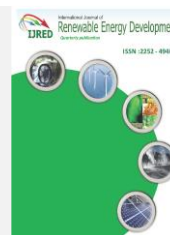




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International Journal of Renewable Energy Development

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Research Article

Preparation of MgO-CaO/SiO₂ catalyst from dolomite and geothermal solid waste for biodiesel production

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Abstract. Energy demand will increase along with the increase in population. The current energy demand is dominated by non-renewable energy as it could reduce dependence on fossil energy sources; hence, it is imperative to be developed. Biodiesel with waste cooking oil as its raw material is one of the renewable energies currently being developed. Catalyst can be utilized to improve the quality of biodiesel product and process. The major content in solid waste of geothermal power plant is silica oxide, while dolomite contains magnesium oxide and calcium oxide. This study aims to test the MgO-CaO/SiO₂ catalyst performance from geothermal waste and dolomite in biodiesel production. The results of catalyst characterization based on FTIR, SEM, and BET tests indicates a successful impregnation method in MgO-CaO/SiO₂ catalyst production. The result shows that the best variable to produce biodiesel is at the ratio of MgO-CaO: SiO₂ is 15:85. The conversion of biodiesel using this variable is 92.63%. The overall results of biodiesel obtained in this study have a good quality and is in accordance with SNI 7182-2015.

Keywords: Catalyst, MgO-CaO/SiO₂, geothermal waste, dolomite, biodiesel, waste cooking oil, catalyst characteristics



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Received: 9th January 2023; Revised: 25th March 2023; Accepted: 10th April 2023; Available online: 15th April 2023

1. Introduction

Energy has an essential role in human life; as the population increases, the energy demand will also increase. The energy needs used today are still dominated by non-renewable resources such as coal, oil, and natural gas, which are limited in availability (Moorthy *et al.*, 2019). This leads to searching and developing alternative fuels, such as biodiesel.

Biodiesel is an alternative fuel that has similar characteristics to conventional diesel. Biodiesel has various advantages compared to fossil fuels. It can reduce carbon monoxide emissions by around 50% and carbon dioxide emissions by up to 78%, has small sulfur content, has a high flash point, and is easy to decompose (Ramos *et al.*, 2019). Biodiesel can be produced from materials that contain fatty acids. Vegetable oils, animal fats, and waste containing fatty acids can be used for biodiesel production (Hadiyanto *et al.*, 2020; Dharma *et al.*, 2016).

Waste cooking oil (WCO) is a mixture of triglycerides and fatty acids contaminated by some of their derivatives during the frying process, such as free fatty acids (Yaakob *et al.*, 2013). Waste cooking oil (WCO) has the potential to be converted into biodiesel. Biodiesel production from waste cooking oil saves 21% of crude oil and 96% of fossil energy savings (Corral *et al.*,

2017; Wahyono *et al.*, 2023). Waste cooking oil has a high content of free fatty acids and water, so it must be pretreated before converting it into biodiesel. This pretreatment is needed before entering the transesterification process because it will cause a saponification reaction. Side reactions such as saponification reactions can reduce the amount of biodiesel produced. The transesterification reaction is sensitive to the presence of free fatty acids; that is the transesterification reaction could not be completed when the fatty acid content in the raw material is above 3% (Yakoob *et al.*, 2013; Satriadi *et al.*, 2022). To produce biodiesel from material that has a high content of free fatty acid, such as waste cooking oil, two reaction processes are required. The first step is esterification reaction and the next step is transesterification reaction. Therefore, it is necessary to modify heterogeneous catalysts that can work simultaneously during esterification and transesterification reactions so that the production of biodiesel is more efficient.

Biodiesel is produced by reacting fatty acids with alcohols, such as methanol or ethanol, through a transesterification reaction to produce alkyl esters and glycerol (Hossain & Al Eissa, 2016; Kusumaningtyas *et al.*, 2022). Biodiesel can also be produced from free fatty acids through esterification reactions (Baroi & Dalai, 2012; Widayat & Suherman, 2012;

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Kusumaningtyas *et al.*, 2023). Esterification is one of the reactions that are usually used in the biodiesel production process and can be used as a pre-treatment of the transesterification reaction to convert free fatty acid (FFA) into methyl esters (Widayat & Suherman, 2012; Kusumaningtyas *et al.*, 2023). The esterification reaction is used to avoid saponification reactions (Mello *et al.*, 2011). Transesterification is the reaction between triglycerides and short-chain alcohols to form alkyl esters and glycerol. Transesterification is a reaction that is reversible and is slow to direct the reaction toward the product using one of the reactants made excessively and by adding a catalyst (Widayat *et al.*, 2020). The catalyst is used to speed up the reaction rate and to produce a high quality of biodiesel. The transesterification reaction can utilize both homogeneous or heterogeneous catalysts (Ogunkunle *et al.*, 2017).

Biodiesel production primarily uses homogeneous catalysts such as KOH and NaOH. One of the problems in using a homogeneous catalyst is the difficulty separating the catalyst and biodiesel due to the same phase (Widayat *et al.*, 2013). In addition, homogeneous catalysts can cause side reactions such as saponification which can affect the biodiesel production. The homogeneous catalyst used will also be difficult to reuse or regenerate (Siregar *et al.*, 2021). Therefore, a heterogeneous catalyst was developed as an alternative.

Heterogeneous catalysts can be a solution to overcome the weaknesses of homogeneous catalysts. Heterogeneous catalysts have several advantages, such as being easier in the separation process if compared to homogeneous catalysts. The separation process is also simple, it can be separated by filtration or precipitation (Hadiyanto *et al.*, 2020; Kusmiyati *et al.*, 2019). One of the catalysts that can be used is MgO-CaO. MgO and CaO are used as heterogeneous catalysts for biodiesel production because it requires only simple operating conditions, inexpensive and environmentally friendly. MgO has special properties, such as high reactivity and high specific surface area, that can be utilized as a catalyst. CaO is often used in transesterification reactions because it has a long catalyst lifetime and has a low solubility in biodiesel, which makes it easier to separate (Lani *et al.*, 2019).

In this research, the MgO-CaO catalyst was obtained from the extraction of dolomite. Dolomite is widely available in Indonesia. The presence of dolomite minerals is widespread in North Sumatra, West Sumatra, Central Java, East Java, Madura and Papua (Budio *et al.*, 2014). Dolomite is one industrial mineral with the chemical formula $MgCa(CO_3)_2$ (Mubarak & Kurniawan, 2015). Dolomite can be used to prepare mixed oxides as a solid base catalyst (Murguía-Ortiz *et al.*, 2021). The main compounds in dolomite are CaO (61.20%), MgO (25.28%), and Na_2O (9.50%) (Sari *et al.*, 2013). The carbonate groups in dolomite will decompose through thermal treatment to form CaO and MgO (Buasri *et al.*, 2013).

The impregnation technique can be used to increase the specific surface area, and it caused improving the characteristics of heterogeneous catalysts. Impregnation is the most common and easy method of catalyst modification for various heterogeneous catalysts (Widayat *et al.*, 2016; Haryono *et al.*, 2020). The basic principle of the impregnation process is to enter the metal catalyst by force into the pores of the support so that there is an exchange of ions contained in the active site of the support with the metal catalyst (Tsao & Yang, 2018).

MgO-CaO was modified with SiO_2 as support to improve the catalyst's performance. Silica is widely used as an inorganic and water absorbent, and can be used as a catalyst because of its large surface area that acts as the active site where the reaction

occurs (Moradi *et al.*, 2014). One of the biggest sources of silica is geothermal waste. Geothermal solid waste was generated from the utilization of a geothermal power plant. The highest component in geothermal waste is SiO_2 , accounting to about 75.08%. Other components found in the waste are Al_2O_3 and Na_2O . The high silica content in geothermal waste makes this material potential to be used as a source of silica in catalyst production (Satriadi *et al.*, 2022).

Previous research by Widayat *et al.* (2017) developed CaO as catalyst in ultrasonic-assisted biodiesel production. Meanwhile, Pandiangan *et al.* (2016) developed MgO/SiO_2 as a catalyst in the transesterification process of castor oil with coconut oil as a co-reactant. Lani *et al.* (2017) developed CaO/SiO_2 through the impregnation method and reported that the use of CaO/SiO_2 in biodiesel production resulted in 87.5% biodiesel. Boonphayak *et al.*, (2021) developed $CaO-SiO_2$ catalyst and resulted in 93% FAME. The use of dolomite to produce $MgO-CaO$ catalyst impregnated with SiO_2 from geothermal solid waste has not been carried out by previous researchers. Catalyst impregnation can be carried out to improve the characteristics of the catalyst, such as increasing the catalyst's surface area and performance. Thus, this research was conducted to determine the effect of the $MgO-CaO/SiO_2$ catalyst impregnation from geothermal waste and dolomite on biodiesel production.

2. Materials and Methods

2.1 Materials

Geothermal solid waste used in this research was obtained from PT Geo Dipa Energi, Wonosobo, Central Java. The waste was chosen for its high content of silica mineral. Dolomite was obtained from Gunung Kidul Regency, Yogyakarta. Sodium hydroxide (NaOH), hydrochloric acid (HCl), and nitric acid (HNO_3) was purchased from Merck Ltd. Catalyst was synthesized via the wet impregnation method using deionized water. Waste cooking oil as the raw material for biodiesel production was collected from restaurants in Tembalang, Semarang City.

2.2 Preparation of $MgO-CaO/SiO_2$ catalyst

Synthesis of the $MgO-CaO/SiO_2$ catalyst begins with the extraction of silica which is contained in geothermal solid waste. Geothermal solid waste is heated using an oven to remove water content. Then it is dissolved in 2 M sodium hydroxide (NaOH) and stirred for 2 h. The solution was then filtered using a vacuum pump and the filtrate was added with HCl until a gel was formed. This gel undergoes a hydrothermal process using an autoclave at 250 °C for 4 h. The hydrothermal product was then calcined at 500 °C for 5 h. Meanwhile, extraction of $MgO-CaO$ from dolomite started with calcination at 900 °C for 4 h. This sample was then dissolved into 2 N nitric acid (HNO_3) and followed by addition Sodium Hydroxide (NaOH) 2 N to form a precipitate. The precipitate was then dried and calcinated at 300°C for 3 h. To synthesize the catalyst, $MgO-CaO$ and SiO_2 was impregnated with deionized water at 70°C for 4 h. After impregnation, the catalyst was then calcinated for 5 h at various temperatures.

2.3 Biodiesel production

The performance of the catalyst can be tested through biodiesel production. In this research, biodiesel production is carried out through simultaneous esterification and

transesterification reactions. It started with mixing methanol, waste cooking oil and the catalyst into the three-necked boiling flask. The ratio of methanol and waste cooking oil was 12:1 with 3%w/w catalyst. This reaction undergoes for 5 h at 65°C. The mixture is separated by a separatory funnel when the reaction is complete. The resulting biodiesel is then heated to evaporate the remaining methanol content.

2.4 Product analysis

The synthesized catalyst was analyzed using Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX) to determine the surface morphology. Fourier Transform Infrared (FTIR) analysis was used to determine which functional groups are present in the catalyst. While surface area and pore radius of the catalyst was analyzed using Brunauer Emmett Teller (BET) method. The Biodiesel product was also analyzed using Gas Chromatography-Mass Spectrometry (GC-MS) to determine the content of Fatty Acid Methyl Esters (FAME) in the biodiesel. Biodiesel characteristics were also analyzed based on density, viscosity, and free fatty acid content. The results of the biodiesel characteristics are then compared with Indonesian National Standard (SNI) 7182-2015.

3. Results and Discussion

3.1 Characteristic of waste cooking oil

The waste cooking oil used in this research contained 6.937% free fatty acid (FFA). Gas Chromatography-Mass Spectrometry (GC-MS) analysis was carried out to determine components contained in raw material. Table 1 shows the composition of waste cooking oil.

Waste cooking oil contains saturated and unsaturated fatty acids. Saturated fatty acids are a type of fatty acid that consists of a single chain of carbon atoms with no double bonds. It has straight chains and usually has higher melting points than unsaturated fatty acids. The types of saturated fatty acids contained are dominated by hexadecanoic acid (palmitic acid) and octadecanoic acid (stearic acid). Palmitic acid is a long-chain saturated fatty acid that has 16 carbon bonds. Stearic acid is a long-chain saturated fatty acid with 18 carbon bonds. Unsaturated fatty acids are a type of fatty acid that has one or more double carbon bonds. The hydrocarbon chains in unsaturated fatty acids are bent and branched, usually this type of fatty acid has a low melting point (Brühl *et al.*, 2014). The unsaturated fatty acids are dominated by 9-Octadecenoic acid (oleic acid) and 9,12-Octadecadienoic acid (linoleic acid). Oleic acid, or 9-octadecenoic acid is a monounsaturated fatty acid because it only has one double carbon bond. The double bond that belongs to oleic acid is located at C-9. Linoleic acid is a fatty acid that has 18 carbon bonds and two double bonds located at C-9 and C-12 with a cis configuration.

Table 1

Composition of waste cooking oil

No.	Compound	Trivial name	Molecular formula	Area%
1.	9-Octadecenoic acid	Oleic Acid	C ₁₈ H ₃₄ O ₂	46.29
2.	Hexadecanoic acid	Palmitic Acid	C ₁₆ H ₃₂ O ₂	34.79
3.	9,12-Octadecadienoic acid	Linoleic Acid	C ₁₈ H ₃₂ O ₂	8.25
4.	Octadecanoic acid	Stearic Acid	C ₁₈ H ₃₆ O ₂	4.08
5.	Dodecanoic acid	Lauric Acid	C ₁₂ H ₂₄ O ₂	1.78
6.	Tetradecanoic acid	Myristic acid	C ₁₄ H ₂₈ O ₂	1.64
7.	Heptadecanoic acid	Margaric acid	C ₁₇ H ₃₄ O ₂	1.43
8.	Docosanoic acid	Behenic acid	C ₂₂ H ₄₄ O ₂	0.87
9.	Tetracosanoic acid	Lignoceric acid	C ₂₄ H ₄₈ O ₂	0.87

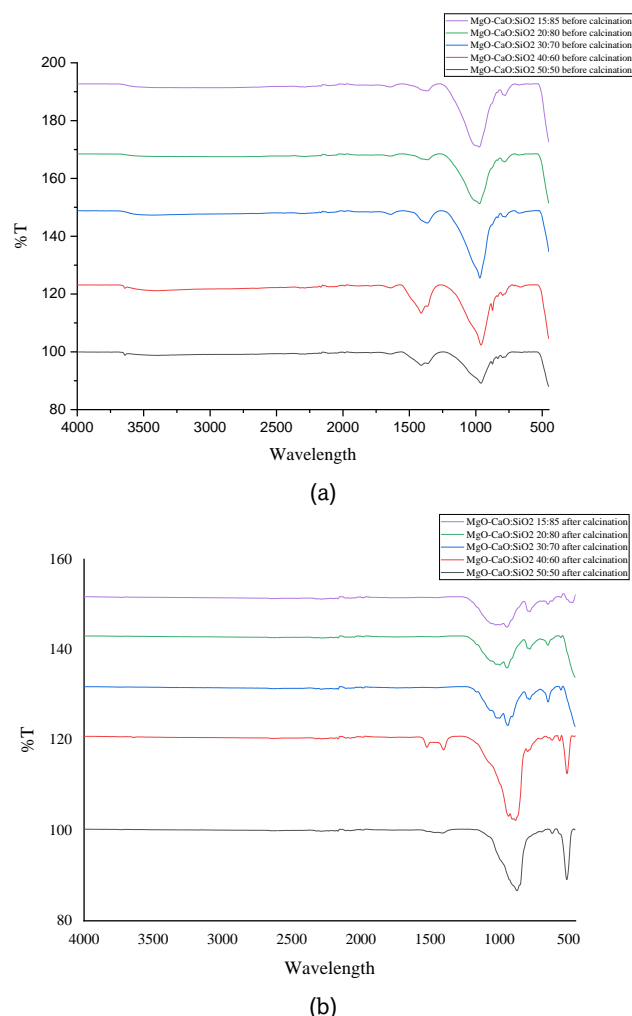


Fig. 1. FTIR spectrum of MgO-CaO/SiO₂ catalyst at various ratios: (a) before calcination (b) after calcination

3.2 Characteristics of MgO-CaO/SiO₂ catalyst

The MgO-CaO/SiO₂ catalyst was analyzed using FTIR, SEM-EDX, and BET. FTIR analysis was used to determine the functional groups present in the catalyst. Each type of bond and functional group in a molecule will have a distinctive and specific infrared absorption band. The functional groups identified are Si-O stretching, O-C-O bond, O-H stretching, Si-O-Ca bond and other functional groups. The results of FTIR showed that before the catalyst was calcinated, there was a wide band in the wavelength range of 3384.71 cm⁻¹ - 3641.2 cm⁻¹, which indicated the adsorbed water molecules. Another functional group identified is the Si-O bond. The absorption band is visible at the wavelength of 873.38 cm⁻¹ - 1068.66 cm⁻¹.

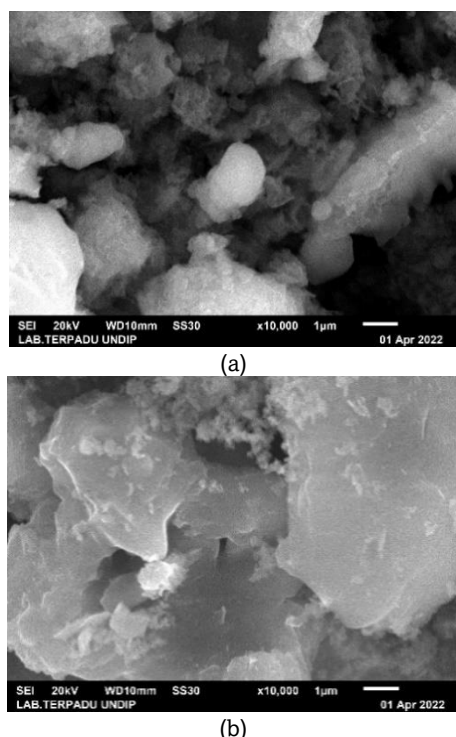


Fig. 2. SEM images of MgO-CaO/SiO₂ catalyst at ratio 15:85: (a) before calcination (b) after calcination

The Ca-O group appears at a wavelength of 588.79 cm⁻¹ - 693.43 cm⁻¹ in the MgO-CaO/SiO₂ catalyst. The Ca-O group was identified at a wavelength of 595 cm⁻¹ (Ajala *et al.*, 2020). There is an absorption at 440 cm⁻¹ - 700 cm⁻¹ and the peak at 1444 cm⁻¹ is the Mg-O strain (Asgari *et al.*, 2019). FTIR spectrum of MgO-CaO/SiO₂ catalyst before and after calcination are shown in Fig. 1.

Changes in the morphological characteristics of the catalyst before and after calcination were studied by SEM in Fig. 2. SEM is an instrument that serves to visualize the chemical composition, material structure and surface morphology of material at the submicron level (Meloni & Bertotti, 2017). SEM is combined with EDX to provide additional input values in determining the distribution of various elements. EDX shows

quantitative analysis in the form of the percentage of constituent elements of a material (Michalak *et al.*, 2014).

The calcination process is the thermal treatment given to solid materials, which is a process that leads to structural transformations such as decomposition, phase transitions, surface reconstruction, or the removal of volatile fractions (Alraddadi, 2020). The calcination process will affect the texture and the specific surface area of the catalyst, consequently affecting the performance of the catalyst (Md Ali *et al.*, 2017). There is a change in the surface structure between the samples before calcination and after calcination. The morphological structure of the catalyst before calcination shows small aggregates without a certain shape. The calcined catalyst showed that the catalyst had a higher crystallinity. The high crystallinity of the catalyst makes the catalyst free from impurities and can improve its physical properties, such as increasing the surface area of the catalyst, better stability at high temperatures and improving its catalytic properties (Afandi *et al.*, 2021).

The catalyst variable with a ratio of 50:50 has a morphological structure in the form of small irregular crystals and is still hollow. The lack of SiO₂ composition, which works as a gap between the active components of the catalyst, causes the particles on the surface of the catalyst to be irregularly dispersed and grouped into lumps (Ndak *et al.*, 2021). Variable catalysts with a composition of 40:60 crystals are larger but still agglomerate in some places. Variable catalyst with a composition of 30:70 has a small crystal size but is more evenly distributed with a closer distance. Variables 20:80 and 15:85 have larger crystal sizes than the previous variables and are more closely spaced. This is because the silica composition which functions as a gap between the particles increases, thereby reducing the particles that cluster together to form clumps (Ndak *et al.*, 2016).

The composition of the catalyst was studied through EDX analysis. Based on the results of the EDX analysis in Fig. 4, it can be seen that the main compounds in the catalyst are SiO₂ (58.14%) and CaO (16.56%). SiO₂ is a compound that has an important role in the esterification process and CaO is a compound that plays an essential role in the transesterification process.

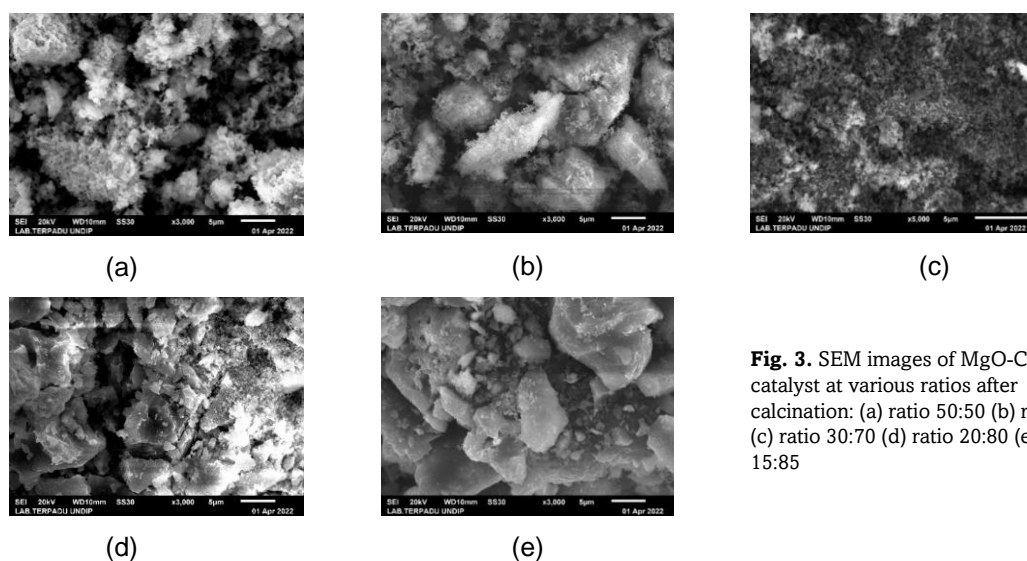


Fig. 3. SEM images of MgO-CaO/SiO₂ catalyst at various ratios after calcination: (a) ratio 50:50 (b) ratio 40:60 (c) ratio 30:70 (d) ratio 20:80 (e) ratio 15:85

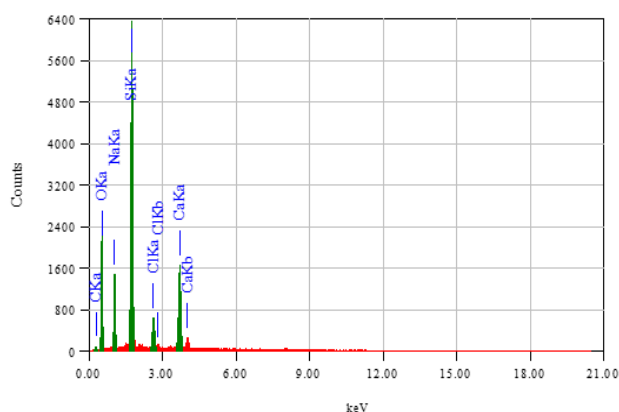


Fig. 4. EDX analysis of MgO-CaO/SiO₂ catalyst

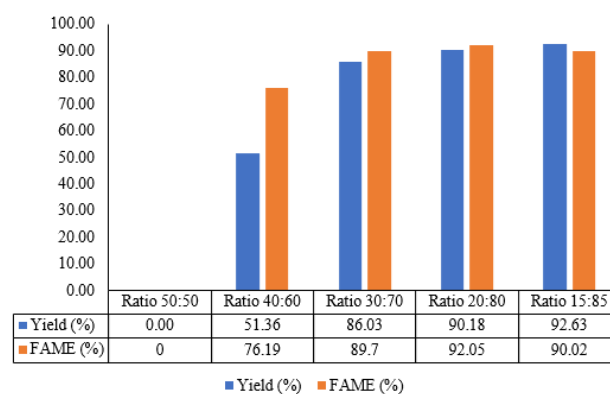


Fig. 5. Effect of MgO-CaO and SiO₂ ratio on biodiesel yield

Table 2

BET analysis of MgO-CaO/SiO₂ catalyst

Sample	Surface Area	Pore Radius
SiO ₂ Catalyst	1.930 m ² /g	15.272 Å
MgO-CaO/SiO ₂ Catalyst	4.022 m ² /g	24.424 Å

Brunauer Emmett Teller (BET) analysis is used to determine the catalyst's specific surface area, the catalyst's average pore diameter, and the catalyst pore volume (Pandit *et al.*, 2017). This analysis refers to the adsorption and desorption of nitrogen gas (N₂) by porous solids (wide pore range) at normal boiling points.

Initially, the surface area of the SiO₂ catalyst was 1.930 m²/g. When the catalyst is modified with MgO-CaO, the surface area becomes 4.022 m²/g. The increase in the surface area of the catalyst indicates the occurrence of catalyst restructuring and that the catalyst impregnation process was carried out successfully. MgO-CaO can stick to the surface of SiO₂. Increased surface area can open new active pore pathways and is able to make better contact between active sites and reactants that leads to better products (Ala'a *et al.*, 2020). The pore radius of the MgO-CaO/SiO₂ catalyst was 24.424 Å, while the pore radius of the SiO₂ catalyst was 15.272 Å. There was an increase in the pore radius of the catalyst after modification. The pore radius of the catalyst is related to its characteristic as a molecular sieve. The larger the pore diameter, the more its ability to adsorb molecules with a bigger size. Conversely, if the pore diameter is small, it will only be able to adsorb small molecules (Dewajani, 2016). The increase in pore radius of the catalyst occurs due to the opening of active SiO₂ pores during the impregnation process with MgO-CaO and the calcination process.

3.3 Effect of MgO-CaO/SiO₂ ratio on biodiesel yield

In this study, MgO-CaO and SiO₂ ratio were varied to determine their effect on the biodiesel production process. The variation in the ratio of MgO-CaO:SiO₂ used are 50:50; 40:60; 30:70; 20:80; dan 15:85. Fig. 5 shows the yield of biodiesel.

According to the experimental result, MgO-CaO/SiO₂ catalyst with a ratio of 50:50 could not produce biodiesel. This reaction forms a thick liquid. The reaction with 50:50 ratio catalyst was unable to produce biodiesel because the acidic composition of SiO₂ was insufficient for the esterification reaction to occur. Hence, free fatty acid (FFA) could not be converted into methyl esters and leads to a saponification reaction. MgO-CaO also reacted with FFA and formed soap

which creates serious problems of product separation and ultimately affects the yield of methyl esters (Lee *et al.*, 2016).

The amount of SiO₂ in the catalyst affects the performance of MgO-CaO/SiO₂ catalyst and the yield of biodiesel produced. An increase of SiO₂ would give a higher biodiesel product as the acid component in the catalyst increases. An acid catalyst is needed in the esterification step to convert the free fatty acid into methyl esters. It also prevents saponification reaction so that the transesterification process can occur completely. Catalyst with a ratio 15:85 has the best performance. The biodiesel produced contains only 0.169% FFA. The decrease of FFA proved that SiO₂ in the catalyst has successfully convert FFA into methyl esters in the esterification reaction. The compounds contained in biodiesel were tested by GC-MS analysis. The result of this analysis can be seen in Fig. 6 with the percentages of each component listed in Table 3.

GC-MS analysis showed the presence of monoglyceride compounds in the biodiesel, such as hexadecanoic acid, 2-hydroxy-1,3-propanediyl ester (CAS) and hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl)ethyl ester (CAS). Biodiesel that is produced also contains Fatty Acid Methyl Ester (FAME) compounds with the main components of methyl palmitate (35.61% area) and methyl oleate (37.30% area). It proves that the MgO-CaO/SiO₂ catalyst has been successfully used for simultaneous esterification-transesterification reactions to produce methyl esters. The catalyst that gave the highest yield was the catalyst with MgO-CaO/SiO₂ ratio of 15:85. This catalyst able to produce 92.63% yield of biodiesel. The catalyst that has the best performance was be used for the next variable.

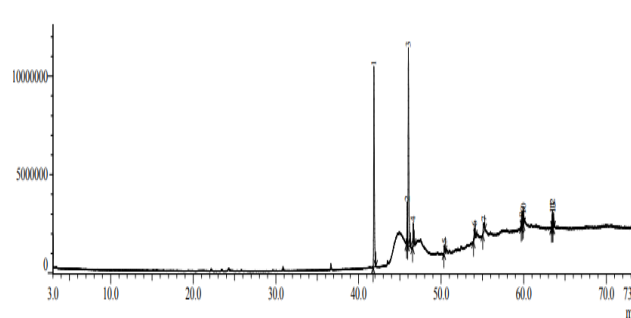


Fig. 6. GC-MS Chromatogram of biodiesel samples

3.4 Effect of catalyst calcination temperature on biodiesel yield

The next variable investigated was the calcination temperature of the catalyst. In this study, the calcination temperature variation used was 500 °C; 600 °C; 700 °C; 800 °C and 900 °C. Fig. 7 shows the yield of biodiesel at various calcination temperature.

Calcination temperature affects the performance of MgO-CaO/SiO₂ catalyst and biodiesel yield. Based on the Fig. 7, it is known that higher calcination temperature will give higher biodiesel and fatty acid methyl ester (FAME) yield. An increase in calcination temperature will cause an increase in the acidity of the catalyst. SiO₂ is the active component in the catalyst which is responsible for the esterification and transesterification reactions to convert waste cooking oil into biodiesel. In this research, the optimum catalytic activity occurred at 700°C of calcination temperature. At this temperature, catalyst can produce 92.63% of biodiesel and 90.02% FAME. The acidity of the catalyst is able to hold the product molecules from being desorbed after the reaction (Farooq *et al.*, 2015). The optimum calcination temperature can increase the resulting catalyst's outer surface area and external acidity, significantly improving its catalytic properties and higher methyl ester conversion (Vieira *et al.*, 2017). However, if the temperature increases continuously and exceeds the optimum temperature, it will decrease biodiesel product. The catalyst which was calcined at 800°C resulted in a lower biodiesel yield. Calcination temperature that is too high can lead to the formation of hard-burned quicklime, making it is more difficult for the reactants to pass the catalyst pores (Suryandari *et al.*, 2019). The most dominant component of biodiesel can be seen in Table 4. It is

known that biodiesel produced contains hexadecanoic acid, methyl ester; 9-octadecenoic acid, methyl ester; octadecanoic acid, methyl ester; 9,12-octadecadienoic acid, methyl ester; and tetradecanoic acid, methyl ester.

3.5 Characteristics of biodiesel produced

Characteristics of biodiesel can indicate the performance of the catalyst used. The results of the characteristic analysis can be seen in Table 5.

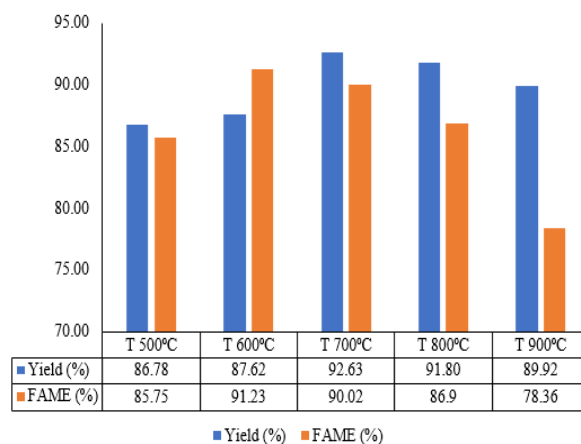


Fig. 7. Effect of catalyst calcination temperature on biodiesel yield


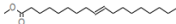
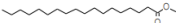
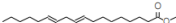
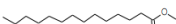
Table 3

Biodiesel components based on GC-MS analysis

Compounds	Molecular formula	Area%	Chemical Structure
Hexadecanoic acid, methyl ester (CAS)	C ₁₇ H ₃₄ O ₂	35.61	
9,12-Octadecadienoic acid (Z,Z)-, methyl ester (CAS)	C ₁₉ H ₃₄ O ₂	6.60	
9-Octadecenoic acid, methyl ester (CAS)	C ₁₉ H ₃₆ O ₂	37.30	
Octadecanoic acid, methyl ester (CAS)	C ₁₉ H ₃₈ O ₂	4.22	
Hexadecanoic acid, 2-hydroxy-1,3-propanediyl ester (CAS)	C ₃₅ H ₆₈ O ₅	1.30	
Hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl)ethyl ester (CAS)	C ₁₉ H ₃₈ O ₄	3.09	
2,6,10-Dodecatriene, 3(E),7(E),11-trimethyl-1-methoxy- (E-Farnesol methyl ether)	C ₁₆ H ₂₈ O	1.90	
9-Octadecenoic acid (Z)- (CAS)	C ₁₈ H ₃₄ O ₂	2.79	
Di-(9-Octadecenyl)-Glycerol	C ₃₉ H ₇₂ O ₅	2.46	
Erythro-7,8-Bromochlorodisparlure	C ₁₉ H ₃₈ BrCl	1.29	
2-Pentyl-cyclohexane-1,4-diol	C ₁₁ H ₂₂ O ₂	0.94	
Tricyclo [20.8.0.0(7,16)]triacontane, 1(22),7(16)-diepoxy-	C ₃₀ H ₅₂ O ₂	0.95	
Geranyl Linalool Isomer B	C ₂₀ H ₃₄ O	1.90	

Table 4

Components of biodiesel

Compounds	Molecular formula	Chemical Structure
Hexadecanoic acid, methyl ester	C ₁₇ H ₃₄ O ₂	
9-Octadecenoic acid, methyl ester	C ₁₉ H ₃₆ O ₂	
Octadecanoic acid, methyl ester	C ₁₉ H ₃₈ O ₂	
9,12-Octadecadienoic acid, methyl ester	C ₁₉ H ₃₄ O ₂	
Tetradecanoic acid, methyl ester	C ₁₅ H ₃₀ O ₂	

The parameter of the purity of the biodiesel product produced is important in determining the quality of biodiesel. The final biodiesel may contain contaminants such as free fatty acids (FFA), residual alcohol, and catalysts. These contaminants can cause operational problems when using biodiesel in engines, such as engine deposits, filter clogging, or fuel damage (Zhang, 2012). The quality of biodiesel can be determined through density, viscosity, free fatty acid (FFA) levels and acid numbers. Through these parameters, the performance of the catalyst in the simultaneous esterification-transesterification reaction can be assessed. These parameters are also compared with the biodiesel quality requirements, SNI 7182: 2015, to assess the performance of MgO-CaO/SiO₂ solid catalyst in biodiesel production.

The density of biodiesel produced using MgO-CaO/SiO₂ catalyst is in accordance with SNI 7182:2015. The lowest density produced was 0.877 gram/cm³ and the highest density is 0.884 gram/cm³. These values indicate that the MgO-CaO/SiO₂ catalyst can convert triglycerides and produce good-quality biodiesel. High biodiesel density (exceeding the standard requirement) will accelerate engine wear and inadvertently cause damage to the engine. Conversely, lower biodiesel densities are needed to control fuel flow at the injection pump and minimize smoke formation when operating at maximum power at higher loads (Rao *et al.*, 2018).

Viscosity is one of the parameters that must be considered in determining the fuel. Viscosity affects fluid transfer by pumps and atomizing machines (Febriana *et al.*, 2020). Too low viscosity will cause bad fuel dispersion in the engine chamber, causing inefficient burning and could also cause leakage in the engine pipe. Meanwhile, high viscosity will cause the flow velocity to be slower; thus, degree of fuel atomization will also be slower in the combustion chamber (Febriana *et al.*, 2020). Referring to the biodiesel quality requirements of SNI 7182: 2015, the viscosity of biodiesel produced using MgO-CaO/SiO₂ catalyst has fulfilled the biodiesel quality requirements. The

results obtained were: 3.341 mm²/s (lowest) and 4.879 mm²/s (highest).

Based on the biodiesel quality requirements listed in SNI 7182:2015, the allowed acid number in biodiesel is 0.5. A high acid number value in biodiesel will cause biodiesel to be corrosive; consequently, causing scale formation in diesel engines (Febriana *et al.*, 2020). The lowest acid value was obtained from the reaction with a catalyst of variable 8 (0.336); nevertheless, the value meets the biodiesel quality requirements.

6. Conclusion

MgO-CaO/SiO₂ catalyst was successfully synthesized using wet impregnation method. MgO-CaO was synthesized from dolomite and SiO₂ was synthesized from geothermal. The optimum catalyst ratio of MgO-CaO:SiO₂ was 15:85 with 92.63% yield of biodiesel, while the variable ratio of 50:50 had low quality because it was unable to convert waste cooking oil into biodiesel. The optimal catalyst calcination temperature was 700 °C with 92.63% yield of biodiesel, while at 500 °C the catalyst was only capable in producing 86.78% of biodiesel.

MgO-CaO/SiO₂ catalyst was characterized using FTIR, SEM-EDX, and BET. The FTIR characterization results showed that the synthesized catalysts contain the expected functional groups. SEM analysis results show that the catalyst has high crystallinity. From the results of the EDX analysis, it can be seen that the main compounds in the catalyst are SiO₂ (58.14%) and CaO (16.56%). BET analysis showed that there was an increase in the surface area of the catalyst after impregnation. The results of biodiesel obtained in this study are in accordance with SNI 7182-2015. Parameters used to determine the quality of biodiesel are density, viscosity, free fatty acid (FFA) content and acid number.

The limitation of this research includes the lack of acid and base characterization in catalysts. The mechanism and reaction

Table 5

Characteristics of biodiesel

No	Variable	Ratio MgO-CaO & SiO ₂	T (°C)	Density (gr/cm ³)	Viscosity (mm ² /s)	Acid Number (mg-KOH/g)	FFA (%)
1.	Variable 1	50::50	700	-	-	-	-
2.	Variable 2	40::60	700	0.880	3.671	0.952	0.479
3.	Variable 3	30::70	700	0.879	3.822	0.672	0.338
4.	Variable 4	20::80	700	0.881	3.459	0.448	0.226
5.	Variable 5	15::85	700	0.877	3.373	0.336	0.169
6.	Variable 6	15::85	500	0.882	3.341	0.504	0.254
7.	Variable 7	15::85	600	0.880	3.496	0.392	0.197
8.	Variable 8	15::85	700	0.877	3.373	0.336	0.169
9.	Variable 9	15::85	800	0.878	3.522	0.56	0.282
10.	Variable 10	15::85	900	0.884	4.879	0.504	0.254
SNI 7182: 2015				0.85-0.89	2.3-6.0	≤ 0.5	-

kinetics in the esterification and transesterification reactions can be studied in more depth in future research.

Acknowledgments

The research was funded by Diponegoro University through International Publication Research Scheme with the Contract Number of : 569-140/UN7.D2/PP/VII/2022.

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