicates the presence of Fe_2O_3 catalyst support which precipitates on CaO [16]. The catalyst composition read in SEM-EDX analysis is CaO (73.15%-wt), Fe (17.53%-wt), and MgO (10.26%-wt).

Figure 2(B) shows an image of the catalyst surface in the form of a wide solid with a fine and shapeless structure that is evenly distributed on the catalyst surface. This indicates that the catalyst performance is relatively well distributed when the biodiesel formation reaction occurs [17]. The change in shape of the surface of the CaO/Fe_2O_3 catalyst after using the reaction for 4 hours occurs due to the sintering process, or damage to the pores and active surface of the catalyst which causes the catalyst to be deactivated [18]. The remaining catalyst composition after use in the reaction for 4 hours is CaO (3.38%-wt), Al_2O_3 (0.46%-wt), and Fe (0.11%-wt).

3.2. Esterification-Transesterification Process

3.2.1. Characteristics of Waste Cooking oil

The chemical composition of waste cooking oil was analyzed using GC-MS, while the analysis of physical properties of waste cooking oil included density, molecular weight, and levels of Free Fatty Acid (FFA). The components of waste cooking oil raw materials are shown in Figure 3 and Table 2.

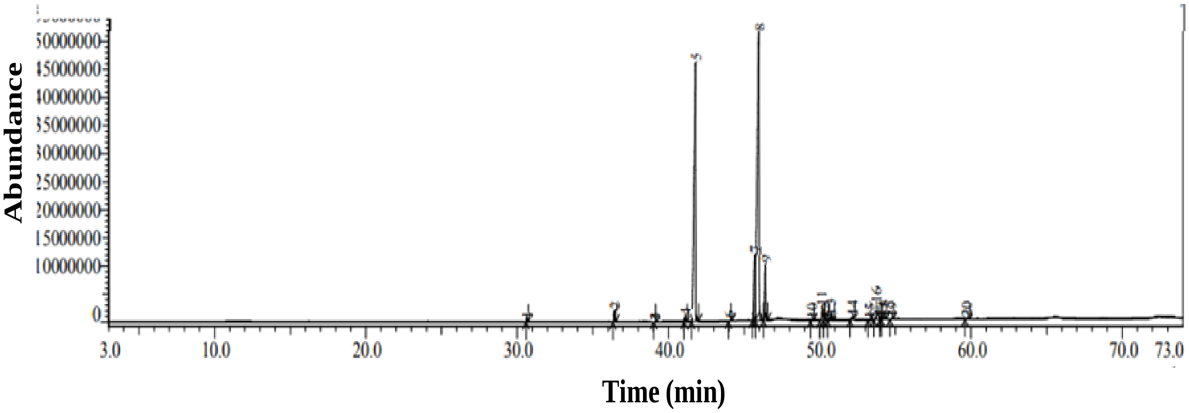

Figure 3.
Results of GC-MS analysis of waste cooking oil raw materials.

DOI: 10.55214/25768484.v9i1.4248

Table 2.
Components of waste cooking oil raw material.

No.	Compound name (IUPAC)	Compound name (Trivial)	Molecular formula	Composition (%)
1	Hexadecanoic acid	Palmitic acid	$C_{16}H_{32}O_2$	34.79
2	9,12-Octadecadienoic acid	Linoleic acid	$C_{18}H_{32}O_2$	8.25
3	9-Octadecenoic acid	Oleic acid	$C_{18}H_{34}O_2$	46.29
4	Octadecanoic acid	Stearic acid	$C_{18}H_{36}O_2$	4.00

The physical characteristics including density, molecular weight, and free fatty acid content of waste cooking oil were 0.9063 gram/ml, 895.2037 gram/mol and 5.076%, respectively. The GC-MS results in Figure 3 show that there are several components in waste cooking oil with quite high % composition, including palmitic acid, lenoleic acid, oleic acid, and stearic acid. Table 2 shows that the palimitic acid content is 34.79%, lenoleic acid is 8.25%, oleic acid is 46.29%, and stearic acid is 4%.

A significant difference between vegetable oil and waste cooking oil is the content of saturated and unsaturated fatty acids. Waste cooking oil has a higher saturated fat content than vegetable oil. This can occur due to the frying process using deep frying [19]. Saturated fatty acids are fatty acids whose hydrocarbon chains do not have double bonds. In waste cooking oil raw materials, saturated fatty acids were found which were characterized by the presence of hexadecanoic acid (palmitic acid) with 16 carbon bonds and octadecanoic acid (stearic acid) with 18 carbon bonds. On the other hand, unsaturated fatty acids are fatty acids that have double bonds. The waste cooking oil raw material used contains unsaturated fatty acids characterized by the presence of the compound 9,12-octadecadienoic acid (lenoleic acid) with double bonds at C-9 and C-12 and 9-octadecenoic acid (oleic acid) with double bonds at C-9 and C-12. The duplicate is in C-9 [20].

3.2.2. Effect of CaO/Fe_2O_3 catalyst calcination temperature on biodiesel yield

The catalyst is one of the factors that has quite an influence on the simultaneous esterification-transesterification reaction. The use of catalysts functions to speed up reactions and reduce activation energy [21]. In this research, the CaO/Fe_2O_3 catalyst was used in the biodiesel production process and variations were made in the calcination temperature of the catalyst to determine its effect on the yield of the biodiesel produced. Variations in the calcination temperature of each catalyst were carried out at temperatures of 750, 800, 850, 900, and 950°C. The results are presented in Figure 4.

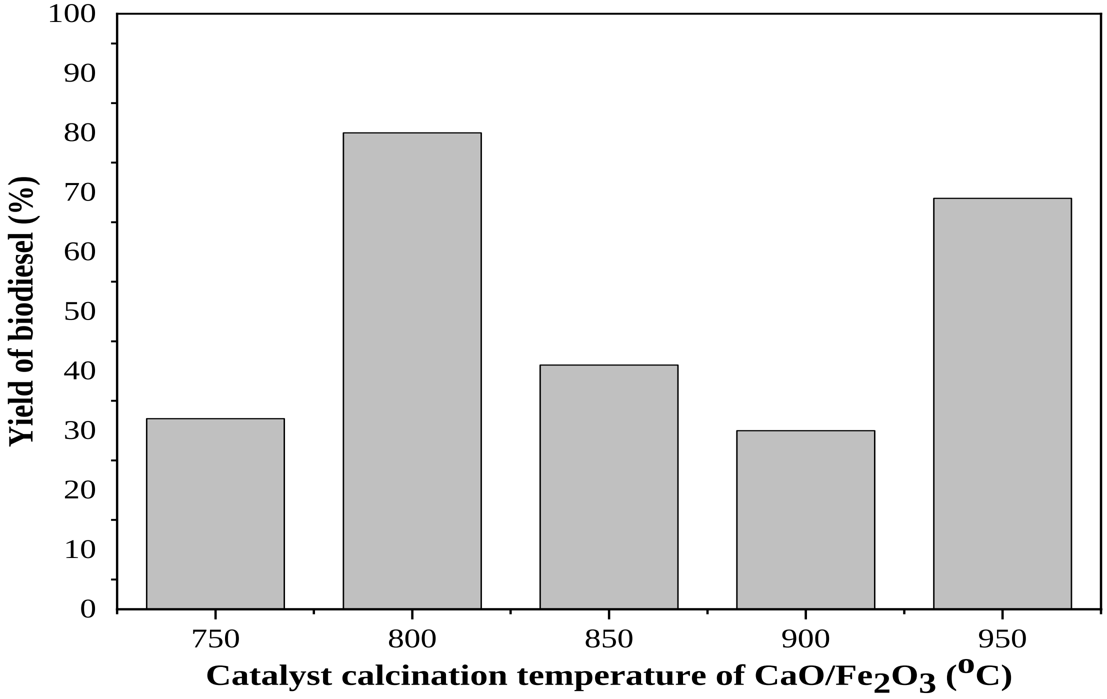

Figure 4.
Effect of catalyst calcination temperature on biodiesel yield.

Based on Figure 4, the biodiesel yield produced is fluctuating or not constant. At a calcination temperature of 750°C, a biodiesel yield of 32% was obtained, then it increased quite significantly at a temperature of 800°C with a biodiesel yield of 80%. Furthermore, there was a constant decrease in biodiesel yield at temperatures of 850°C and 900°C of 41% and 30%, respectively. At the highest calcination temperature variation, namely 950°C, biodiesel yield experienced a significant increase of 69%. Figure 4 also shows the optimum catalyst calcination temperature in this study, namely at a calcination temperature of 800°C.

According to Aleman-Ramirez, et al. [22] variations in the use of catalyst calcination temperature have a huge influence on catalyst performance in biodiesel production. Catalyst activation occurs at the appropriate catalyst synthesis temperature. The CaO/Fe_2O_3 catalyst goes through a calcination process first before finally being used to form biodiesel. The purpose of this calcination is to change the composition of the catalyst so that the active side of the catalyst is obtained which can work effectively in biodiesel production. During the calcination process, water (H_2O) is removed from the catalyst surface resulting in expansion of the crystallites and then an increase in the particle size of the catalyst [23]. The higher the calcination temperature is ideally successful in opening up more active sites on the catalyst so that it can produce more biodiesel yield. However, a calcination temperature that exceeds the resistance limit of a catalyst, usually up to 1000°C, will cause a decrease in the yield of biodiesel produced due to the sintering process, resulting in catalyst deactivation [24].

Calcination of the CaO/Fe_2O_3 catalyst at various temperature variations causes changes in the morphology of the catalyst as shown by the results of the XRD analysis in Figure 1. At 750°C calcination, the CaO composition is not completely formed and the Fe_2O_3 catalyst support is still not detected so the reaction cannot proceed perfectly and produces low biodiesel yields. Furthermore, at 800°C calcination, the CaO/Fe_2O_3 composition began to emerge, namely CaO and Fe_2O_3 appeared with quite high intensity so that the yield of biodiesel produced was also high. At the next calcination temperature variation, namely at 850°C and 900°C, there was a decrease in the yield of biodiesel produced as a result of the presence of $Ca(OH)_2$ content in the catalyst which came from contact with

DOI: 10.55214/25768484.v9i1.4248

outside air and caused a decrease in the catalytic activity of the catalyst [25]. The nature of CaO which easily absorbs water means that $Ca(OH)_2$ content cannot be avoided [15].

At a catalyst calcination temperature of 950°C, there was an increase in biodiesel yield from the previous 2 variables, but it still did not match the amount of biodiesel yield produced by a catalyst with a calcination temperature of 800°C. If we look at its composition, the catalyst at a calcination temperature of 950°C is not disturbed by the presence of $Ca(OH)_2$ compounds and still contains CaO and sufficient catalyst support so that it is able to produce good biodiesel yields. This also happened in research conducted by Yusuff, et al. [26] where the biodiesel yield produced from a catalyst with a calcination temperature of 800°C is greater than a catalyst calcined at a higher temperature (900–1000°C). When calcining a catalyst at a high temperature, the pores of the catalyst will become more open and the surface area of the catalyst will become wider. However, at calcination temperatures that exceed the maximum limit of catalyst resistance, the catalyst pores formed under previous conditions will experience damage due to the sintering process. The sintering process, which is a process to form a solid using heat without melting it first, is one of the factors causing catalyst deactivation. The sintering process can cause damage to the catalyst pores and loss of the active surface of the catalyst, causing the catalyst to be deactivated [18].

3.2.3. Effect of Esterification-Transesterification Reaction Time on Biodiesel Yield

One of the factors that influences the process of making biodiesel, especially using the simultaneous esterification-transesterification method, is reaction time. In this research, variations in reaction time were carried out to determine the effect on the biodiesel yield obtained. Variations were carried out at reaction times of 1, 2, 3, 4, and 5 hours. The results are depicted in Figure 5.

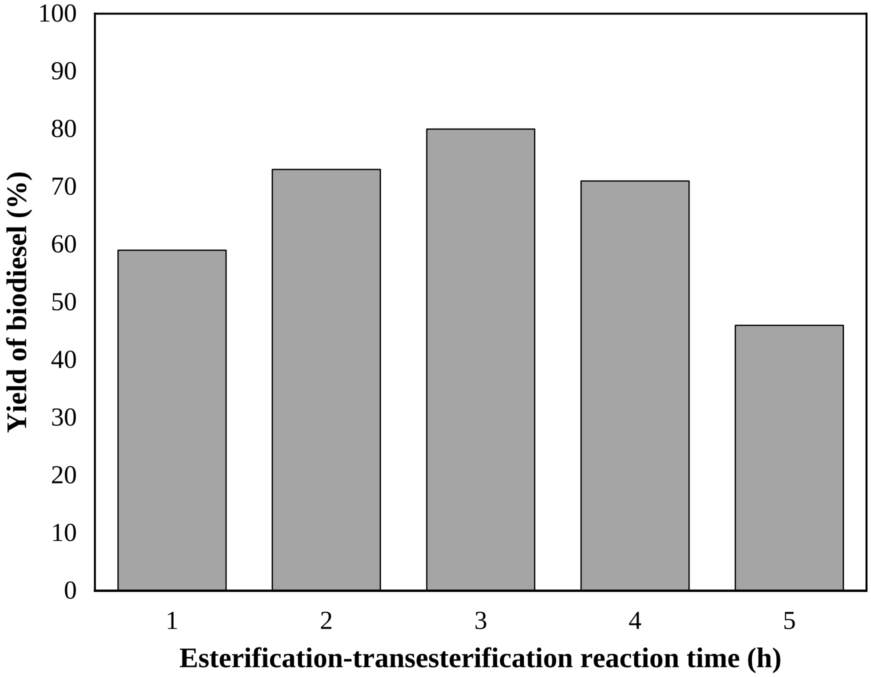

Figure 5.
Effect of reaction time on biodiesel yield.

Figure 5 shows that biodiesel yield increased quite significantly at the beginning and then decreased at the end. At reaction time 1, 2, 3, and 4 hours, the biodiesel yield was 59%, 73%, 80%, and 82%, respectively. Meanwhile, with a reaction time variation of 5 hours, the biodiesel yield obtained was lower than before, namely 46%. Figure 5 also shows that the optimum reaction time to produce biodiesel is a reaction time of 4 hours.

The transesterification reaction of methanol and triglycerides is an equilibrium reaction that requires interaction time between reactants to form a product [22]. This is in accordance with the research results obtained, namely the formation of a greater biodiesel yield when the reaction time is longer.

The mismatch occurred in the biodiesel formation reaction at the longest time, namely 5 hours, where there was a decrease in the yield of the biodiesel produced. Ideally, the longer the reaction time will produce better biodiesel yields because complete product transformation occurs [27]. Deviations occur because equilibrium in the reaction has been reached and causes the purity of the product to decrease [28].

3.2.4. Characterization of Biodiesel Product

The characteristics of biodiesel products can be determined based on several parameters including density, viscosity, %FAME and biodiesel yield values. In this study, the characteristics of biodiesel are determined based on the parameters of density and viscosity values. This value is then compared with the Indonesian National Standard (SNI) 7182-2015 value to determine the success of the CaO/Fe_2O_3 catalyst in producing biodiesel products and to determine the quality of the biodiesel products produced. The results of density and viscosity analysis of biodiesel products are presented in Tables 3 and 4.

Table 3.
Characteristics of biodiesel products at a reaction time of 3 hour.

Catalyst calcination températur (°C)	Parameter		
	Density (gr/ml)	Viscosity (cSt)	Yield of biodiesel (%)
750	0.8936	4.1250	32
800	0.8551	2.3744	80
850	0.8566	2.3695	41
900	0.8988	4.1928	30
950	0.8562	2.3824	69

Table 4.
Characteristics of biodiesel products at a calcination temperature of 800°C.

Reaction time (h)	Parameter		
	Density (gr/ml)	Viscosity (cSt)	Yield of biodiesel (%)
1	0.8542	2.3722	59
2	0.8573	2.3926	73
3	0.8551	2.3744	80
4	0.8509	2.3964	82
5	0.8628	2.6005	46

According to SNI 7182-2015, the biodiesel product permitted for use is biodiesel with a density value range of 0.85-0.9 gr/mL and a viscosity value of 2.3-6 cSt. Based on Tables 3 and 4, the biodiesel products produced from this research are in accordance with SNI 7182-2015. The highest density produced was 0.8988 gr/mL and the lowest was 0.8509 gr/mL If calculated, the average density produced from the biodiesel product as a whole is obtained by a density value of 0.8655 gr/ml. This shows that the CaO/Fe_2O_3 catalyst can be used to convert triglycerides while producing biodiesel products of fairly good quality. The resulting density is related to the calorific value of biodiesel. When the density is high, the calorific value will also be high and makes biodiesel difficult to burn [29]. The high density can be caused by the presence of soap in the methyl ester compound and will affect the combustion power of the methyl ester product [30]. A lower density value (not exceeding the standard) is actually needed to be able to control fuel flow in the injection pump and minimize smoke formation when operating at maximum power at higher loads [31].

Regarding the viscosity value parameters, it can be seen in Tables 3 and 4 that the viscosity of the biodiesel produced meets the SNI 7182-2015 standard. The highest viscosity value was 4.1928 cSt and the lowest was 2.3695 cSt. When the viscosity value of a solution is high, the solution will tend to be more liquid. Vice versa. Apart from that, the solution will have a higher ability to flow. Biodiesel with a high viscosity value will affect the performance of injectors in diesel engines and will have better lubricating or fuel lubrication properties. Viscosity, pressure, injection conditions and injector hole size will affect fuel atomization. When the viscosity is high, it will atomize the fuel into larger droplets with high momentum and have a tendency to collide with the relatively cooler cylinder walls and cause flame extinction and increased deposits, fuel spray penetration and engine emissions [32].

The best biodiesel product obtained with the highest yield value was then subjected to GC-MS analysis to determine the methyl ester content. The results of GC-MS analysis of biodiesel products are shown in Figure 6 and Table 5.

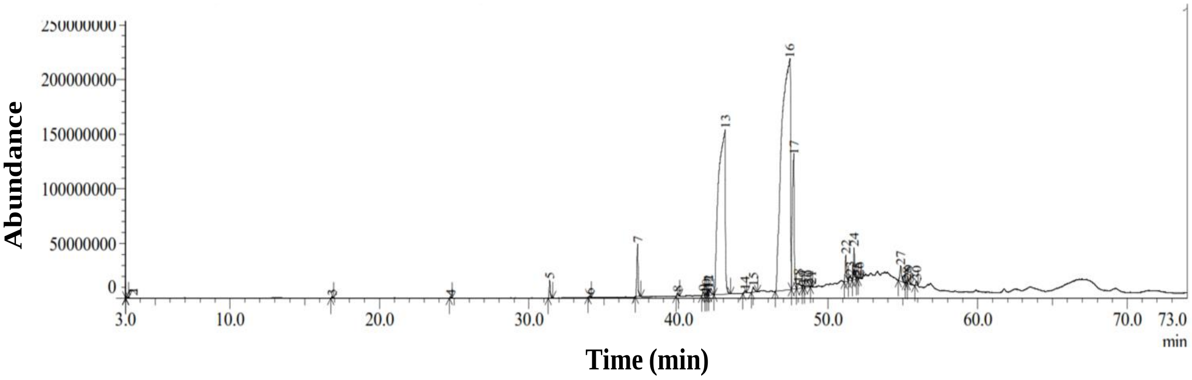

Figure 6.
Results of GC-MS analysis of biodiesel products with the highest yield.

Table 5.
Components of biodiesel products.

No.	Compound name	Synonym	Molecular formula	Composition (%)
1.	1,14-Octadecadienoic acid, methyl ester (CAS)	1,14-Octadecadienoic acid, methyl ester	$C_{19}H_{34}O_2$	0.05
2.	Octanoic acid, methyl ester (CAS)	Methyl Octanoate	$C_9H_{18}O_2$	0.04
3.	Decanoic acid, methyl ester (CAS)	Methyl Decanoate	$C_{11}H_{22}O_2$	0.04
4.	Dodecanoic acid, methyl ester (CAS)	Methyl Dodecanoate	$C_{13}H_{26}O_2$	0.51
5.	Tetradecanoic acid, methyl ester (CAS)	Methyl Myristate	$C_{15}H_{30}O_2$	1.80
6.	Pentadecanoic acid, methyl ester (CAS)	Methyl Pentadecanoate	$C_{16}H_{32}O_2$	1.10
7.	Oxiraneoctanoic acid, 3-octyl-, methyl ester (CAS)	Methyl 8-[(2R,3R)-3-octyloxiran-2-yl]Octanoate	$C_{19}O_{36}O_3$	0.07
8.	9-Hexadecenoic acid, methyl ester, (Z)- (CAS)	Methyl (Z)-pentadec-8-enoate	$C_{16}H_{30}O_2$	0.16
9.	9-Hexadecenoic acid, methyl ester, (Z)- (CAS)	Methyl (Z)-pentadec-8-enoate	$C_{16}H_{30}O_2$	0.32
10.	Hexadecanoic acid, methyl ester (CAS)	Methyl Palmitate	$C_{17}H_{34}O_2$	30.14
11.	9-Octadecenoic acid (Z)-, methyl ester (CAS)	Methyl Oleate	$C_{19}H_{36}O_2$	0.08
12.	Heptadecanoic acid, methyl ester (CAS)	Methyl Heptadecanoate	$C_{18}H_{36}O_2$	0.26
13.	9-Octadecenoic acid (Z)-, methyl ester (CAS)	Methyl Oleate	$C_{19}H_{36}O_2$	54.56
14.	Octadecanoic acid, methyl ester (CAS)	Methyl Stearate	$C_{19}H_{38}O_2$	7.22
15.	9,12-Octadecadienoic acid, methyl ester, (E,E)- (CAS)	Methyl trans,trans-9,12-Octadecadienoate	$C_{19}H_{34}O_2$	0.03
16.	11-Eicosenoic acid, methyl ester (CAS)	11-Eicosenoic acid, methyl ester	$C_{21}H_{40}O_2$	0.99
17.	Eicosanoic acid, methyl ester (CAS)	Methyl Arachidate	$C_{21}H_{42}O_2$	1.09
18.	Docosanoic acid, methyl ester (CAS)	Methyl Behenate	$C_{23}H_{46}O_2$	015

Based on Figure 6 and Table 5, it is found that biodiesel is formed from several main components which have the highest percentage composition, including methyl palmitate (30.14%), methyl oleate (54.56%), methyl stearate (7.22%), and methyl myristate. (1.80%). The percentage of the total composition of methyl esters contained in the biodiesel product was obtained at 97.61%. According to

SNI 7182-2015, the minimum methyl ester content for biodiesel products is 96.5%. This proves that the biodiesel product produced meets SNI standards. Meanwhile, the FAME yield calculation results obtained a value of 80.30%.

4. Conclusion

The calcination temperature of the CaO/Fe_2O_3 catalyst and the reaction time for biodiesel formation influence the yield of the biodiesel produced. If the calcination temperature exceeds the resistance limit of the CaO/Fe_2O_3 catalyst, sintering process occurs which causes catalyst deactivation and a decrease in biodiesel yield. The reaction time for biodiesel formation that exceeds the length of the equilibrium condition of a reaction causes the purity of the product to decrease, thereby causing a decrease in biodiesel yield.

In this research, the best biodiesel product was obtained with a biodiesel yield of 82% at a catalyst calcination temperature of 800°C and a simultaneous esterification-transesterification reaction time of 4 hours. The methyl ester composition formed was 97.61% with a FAME yield of 80.30%. This shows that the CaO/Fe_2O_3 catalyst has been successfully used in biodiesel production using the simultaneous esterification-transesterification method.

Funding:

This research was supported by the RIIM LPDP Grant and BRIN, grant number 947-03/UN7.D2/KS/XI/2022. We also thanks to the Diponegoro University.

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