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Study of green and sustainable heterogeneous catalyst produced from Javanese *Moringa oleifera* leaf ash for the transesterification of *Calophyllum inophyllum* seed oil

Destania Ayu Ramdhani, Wega Trisunaryanti*, Triyono

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Yogyakarta 55281, Yogyakarta

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Abstract

The transesterification of *Calophyllum inophyllum* seed oil into biodiesel using Javanese *Moringa oleifera* leaf ash catalyst with various reaction conditions has been completed. MA-500 (Moringa ash at 500°C for 3 h) and MA-900 (Moringa ash at 900°C for 3 h) catalysts were obtained by grinding Javanese old *Moringa oleifera* leaf (MP) and then calcined for 3 h at 500 and 900°C. The crude *Calophyllum inophyllum* seed oil was degummed (OD) prior to continue the esterification process (ODE). The MA-500 and MA-900 catalysts were tested for their activity and selectivity through the ODE transesterification with various catalyst weights (3, 6, and 9% (w/w)), reaction temperature (55, 60, and 65°C), oil: methanol mole ratio (1:3, 1:6, and 1:9), and reaction time (60, 90, 120, and 150 minutes). The results showed that the MA-500 and MA-900 catalysts contained 18.17% and 52.91% Ca respectively. The esterification reaction could reduce FFA levels to 89.82%, from 19.46% to 1.98%. ODE transesterification with MA-900 catalyst optimum reaction conditions with a catalyst weight of 3%, reaction temperature of 60°C, oil: methanol mole ratio of 1:9, and reaction time of 120 min, 76.17% FAME yield was observed. The MA-900 catalyst has the potential to be an effective green catalyst.

Keywords: Biodiesel; *Calophyllum inophyllum*; *Moringa oleifera*; transesterification

1. Introduction

Along with economic development, population growth, and regional development, most countries use the main energy source in the form of fossil fuels. In fact, for being non-renewable, fossil fuel reserves are dwindling [1,2]. An alternative to fossil fuels, therefore, is required such as through biodiesel production. Biodiesel is considered an alternative fuel that can overcome the problem related to the availability of non-renewable fossil fuels [3,4]. Compared to other conventional fossil fuels like petroleum, it also has a higher flash point and lower carbon monoxide emissions, which can reduce air pollution [5]. Biodiesel, also called as ‘green’ diesel, has the advantage of having good sustainability due to its renewable source [6]. It possesses a number of properties including being easily decomposed, non-toxic, having a high cetane number, and having good engine lubrication properties [1, 7]. Biodiesel is made from renewable sources such as vegetable oils or animal fats and is more easily decomposed compared to animal fossil fuels [8,9].

In general, biodiesel can be produced through the transesterification reaction of vegetable or animal oils using short-chain alcohols such as methanol or ethanol with the help of a catalyst [10]. The basic principle of transesterification is that one alcohol occupies a fatty acid to produce an ester. The reactions occurred are reversible and require excess alcohol to accelerate the equilibrium toward the products. The stoichiometry for this reaction is 3:1 alcohol to fat. However, in practice, this ratio commonly increases from 6:1 to 12:1 to achieve product yields [11]. Generally, ethanol or methanol is used, with methanol preferred because mild reaction conditions could be realized with methanol [12]. Also, when methanol is used in the transesterification process, the viscosity of the biodiesel obtained is lower than that of the biofuel obtained from other alcohols (ethanol, butanol) [1].

The biodiesel production through a transesterification reaction requires a catalyst to produce a reasonably high yield of the fuel under milder conditions. Generally, it involves homogeneous catalysts, but this treatment is susceptible to corrosion and the difficulty of product separation [13,14]. Hence, the heterogeneous catalyst is more suitable for biodiesel production with the benefit of desirable economic value and profitability, as it can be easily separated and regenerated [15]. In many studies, heterogeneous catalyst has been promoted as a good catalyst due to their excellent properties (environmentally friendly and non-toxic) [16]. For the purpose of green chemistry, some researches have focused on the exploration and development of new heterogeneous catalysts from renewable sources [17] to add value to them and reduce the environmental pollution they generate when they are burnt as a cheap fuel. Also, catalysts derived from biomass have

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* Corresponding author.
Email: wegats@ugm.ac.id
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certain characteristics such as non-toxicity, biodegradability, containing a variety of mineral constituents, surface area, and pore structure that can be tuned [18].

Several biomass residues such as eggshells [19], fruit peels [20], and waste oyster shells [21] have been used as a sustainable precursor for catalyst development to synthesize biodiesel. The use of biomass residues as catalysts, for this reason, will significantly impact the market value of biodiesel production [22, 23]. In this study, a catalyst derived from biomass in the form of Javanese old *Moringa oleifera* leaf was used. Javanese old *Moringa oleifera* leaf has a high content of Ca metal. Every 100 g of Moringa leaf contains Ca (2.003%), K (1.324%), Mg (0.368%), P (0.204%), and Na (0.87%) [24]. It also contains polyphenols, alkaloids, tannins, carotenoid, flavonoids, and ascorbic acid [25]. Moreover, the use of the Javanese old *Moringa oleifera* leaf as a catalyst is valued as more green and renewable. The high CaO content in Javanese old *Moringa oleifera* leaf is obtained after calcining Moringa leaf powder at high temperatures into Moringa leaf ash to be used as a catalyst [8]. CaO is a non-corrosive, environmentally friendly, and nontoxic heterogeneous catalyst with a high basicity property. It has been discovered to be an excellent base catalyst candidate, such as for biodiesel production [26]. This makes Moringa leaf ash as a sustainable competitive precursor in the development of heterogeneous catalysts.

As an agricultural country, Indonesia has many types of plants as a source of biodiesel, spread specifically throughout the archipelago, one of which is *Calophyllum inophyllum* plant. *Calophyllum inophyllum Linn* seed oil is a vegetable oil that has the potential to be used as a raw material in biodiesel production. It is composed of four main types of fatty acids, namely oleic acid (58.13 wt%), palmitic acid (18.46 wt%), linoleic acid (12.26 wt%), and stearic acid (11.41 wt%) [27]. *Calophyllum inophyllum* seed oil is a non-toxic substance with better lubrication than petroleum oil and is easy to decompose due to high flash points [28,29].

One of the advantages of *Calophyllum inophyllum* seed oil is that it is a non-edible oil, so its use in biodiesel production does not compete with food needs [30, 31]. *Calophyllum inophyllum* seed oil can produce relatively high yields compared to other types of plants (palm 46-54%, *jatropha curcas* 40-60%, and *Calophyllum inophyllum* 40-73%) [2]. The most attractive part of utilizing *Calophyllum inophyllum* is that its primary natural habitat grows along the coastal line, which hardly interferes with agricultural land [17,31]. However, *Calophyllum inophyllum* seed oil has a number of weaknesses: a dark green appearance, dirty, and high levels of FFA. The high level of FFA and water content could support the saponification reaction, resulting in the deactivation of the catalyst; thus reducing the methyl ester or biodiesel yield [32]. Therefore, it is necessary to pre-treat *Calophyllum inophyllum* seed oil before being used for transesterification, namely degumming and esterification processes. The degumming process aims to separate sap or dirt from carbohydrates, resin, proteins, and residues. Meanwhile, the esterification process aims to reduce the levels of Free Fatty Acid (FFA) in the oil [33]. Pre-treatment on *Calophyllum inophyllum* seed oil aims to reduce the contents of FFA and water contained in the oil [34], and the conversion of *Calophyllum inophyllum* seed oil into biodiesel in the second step reaction (transesterification) can be maximized because all the fatty acid contents in *Calophyllum inophyllum* seed oil can be converted into biodiesel [14].

Based on the above background, in this research synthesis, characterization, activity, selectivity tests, and usability tests (lifetime) of Moringa leaf ash catalysts were carried out in the transesterification of *Calophyllum inophyllum* seed oil under various reaction conditions to biodiesel. The hope in this study is to follow the principle of the green economy, which focuses on green economic growth that is environmentally friendly, enabling it to be developed as a sustainable energy source.

2. Materials and Methods

2.1. Materials

Javanese old *Moringa oleifera* leaf from Yogyakarta, *Calophyllum inophyllum* seed oil from the Physical Chemistry Laboratory FMIPA UGM, H_3PO_4 (85%), H_2SO_4 (98%), isopropyl alcohol, phenolphthalein indicator, KOH (0.1N), methanol (97%) from Merck & Co., and distilled water from CV Progo Mulyo.

2.2. Catalyst preparation

Our method was adapted from Taslim's method [35]. This stage started by washing Javanese old *Moringa oleifera* leaf using distilled water. Javanese old Moringa leaves were then dried for 1 day in the sun before going to the drying process using an oven at 105˚C for 45 min. Dried Moringa leaves were crushed using a mortar to obtain Moringa leaf powder (MP). Furthermore, MP was calcined in a furnace for 3 h at 500°C (MA-500) and 900°C (MA-900).

2.3. Catalyst characterization

MA-500, MA-900, MP, and CaO catalysts were characterized using Fourier-Transform InfraRed (FT-IR, SHIMADZU Prestige 21) to analyze functional groups, X-Ray Diffraction (XRD, Bruker D2 Phase 2 Gen) to identify the compositions of the catalysts and to recognize the forms of crystal catalysts, and Scanning Electron Microscope (SEM-EDX, JEOL JSM-6510) to see the surface morphology and identify mineral composition in the developed catalysts.

2.4. Pre-treatment Calophyllum Inophyllum seed oil

2.4.1. Degumming crude Calophyllum Inophyllum seed oil (OD)

Our method was adapted from Atabani's method [36]. Crude *Calophyllum inophyllum* seed oil was heated at a temperature of 60˚C, and then 2% (wt/wt) of 85% H_3PO_4 solution was added to the weight of the oil, accompanied by stirring for 2 h. The mixture was then put into a separatory funnel and washed using warm distilled water (60˚C). The top layer (oil) was heated at 105˚C (OD). OD oil was tested for FFA levels, and then characterized using FTIR and GC-MS. Acid number, conversion factor, and FFA content were then calculated using the following equation:

$$\text{Acid number} = \frac{\text{V KOH (mL)} \times \text{N KOH (N)} \times \text{Mr KOH}}{\text{Weight of oil (g)}} \quad (1)$$

$$\text{Conversion factor} = \frac{\text{Mr KOH} \times 10}{\text{Mr FFA } (278.0329 \frac{\text{g}}{\text{mol}})} \quad (2)$$

$$\text{FFA content (\% FFA)} = \frac{\text{Acid number}}{\text{Conversion factor}}\% \quad (3)$$

2.4.2. *Calophyllum inophyllum seed oil esterification* (ODE)

Our method was adapted from Atabani's method [36]. OD oil was mixed with methanol (oil: methanol mole ratio 1:40) and 13% (v/v) H_2SO_4 solution to the volume of oil in a three-neck flask. The mixture was refluxed at 60˚C for 60 min accompanied by stirring at 300 rpm. The mixture was put in a separatory funnel, and then the lower layer was washed using warm distilled water (60˚C). The top layer was taken and heated at a temperature of 105˚C (ODE). ODE oil was tested for FFA levels, and characterized using GC-MS.

2.5. Catalyst activity test

2.5.1. Best catalyst test

Our method was adapted from Betiku's method [37]. The best catalyst test used catalysts in the form of CaO, MA-500, and MA-900, which were tested through the transesterification process. The best catalyst test was carried out to obtain methyl ester conversion with MA-500 catalyst or MA-900 catalyst which was close to the conversion of methyl ester produced from CaO catalyst. The catalyst was weighed at 3% by weight of the oil and added methanol (oil: methanol mole ratio 1:6), and then stirred at 250 rpm for 30 min. ODE oil was put into a three-neck flask and added to the methanol-catalyst mixture, and then refluxed at 60˚C for 120 min accompanied by stirring at 300 rpm. The mixture was put in the falcon and left for 24 h until 3 layers were formed. The top layer was a liquid product, the middle layer was glycerol, and the bottom one was a catalyst. The top layer was centrifuged for 15 min at 3500 rpm and washed using warm distilled water (60˚C). It was taken and heated at a temperature of 105˚C. The transesterified liquid product was characterized using GC-MS. The conversion of transesterified liquid products, methyl esters, and non-methyl esters, was then carried out by testing the activity and selectivity of the catalyst.

$$\text{Liquid product (LP) (wt\%)} = \frac{\text{WPC}}{\text{WODE}} \times 100\% \quad (4)$$

$$\text{Methyl ester (ME) (wt\%)} = \frac{\text{WPC} \times \text{LME}}{\text{WODE}}\% \quad (5)$$

$$\text{Non methyl ester (wt\%)} = \%\text{LP} - \%\text{ME} \quad (6)$$

where:
W_{PC} = Weight of liquid product transesterification (g)
W_{ODE} = Weight of oil used during transesterification (g)
L_{ME} = Area of methyl ester on GC-MS analysis (%)
W_{ODE} = Weight of oil used during transesterification (g)

2.5.2. Variation of transesterification conditions

Our method was adapted from Betiku's method [37]. MA-900 catalyst was used in the transesterification of *Calophyllum inophyllum* seed oil to determine the optimum reaction conditions for various variations. MA-900 catalyst (3, 6, and 9% wt of oil) was added in methanol (oil: methanol mole ratio 1:3, 1:6, and 1:9), and stirring was carried out at 250 rpm for 30 min. ODE oil was put into a three-neck flask, added to the methanol-catalyst mixture, and refluxed at (55, 60, and 65˚C) for (60, 90, 120, and 150 min) accompanied by stirring at 300 rpm. The mixture was put into the falcon and left for 24 h until 3 layers were formed.

The top layer was a liquid product, the middle layer was glycerol, and the bottom one was a catalyst. The top layer was centrifuged for 15 min at 3500 rpm and washed using warm distilled water (60˚C). The top layer was taken and heated at a temperature of 105˚C. The transesterified liquid product was characterized using GC-MS. A catalyst usability test was carried out with the repeated use of MA-900 catalyst by 3 times in the transesterification of *Calophyllum inophyllum* seed oil with optimum reaction conditions in producing transesterified liquid products. The transesterified liquid product was characterized using GC-MS. The conversion of transesterified liquid products, methyl esters, and non-methyl esters, was then carried out by testing the activity and selectivity of the catalyst.

A catalyst usability test was carried out with the repeated use of MA-900 catalyst by 3 times in the transesterification of *Calophyllum inophyllum* seed oil with optimum reaction conditions in producing transesterified liquid products. The transesterified liquid product was characterized using GC-MS. The conversion of transesterified liquid products, methyl esters, and non-methyl esters, was then carried out by testing the activity and selectivity of the catalyst. A catalyst usability test was carried out with the repeated use of MA-900 catalyst by 3 times in the transesterification of *Calophyllum inophyllum* seed oil with optimum reaction conditions in producing transesterified liquid products. The transesterified liquid product was characterized using GC-MS. The conversion of transesterified liquid products, methyl esters, and non-methyl esters, was then carried out by testing the activity and selectivity of the catalyst.

3. Results and Discussion

3.1. Characterization of MP, MA-500, MA-900, and CaO Catalysts

3.1.1. FTIR analysis

Characterization with FTIR on the catalyst material was carried out to determine the functional groups present in the sample. For structure elucidation, the region with a wave number of 400-4000 cm^{-1} on the left side of the IR spectra was useful for identifying functional groups. Figure 1 shows the results of the infrared spectrophotometer analysis for MP, MA-500, MA-900, and CaO catalysts. FTIR analysis results for MP are shown in the spectrum (a), MA-500 is shown in the spectrum (b), MA-900 is shown the in spectrum (c), and CaO is shown in the spectrum (d).

The use of MA-500 and MA-900 materials as catalyst were obtained from the calcination process at 500 and 900°C for 3 h to obtain the highest metal oxide content.

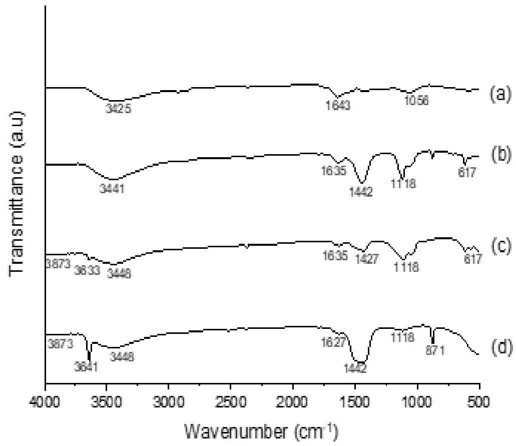

Fig. 1. FTIR spectra of (a) MP, (b) MA-500, (c) MA-900, and (d) CaO

In the MA-900 and CaO materials, an absorption band in the form of -OH stretching vibrations appeared at wave number 3873.06 cm^{-1}. The -OH group with a sharp peak was the characteristic of CaO [35]. Then, in MA-500, MA-900, and CaO materials, absorption bands appeared in the form of vibrations from alkane bond (-C-H) at wave numbers 1427.32 and 1442.75 cm^{-1}. In the four samples, the stretching vibrations of the ester group (-CO-) were found at wave numbers 1080-1200 cm^{-1} [38]. Then, the O-C-O stretching bond from carbonate appeared at wavenumbers 1627.92; 1635.64; and 1643.35 cm^{-1} [5]. At wave numbers 400-1040 cm^{-1}, the -O group binds to metals [39]. The presence of the -O group indicated the success of the calcination due to the formation of metal oxide compounds [40] in the MA-900 material, which had a higher intensity compared to the MA-500 material.

3.1.2. XRD analysis

Characterization by XRD of the catalyst material was carried out to identify the crystalline phase in the material from the sample used. This characterization also served to determine the regularity of the structure of the catalyst material before and after calcination. The results of the MP analysis using XRD are shown in Figure 2.

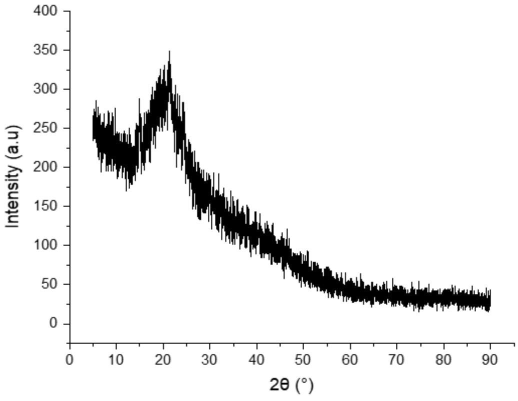

Fig. 2. MP diffractogram

The 2θ value on the diffractogram could be compared with the characteristic 2θ value on the Joint Committee on Powder Diffraction Standard (JCPDS). Based on the XRD diffractogram of the MP material, it could be seen that MP displayed the characteristic peaks of dolomite ($CaMg(CO_3)_2$), which was confirmed according to JCPDS standard data 01-071-1662 and calcite ($CaCO_3$), which corresponded to JCPDS standard data 00-017-0763. The characteristic peaks of dolomite were at 2θ =14.8380° and 24.3212°. Whereas, the characteristic peaks of calcite were at 2θ =21.3947° and 29.8842°. The analysis results for MA-500, MA-900, and CaO catalysts using XRD are shown in Figure 3.

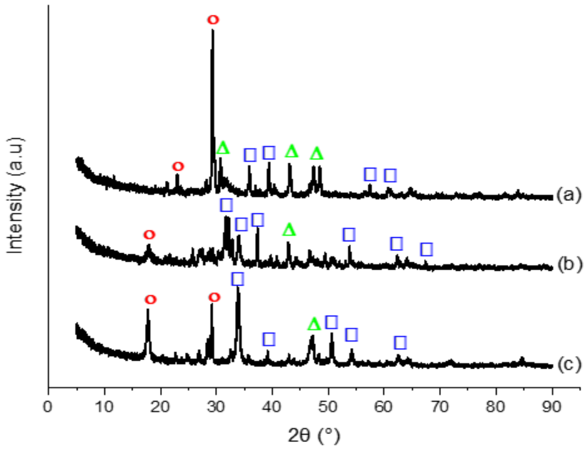

Fig. 3. Diffractogram of (a) MA-500, (b) MA-900, and (c) CaO with o ($CaCO_3$),Δ ($CaMg(CO_3)_2$), and □ (CaO)

On the diffractogram of the MA-500 material, a new peak appeared and indicated as a characteristic peak of calcium oxide (CaO). The peak was expected to start appearing at 2θ = 37.3333°. Meanwhile, on the diffractogram of the MA-900 material the characteristic peaks of CaO started to appear at 2θ = 32.1511°; 37.3333°; and 53.8298°, which was confirmed according to the CaO standard (JCPDS No. 00-037-1497). This matter indicated that at a temperature of 900°C, most of the $CaCO_3$ has been converted to CaO [43]. The $CaCO_3$ compound remained, but with very low intensity. From the XRD pattern of the MA-900 material, the calcination temperature was at 900°C as a suitable condition to produce a CaO catalyst from old Moringa leaf powder [44]. The high content of CaO contributes to the efficiency of the transesterification process.

3.1.3. SEM-EDX analysis

Characterization with SEM-EDX on the catalyst material was carried out to determine the morphological structure of the catalyst surface and the elements contained in the catalyst material. The results of the identification of MP, MA-500, MA-900, and CaO materials using SEM-EDX are shown in Figure 4.

As shown in Figure 4, the morphological changes between Moringa leaf powder and Moringa leaf ash could be observed. The surface of Moringa leaf powder had a smoother appearance with non-uniform particle shapes. Meanwhile, Moringa leaf ash had a regular surface appearance, looked rougher, porous, and had smaller particles. On the surface, the MA-900 material had a rougher and more porous appearance than the MA-500 material. This was due to the high calcination temperature used to turn the powder into Moringa leaf ash. Calcination caused the particles to become uniform with a more regular distribution of particles. In addition, the temperature-increased calcination caused the volatile components contained to evaporate [43]. They resulted in the formation of more and more pores. The composition of the constituents in MP, MA-900, and CaO as presented in the EDX data can be seen in Table 1.

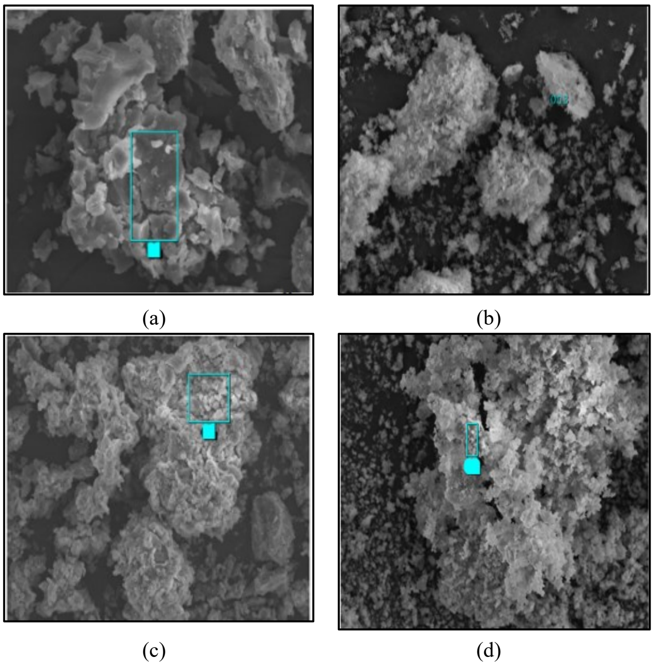

Fig. 4. SEM images of (a) MP, (b) MA-500, (c) MA-900, and (d) CaO

Table 1. Analysis of elemental content in MP, MA-500, MA-900, and CaO with EDX

Component	Composition (%)			
	MP	MA-500	MA-900	CaO
C	85.57	12.68	9.40	-
O	4.90	50.80	27.28	28.53
Mg	1.14	3.43	2.09	-
Al	0.21	0.04	0.11	-
S	1.30	2.25	2.13	-
K	3.71	3.26	5.82	-
Ca	3.18	26.94	52.91	71.47
Si	-	0.35	0.16	-
P	-	0.26	0.11	-

In MP material, it can be seen that the element carbon dominated the composition of the material. It was possible since most of the composition of living things are composed of carbon and oxygen. In MA-500, MA-900, and CaO the levels of metal oxides increased after the calcination process because the volatile and carbon content in Moringa leaf ash decreased after going through the calcination process so that Moringa leaf ash was obtained which is a mixture of metal oxides, such as CaO and K_2O that acted as a catalyst in the production of methyl esters. The calcination process aims for thermal decomposition and reduces the volatile fractions in a material [44].

3.2. Characterization of Calophyllum Inophyllum seed oil

In biodiesel production, the determination of the acid number in oil becomes an important factor. The presence of an acid number indicates the amount of free fatty acids in the oil calculated based upon the molecular weight of the fatty acids. In general, pure oil has an FFA content of about 2%, so it can be directly processed by transesterification. However, if the FFA content of the oil is above 2%, it will cause a saponification reaction [45]. Ma and Hanna [46] stated that the production of biodiesel yield is highly dependent upon the FFA content, where the conversion will decrease as the FFA content increases. Therefore, it is necessary to carry out the pre-treatment stages in the form of degumming and esterification processes first.

Degumming aims to remove gum, which consists of phosphatides and impurities. Meanwhile, the esterification stage is used to convert FFA to methyl ester and reduce the FFA content in the oil. Thus, it can proceed to the transesterification stage for biodiesel production [47]. In this esterification step, the mole ratio of oil: methanol 1:40 is used. This is because the FFA of oil will be reduced as a result of the excessive use of methanol. The reversible esterification reaction caused by methanol forces the reaction to shift the equilibrium toward the product, resulting in a decrease in the oil's FFA [48]. Therefore, it is necessary to figure out the FFA content in *Calophyllum inophyllum* seed oil by testing it to determine the transesterification method to be used. FFA levels were determined by titrating with a KOH base. The results of the FFA level test can be seen in Table 2.

Table 2. Characteristics of FFA levels in *Calophyllum inophyllum* seed oil

Test Parameters	Test result	
	Before esterification	After esterification
Color	Reddish brown	Reddish yellow
Acid number (mg KOH/g *Calophyllum inophyllum* seed oil)	39.27	4.0018
FFA content (%)	19.46	1.98

As seen in the table above, after the pre-treatment of *Calophyllum inophyllum* seed oil, the FFA content decreased by 89.82% from 19.46% to 1.98%. As a result, *Calophyllum inophyllum* seed oil could proceed to the transesterification stage.

3.3. Effect of reaction conditions on fatty acid methyl ester (FAME) yield

3.3.1. Effect of catalyst weight

In this study, variations in catalyst weight were carried out, namely 3, 6, and 9%. The existence of this variation aimed to determine the effect of each catalyst weight variation on the resulting methyl ester. The catalyst promotes the transesterification reaction by accelerating the reaction rate to realize high biodiesel without being consumed in the reaction [49]. The effect of catalyst weight was studied using a fixed variable oil: methanol ratio of 1:9, a temperature of 60°C, and a time period of 120 min. The effect of catalyst weight on methyl ester conversion can be seen in Figure 5.

Variations in the catalyst weight of 3, 6, and 9% each resulted in a methyl ester conversion of 76.17; 74.49; and 69.98%. Based on the research results, 3% catalyst weight resulted in the highest conversion of methyl esters. Meanwhile, the weight of the catalyst above 3% caused a decrease in the conversion of the methyl ester obtained. This was because the use of a catalyst above 3% caused the catalyst and reactant mixture to become thicker, and the viscosity increased, making it difficult for the mass transfer process due to the collisions between the molecules which are not free. Therefore, the intermolecular interaction forces weaken and cause a decrease in the methyl ester conversion [50]. The study from Oladipo et al. [51] showed that the optimum amount of catalyst from papaya peel was 3.5%. From this description, it is necessary to use the smallest amount of catalyst that produces the highest biodiesel yield.

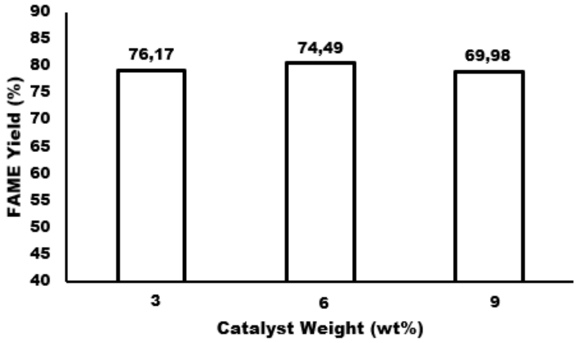

Fig. 5. Effect of catalyst weight on methyl ester conversion at 60 °C, 1:9 mole ratio of oil to methanol, and 120 min of reaction time

3.3.2. *Effect of reaction temperature*

In this research, the variations of reaction temperature were carried out, namely 55, 60, and 65°C. To study the effect of temperature, the reaction was carried out using a constant variable catalyst weight of 3% (optimum from run 1), a ratio of oil to methanol 1:9, and a time of 120 min. The effect of reaction temperature on the conversion of methyl esters can be seen in Figure 6.

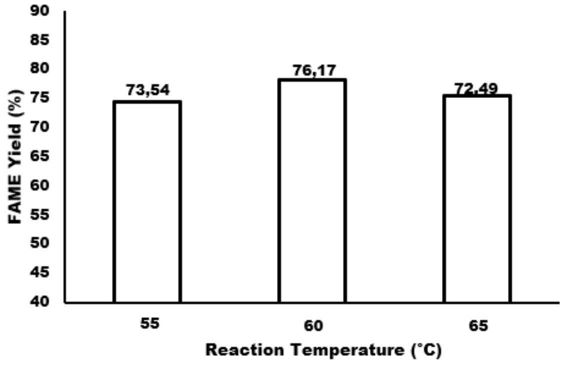

Fig. 6. Effect of reaction temperature on methyl ester conversion under conditions of 3% catalyst weight, 1:9 mole ratio of oil to methanol, and 120 min of reaction time

The existence of this variation aims to determine the effect of each reaction temperature variation on the resulting methyl ester. The transesterification reaction of oil and methanol to produce biodiesel is an endothermic reaction that requires an elevated temperature. Besides, reaction temperature facilitates the collision of reactants' molecular species to enhance miscibility and interactions that result in bond breaking and cleavages [52].

Variations in reaction temperature of 55, 60, and 65°C each resulted in a methyl ester conversion of 73.54; 76.17; and 72.49%. Based on the research results, the reaction temperature of 60°C produced the highest conversion of methyl esters. This occurred because, in the oil-methanol-catalyst system, three phases would form due to diffusion resistance. As a result, sufficient heat energy is required to mix and react with the three phases [53]. However, at temperatures above the boiling point of methanol (64.7°C) it caused a decrease in the methyl ester conversion. This was due to the uncontrolled evaporation of methanol, making the availability of methoxy decreased [54,55].

3.3.3. *Effect of mole ratio of oil to methanol*

In this research, the variations of the mole ratio of oil to methanol namely 1:3, 1:6, and 1:9 were carried out. The existence of this variation aimed to determine the effect of each variation in the mole ratio of oil to methanol in producing methyl ester. To study the effect of the mole ratio of oil to methanol, a fixed variable weight of the catalyst was 3% (optimum run 1), the reaction temperature was 60°C (optimum run 5), and the time period was 120 min. The effect of the mole ratio of oil to methanol in producing methyl ester conversion can be seen in Figure 7.

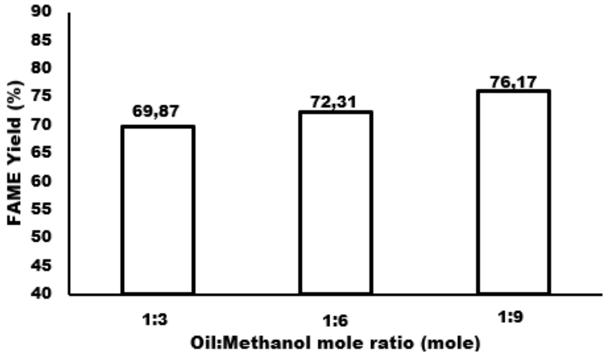

Fig. 7. Effect of the oil: methanol mole ratio on methyl ester conversion at 3% catalyst weight, temperature 60°C, and reaction time of 120 min

Variations in the mole ratio of oil to methanol, namely 1:3, 1:6, and 1:9 respectively resulted in a methyl ester conversion of 69.87; 72.31; and 76.17%. Based on the research results, the mole ratio of oil: methanol 1:9 resulted in the highest conversion of methyl esters. The increasing methanol could shift the equilibrium-based transesterification to produce more biodiesel by promoting the formation of methoxy groups on the catalyst surface [56]. Stoichiometrically, it took 3 moles of methanol and 1 mole of triglyceride to produce 3 moles of methyl ester and 1 mole of glycerol. However, the transesterification reaction is reversible, so to produce more alkyl esters, the equilibrium must be shifted towards the product. The method commonly used is to use methanol in excess [57]. This is because the conversion of methyl ester will increase as the mole ratio of oil to alcohol increases [58]. However, the use of excess methanol is only effective to a certain extent in increasing the conversion of methyl esters.

3.3.4. *Effect of reaction time*

In this study, the variations of reaction time were carried out, namely 60, 90, 120, and 150 min. The existence of this variation aimed to determine the effect of each reaction time variation in producing methyl ester. To study the effect of reaction time, the catalyst weight fixed variable was 3% (optimum from run 1), the reaction temperature was 60°C (optimum run 5), and the mole ratio of oil to methanol was 1:9 (optimum from run 9). The effect of reaction time in producing methyl ester conversion can be seen in Figure 8.

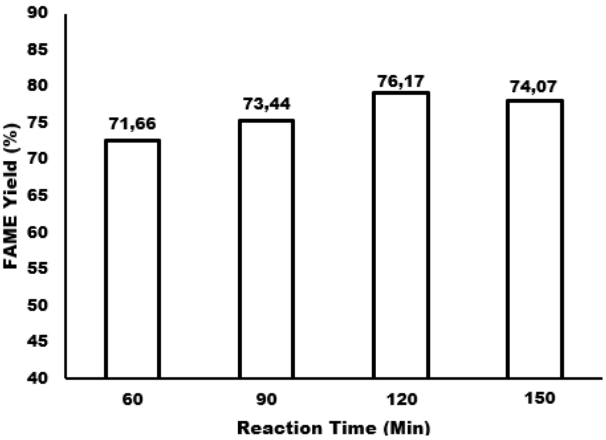

Fig. 8. The effect of reaction time on the conversion of methyl esters under conditions of 3% catalyst weight, the temperature of 60 °C, and a mole ratio of oil to methanol of 1:9

The variations of reaction time, namely 60, 90, 120, and 150 min each resulted in a methyl ester conversion of 71.66; 73.44; 76.17; and 74.07%. Based on the research results, the reaction time of 120 min resulted in the highest conversion of methyl esters. In transesterification, using heterogeneous catalysts to produce methyl esters requires a longer reaction time than homogeneous catalysts. This is because the existence of obstacles in mass transfer [59]. Increasing the reaction time can cause the viscosity of the methyl ester to decrease, thereby increasing the conversion of methyl ester. However, when the reaction time continues to increase, the transesterification reaction will shift towards the reactants and cause an increase in the viscosity of the methyl ester. The increase in the viscosity of this methyl ester can cause the conversion of methyl ester to decrease [60].

3.4. Catalyst Selectivity and activity test

3.4.1. Activity and selectivity tests on MA-900 and CaO catalyst

The activity and selectivity tests of the MA-900 catalyst were carried out under various conditions of *Calophyllum inophyllum* seed oil transesterification reaction and repeated use of MA-900 catalyst at optimum reaction conditions (3% catalyst weight, 60°C reaction temperature, 1:9 oil: methanol mole ratio, and reaction time of 120 min). The catalyst activity test was defined as the conversion of the liquid product obtained from the transesterification process of *Calophyllum inophyllum* seed oil before being characterized using GC-MS. Meanwhile, the catalyst selectivity test was defined as the actual amount of methyl ester compound contained in the transesterification liquid product. The activity and selectivity test results of the MA-900 catalyst in the *Calophyllum inophyllum* seed oil transesterification process can be seen in Table 3.

Table 3. Results of transesterification of *Calophyllum inophyllum* seed oil

Information	Liquid product ((%wt/wt)a))	Methyl ester ((%wt/wt)b))	Non-methyl ester (%wt/wt)
Best catalyst test c)			
(a) CaO	77.60	73.08	4.52
(b) MA-900	77.93	72.31	5.62
Transesterification of *Calophyllum inophyllum* seed oil under various reaction conditions			
MA-900 catalyst weight (%)			
(a) 3	80.00	76.17	3.83
(b) 6	76.20	74.49	1.71
(c) 9	71.93	69.98	1.95
Reaction temperature (°C)			
(a) 55	77.20	73.54	3.66
(b) 60	80.00	76.17	3.83
(c) 65	76.87	72.49	4.38
Oil: methanol mole ratio			
(a) 1:3	74.73	69.87	4.86
(b) 1:6	77.93	72.31	5.62
(c) 1:9	80.00	76.17	3.83
Reaction time (min)			
(a) 60	73.13	71.66	1.47
(b) 90	75.13	3.44	1.69
(c) 120	80.00	76.17	3.83
(d) 150	75.87	74.07	1.80
MA-900 catalyst usability test			
(a) *run*1d)	80.00	76.17	3.83
(b) *run*2e)	78.60	76.49	2.11
(c) *run*3f)	73.93	71.65	2.28

Notes: a) shows the activity of the catalyst; b) indicates the selectivity of the catalyst; c) 3% catalyst weight condition; temperature 60°C; the ratio of oil moles to methanol 1:6; and time 120 min; d) new catalyst; e) used catalyst 1; f) used catalyst 2 (3% catalyst weight; temperature 60°C; mole ratio of oil to methanol 1:9; and time period of 120 min)

Table 3 shows the activity and selectivity of the catalyst for the transesterification liquid product and the methyl ester conversion contained therein. In the best catalyst test, the use of the CaO catalyst resulted in higher methyl ester conversion than the MA-900 catalyst. However, after varying the conditions of the transesterification reaction on the MA-900 catalyst, an increase in methyl ester conversion was obtained at the reaction conditions in the form of 3% catalyst weight, reaction temperature of 60°C, oil: methanol mole ratio of 1:9, and reaction time of 120 min. Previously, the esterification process was also carried out to determine the amount of esterified liquid product produced and the conversion of the methyl ester contained therein. In the esterification process, 55.07% esterified liquid product was produced with a methyl ester conversion of 54.63%. This showed that there was an increase in the conversion of methyl ester after the transesterification of *Calophyllum inophyllum* seed oil.

3.4.2. Usability test on MA-900 catalyst

In the MA-900 catalyst usability test, the catalyst was used repeatedly by 3 times in the *Calophyllum inophyllum* seed oil transesterification process under optimum reaction conditions (3% catalyst weight, reaction temperature 60°C, oil: methanol mole ratio 1:9, and reaction time of 120 min) using the reflux method. This is one of the advantages of using heterogeneous catalysts in biodiesel production [61]. The results of the MA-900 catalyst usability test in Table 3 showed that in the first transesterification, a methyl ester conversion of 76.17% was obtained. Interestingly, the conversion of methyl esters increased in the second use and decreased in the third one.

The increase in the amount of methyl ester product obtained can be caused by the loss of impurities in the MA-900 catalyst together with the first transesterification process. This was because during the first transesterification process the catalyst was assisted by the high temperature of the transesterification process to remove any remaining impurities. As a result, in the second transesterification process the catalysts could work more effectively and leafless glycerol than the first transesterification. In the third transesterification, the conversion of the methyl ester obtained decreased. This was because there was a decrease in the active side of the MA-900 catalyst after being used repeatedly [62]. From these results, it can be concluded that the MA-900 catalyst that has been synthesized had an optimum activity after being used for transesterification twice.

3.4.3. MA-900 catalyst morphology before (fresh) and after 3X runs

The results of the SEM-EDX analysis on the MA-900 catalyst before and after 3X runs showed changes in the surface morphology of the catalyst and the elements contained in the catalyst material before and after three times transesterification using the reflux method. The results of the MA-900 catalyst identification before and after the 3X run can be seen in Figure 9.

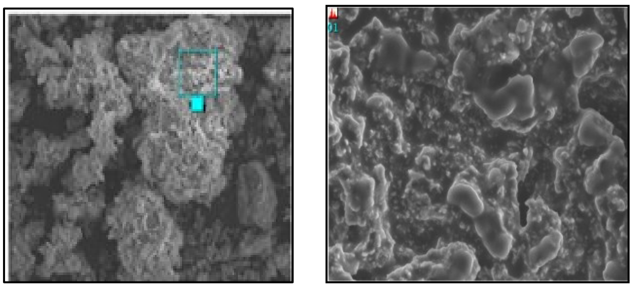
(a) (b)

Fig. 9. SEM image on MA-900 (a) before 3X runs (Fresh) and (b) after 3X runs

As shown in Figure 9, the surface of the fresh MA-900 catalyst had a regular surface appearance, looked rougher, porous, and had smaller particles. Meanwhile, the surface of the MA-900 after 3X runs had a non-uniform and irregular pore appearance. This indicated that the surface of the MA-900 catalyst after 3X runs has been saturated as characterized by a decrease in CaO content. As seen in Table 4 the composition of the material on the MA-900 catalyst after 3X runs decreased in some metal oxide, such as Ca, K, and Mg where these metal oxide acted as a catalyst in biodiesel production. The repeated use of the catalyst caused the catalyst side to experience deactivation and caused a decrease in the conversion of the methyl ester obtained. The composition of the MA-900 catalyst material before and after the 3X run can be seen in Table 4.

Table 4. Analysis of elemental content in MA-900 catalyst before (fresh) and after 3X runs with EDX

Component	Composition	
	MA-900 before 3X runs (Fresh)	MA-900 after 3X runs
C	9.40	72.53
O	27.28	10.67
Mg	2.09	1.55
Al	0.11	0.02
Si	0.16	0.15
P	0.11	1.28
S	2.13	2.56
K	5.82	2.65
Ca	52.91	8.59

4. Conclusion

In conclusion, the catalyst of Moringa leaf ash has been successfully synthesized in our experiments through a calcination process. The calcination process for 3 hours was able to increase Ca level in *Javanese* old *Moringa oleifera* leaf from 3.18 to 26.94 (MA-500) and 52.91 (MA-900). The increased Ca content in the calcined Moringa leaf powder could be used as a catalyst in the form of CaO, contributing to the efficiency of the transesterification reaction of *Calophyllum inophyllum* seed oil into biodiesel. In FTIR data, the MA-900 catalyst had a higher intensity at wave number 617 cm-1 than the MA-500 catalyst, which indicated the formation of metal oxide compounds as a result of the calcination process. This was also supported by the results of SEM-EDX analysis, which stated that the MA-900 catalyst had a higher Ca content. From the XRD data, the MA-500 catalyst began to appear with a characteristic peak of CaO at 2θ = 37.3333°. Meanwhile, the MA-900 catalyst began to show the characteristic peaks of CaO at 2θ = 32.1511°, both of which were confirmed according to the CaO standard (JCPDS No. 00-037-1497). The degumming and esterification processes in *Calophyllum inophyllum* seed oil were able to reduce the high FFA levels in *Calophyllum inophyllum* seed oil by up to 1.98% so that the transesterification process could be continued. The transesterification process of *Calophyllum inophyllum* seed oil with MA-900 catalyst produced the most liquid product of 80% and a high selectivity to methyl ester conversion of 76.17% under reaction conditions of 3% catalyst weight, a reaction temperature of 60°C, an oil: methanol mole ratio 1: 9, and a reaction time of 120 minutes. The repeated use of the MA-900 catalyst at optimum transesterification reaction conditions resulted in ODE without any significant decrease in the methyl ester conversion. Therefore, the MA-900 catalyst can be used as a promising catalyst.

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