Biodiesel production from Kesambi (*Schleichera oleosa*) oil using multi-walled carbon nanotubes supported zinc oxide as a solid acid catalyst

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Abstract. The development of heterogeneous catalysts for biodiesel production became a hot topic among scientists because of its many advantages including easy separation and catalyst reusability. In this study, multi-walled carbon nanotubes supported zinc oxide (MWCNTsZ) as a solid acid catalyst had been successfully prepared via the stober-like process. There are several % loading of ZnO variations ranging from 10 – 35 % of catalyst weight. These catalysts were characterized by x-ray diffraction (XRD), BET surface area analysis, and scanning electron microscope with energy-dispersive x-ray spectroscopy (SEM-EDX) analysis. Transesterification of kesambi (*Schleichera oleosa*) oil also had also been done to test the activity of the solid catalyst. The potential of this catalyst is shown from its large surface area with the maximum surface area until 409 m²/gram. However, the quantity of dispersed zinc oxide (ZnO) on multi-walled carbon nanotubes (MWCNTs) via that modified Stober preparation is quite small lower than 5% weight. This phenomenon is resulting in a low yield of biodiesel after 3 h of transesterification reaction. The highest yield of biodiesel is obtained with 20% weight of loading ZnO variable producing 13.82% yield of methyl ester.

1. Introduction
All this time, energy needs in the world are depending on fossil fuel availability. It has impacted not only on depletion of petroleum reserves but also on environmental issues like global warming, greenhouse gas effect, and air pollution [1]. This energy sustainability problem can be resolved by three key solutions that are enhancing fossil fuel technologies, developing renewable energy technologies, and proposing energy efficiency measurement for energy conservation [2]. In the forthcoming years, renewable energy technologies development will be an important solution for sustainable energy systems in the world due to steadily escalating energy demands by year to year [3].
Indonesia has so many abundant biomass resources that can be developed as renewable energy sources. One of them is biodiesel which shows great potential as a fossil-based diesel fuel substitution [4]. Biodiesel is bio-based diesel usually developed from vegetable oils or animal fats. There are so many vegetable oil sources in Indonesia such as palm, coconut, rubber, kapok seed, nyamplung (Calophyllum inophyllum), kesambi (Schleicheria oleosa), jatropha (Jatropha curcas), and many more. However, due to its expensive cost production, biodiesel is still difficult to commercialize in Indonesia, resulting in a higher and less competitive price than fossil-based diesel oil [3].

There are two reasons for the high cost of biodiesel production in Indonesia. Firstly, vegetable oils that usually used as raw material for biodiesel production are edible oil groups like palm oil and coconut oil. These oil groups always processed in the food industry for human food ingredients. Because of that, it is not wise if edible oils utilized for biodiesel synthesis competing with the food sector and making national food security destabilization [3]. Finding alternative raw materials and substituting its edible oils is one of the solutions to reduce biodiesel production cost. Secondly, biodiesel was usually synthesized through the transesterification of vegetable oils utilizing homogeneous acid/alkaline catalyst [5]. This process has many disadvantages like by-products formation, difficult separation of catalyst from the product, and a large amount of alkaline waste output [6]. These side products need other treatment processes consuming much energy and increasing production cost [7]. Moreover, the separation of homogeneous catalysts from the products also makes its production cost getting higher [7].

Heterogeneous catalyst development for transesterification reactions will be the right solution to overcome this problem. A heterogeneous catalyst is easily separated from the products and can be reused many times so it will reduce biodiesel production cost [7]. Furthermore, waste alkaline products like soap will not form and high purity of glycerol (more than 98% wt) is produced having different phases with the main product so it can be separated easily [3]. Hence, utilizing a heterogeneous catalyst for transesterification make this process more environmentally friendly so it can be identified as the green process. There are many various types of solid catalysts had been developed by the researcher for transesterification. These catalysts had been investigated as an acid or base catalyst depending on its active site [7]. Some of developed solid base catalyst for transesterification is CaO based oxide [8,5], MgO base oxide [9], alumina-based catalyst [10,3], amorphous-zirconia based catalyst (Ti/ZrO2, K2O/ZrO2, and WO3/ZrO2) [5], zeolite-based catalyst [11], and hydrotalcite based catalyst [12]. Many researchers showed that solid base catalyst is suitable for transesterification especially mixed-oxide based catalyst producing a high yield of methyl ester. One of the mixed-oxide based catalysts that shown great potential for this reaction is calcium oxide, CaO. It showed great results with a 99% yield of fatty acid methyl ester (FAME) from transesterification of sunflower oil at a reaction temperature of 252 °C [9]. Asri et al. introduced double promoted catalyst, CaO/KI/Al2O3, to reduce the reaction temperature until mild condition resulting 94.94% yield of biodiesel from transesterification of refined palm oil at 65 °C [4].

Refined palm oil (RPO) used in previous research is edible oil and has low free fatty acid (FFA) content (lower than 1% wt). In order to gain low-cost biodiesel production, Asri et al. also investigated the same catalyst for transesterification of waste cooking oil which has FFA content more than 1% wt. Because of high FFA content, small quantities of soap were formed giving a lower yield of produced FAME that is 83.26% [4]. From this previous study, it can be concluded that CaO/KI/Al2O3 solid base catalyst is less suitable for transesterification of vegetable oils having high FFA content like low-grade oil and other non-edible oil. The solid acid catalysts for the transesterification reaction of low-grade oil would be explored by biodiesel researchers due to its strong potential compared to base catalysts. Solid acid catalyst has many advantages that are its FFA content insensitivity, stimulating esterification and transesterification reaction simultaneously, and eliminating the washing step of FAME product [13]. The main characteristics of that catalyst are having large pores, moderate to the high concentration of strong acid active sites, and hydrophobic surface [13,14]. However, widely utilization of that catalyst for biodiesel production still has limitations like slow reaction rate and appearing undesirable parallel reactions [13].
There have been several mixed-oxyde metal group that reported suitable as acid solid catalyst for biodiesel production, e.g. zirconium oxide (ZrO$_2$) [15], modified zirconium oxide with tungsten oxide (WO$_3$) [16], titanium oxide (TiO$_2$) [17], zinc oxide (ZnO) [18], and tin oxide (SnO$_2$) [19]. All of these metal oxides reside on the group of transition metals and earth metals. Zinc that belongs to a group of transition metals had been directly investigated as the promising solid acid catalyst for biodiesel synthesis. Istadi et al. [18] reported the activity of sulfated zinc oxide (SO$_4^2-$ZnO) catalyst that shown great potential as a catalyst for transesterification of soybean oil under low-temperature conditions obtaining 80.19% yield of FAME. Meanwhile, because of its high activity on the last research, modified ZnO was also investigated as an acid solid catalyst for biodiesel production from rapeseed oil [18].

The catalytic activity of the heterogeneous catalyst depends on some important factors, e.g. solid morphology including specific surface area and pore size, crystallinity, and active site concentration on the surface of the solid catalyst [20]. Active surface areas per volume unit of the catalyst can be improved using various methods. One of the methods to enhance its parameter is combining the solid catalyst with another material that has a large specific surface area and pore volume called catalyst support or carrier. Utilizing catalyst support could reduce the resistance to the three-phase reaction increasing its mass transfer rate [3]. Asri et al. [3] developed heterogeneous acid catalysts using alumina as catalyst support namely ZnO/γ-Al$_2$O$_3$ (ZA) and ZnO-CuO-SO$_4$/γ-Al$_2$O$_3$ (ZCSA) for transesterification of kesambi (Schleichera oleosa) oil. This previous study showed less satisfying results-producing 35% yield of biodiesel from the reaction at 65 °C. That catalyst will work well at high-temperature conditions (>200 °C) because its active site is easily reduced by hydration of acid hydroxyl (OH) group in the presence of water [3].

A carbon-based acid catalyst can be an alternative solution due to hydrophobic property inside its carbon sheet preventing hydration of hydroxyl group [21]. Among several catalyst support like γ-alumina, silica and various kinds of carbon, multi-walled carbon nanotubes (MWCNTs) show good potential for catalyst support utilization. MWCNTs have some beneficial intrinsic properties for catalysis, e.g. high surface area, high purity, and well-developed surface morphology and porosity [22]. Shuit et al. investigated MWCNTs utilization as catalyst support with the sulphuric group as an active site on esterification of palm fatty acid distillate (PFAD) resulting 93.5% yield of biodiesel [22]. Otherwise, there are no previous researches that develop MWCNTs supported zinc oxide as a solid catalyst for transesterification. Development of MWCNTs supported zinc oxide catalyst (MWCNTsZ) needs to be further studied to enhance the yield of biodiesel production especially from non-edible oil and other waste cooking oil.

In this study, multi-walled carbon nanotubes (MWCNTs) supported zinc oxide (ZnO) as a solid acid catalyst was prepared via a modified Stober process and precipitation method. Then, this catalyst was analyzed and characterized by some methods in order to observe the catalyst properties. Furthermore, the authors also focus on kesambi (Schleichera oleosa) oil utilization as a non-edible oil feedstock for biodiesel production. It shows great potential because it has high natural fat content, low price, abundant availability, and not competing with food sources. The activity of catalyst was also tested into biodiesel production from kesambi oil for investigating the influence of ZnO loading into catalyst support towards yield of FAME.

2. Materials and methods

2.1. Materials

The multi-walled carbon nanotubes (MWCNTs) as catalyst support was supplied by Advanced Material Esoterica, China. Other analytical grade reagents for MWCNTsZ catalyst preparation including methanol, sodium hydroxide, zinc chloride, ammonia, and ethanol were purchased from Merck, Germany. Those reagents were utilized directly with no further purification. Kesambi (Schleichera oleosa) oil as a non-edible oil feedstock for biodiesel synthesis was supplied from the local market. Moreover, methanol with commercial-grade level as a reactant for transesterification reaction was
provided from the domestic chemical supplier. Last, all standard reagents for Gas Chromatography (GC) analysis were also provided by Merck, Germany.

2.2. Methods

2.2.1. The preparation of multi-walled carbon nanotubes supported the zinc oxide (MWCNTsZ) catalyst. MWCNTsZ catalyst was prepared using a modification of the Stober gel-based process that was proposed by Mukenga, et al. with simultaneously impregnation and precipitation method [20]. Firstly, zinc methoxide as a precursor was synthesized by mixing 3 g of sodium hydroxide in 100 mL of methanol (90% v/v) to form sodium methoxide. Then, this formed sodium methoxide was reacted with 1 M zinc chloride solution at room temperature and stirred for 3 h. After 3 h, solid materials were formed and the solution was centrifuged for 5 minutes to separate this solid from its mother liquor. This produced solid that is zinc methoxide, then, was washed twice by methanol solution and dried at 45 °C.

In order to introduced nano ZnO to MWCNTs, two solutions were prepared. The first solution contains zinc methoxide as a precursor in ethanol solvent with various concentrations based on % loading ZnO variable ranging from 10%wt until 35%wt in catalyst support. In the other solution, 10 grams of MWCNTs with 59 mL of ammonia as the catalyst was dispersed into 100 mL of distilled water. This first solution containing precursor was introduced slowly using the dropwise technique into the second solution and stirred for 3 h to form ZnO nanoparticle inside MWCNTs pore. The solid precipitated product then was separated, washed with methanol solvent, and dried overnight at 80 °C. The dried solid catalyst was crushed into powder form and calcined at 500 °C for 5 h in a muffle furnace.

After the calcination process, the prepared catalyst was characterized to investigate its properties. The morphology of solid acid catalysts like total specific area, pore-volume, and average pore size diameter was measured by the Brunauer-Emmett-Teller (BET) method. Furthermore, X-Ray Diffraction (XRD) analysis was used for the detection of the crystal structure of the solid catalyst. Solid catalyst surface morphology appearance was captured by scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM-EDX) analysis. SEM-EDX analysis also was used to investigate the catalyst composition.

2.2.2. Transesterification of kesambi (Schleicheria oleosa) oil in the batch reactor. Kesambi oil which is one of non-edible oil must be purified before used as the feed of biodiesel production. This purification was called by degumming because kesambi oil contains a lot of gum impurities. The degumming process was carried out by oil heating at 70 °C in beaker glass. Phosphate acid (H₃PO₄) solution was added with an amount of 0.1% (v/v of oil) while stirred over 30 min. at 70 °C. This mixture subsequently was washed with aquadest and stirred slowly over 5 mins. dissolving residual H₃PO₄. After 48 h, there are formed three layers in this mixture that is oil in the top layer, gum in the middle, and water with a little dissolved H₃PO₄ in the bottom. Oil was separated from this mixture and heated at 110 °C in the oven for 12 h to release its water content.

Transesterification of kesambi oil was conducted in a batch reactor using prepared MWCNTsZ solid catalyst. A three-necked round bottom flask equipped with a reflux condenser was utilized as the batch reactor in this experiment. The batch reactor afterward was immersed in water bath heating this system until 65 °C as the operating temperature of this experiment. MWCNTsZ catalyst with the amount of 3% (w/w of oil) and 1:15 of oil to methanol molar ratio was used in this experiment. There are various loading of ZnO on MWCNTs applied in this experiment namely Z10 for 10%, Z15 for 15%, Z20 for 20%, Z25 for 25% and Z35 for 35% loading of ZnO.

The transesterification reaction was carried out at refluxed methanol condition (65 °C) under vigorous stirring at 150 rpm of speed for 3 h. After the reaction was terminated, the reactor was naturally cooled down to room temperature. Afterward, the liquid mixture was withdrawn from the reactor and filtered to separate the solid catalyst from this mixture. There are two layers formed in this liquid mixture, that is FAME and the rest of oil having a lower density in the top layer and glycerol and residual
methanol at the bottom. The product of the reaction was separated using centrifugation and evaporated to relieve the excess methanol.

Fatty acid methyl ester (FAME) content in biodiesel product was analyzed with a gas chromatography flame ionization detector (GC-FID) using a GC HP 5890 equipped with 20 m carbowax column. Nitrogen with a flow of 28 mL min\(^{-1}\) was used as the carrier gas in this analysis. The initial temperature was set by 150 °C and the initial time was 3 min, while the increment temperature was about 7.5 °C per minute until 275 °C as a final temperature was reached. The same procedure of GC analysis for biodiesel products had been used in the previous work [3]. The FAME content in the product from GC analysis was used to calculate the yield of biodiesel and the conversion of transesterification.

3. Results and discussion

3.1. MWCNTs-Z catalyst properties

The crystal structure of the catalyst was measured by X-Ray Diffraction (XRD) analysis. XRD method also detects the presence of zinc oxide compounds on the pore surface of multi-walled carbon nanotubes (MWCNTs). The dispersed of zinc oxide would increase the activity of catalysts towards transesterification. There are various loading of ZnO into MWCNTs ranging from 10%, 15%, 20%, 25%, and 35% weight of its support. The result was confirmed that ZnO was successfully loaded into MWCNTs surface regarding peak reference of ZnO and MWCNTs itself as shown in figure 1. The peak reference of the ZnO diffractogram was given by JCPDS (Joint Committee of Powder Diffraction Standard) card no. 00-036-1451 having diffraction peak at 2\(\theta\) (31.4; 33.8; 35.8; 46.8; 55.9; 61.7; 65.5; 66.9; 68.2; 71.5; 75.8; 79.7; 88.04 degree of angle). This XRD pattern had been indexed to the ZnO wurtzile structure and was seen more crystalline [23].

![Figure 1. Comparison of sample diffractogram, (a) MWCNTs; (b) Z15; (c) Z25.](image)

Meanwhile, the diffractogram of MWCNTs indicates the amorphous structure and has less crystallinity compared to ZnO. More ZnO loading into MWCNTs surface gives sharper peaks of ZnO diffractogram that means the more crystalline structure is formed. This is a similar result with the previous study that used ZnO/\(\gamma\)-Al\(_2\)O\(_3\) as the solid catalyst and reported by Asri et al. [3]. Unfortunately,
the unknown peaks were seen at 38; 44; 64; 77 degrees of 2θ angle meaning there are some impurities substances in the catalyst. These unknown peaks somehow have the same pattern with synthesized aluminum patterns that are given by JCPDS card no. 00-04-0787 [24]. These impurities were also indicated by SEM-EDX analysis that shown Al2O3 inside MWCNTs itself (table 1). The impurities inside of the MWCNTs is not significant because it was synthesized by chemical vapor deposition (CVD) techniques. The synthesis of carbon nanotubes by CVD is the most efficient method yielding high purity of the product and requiring no further purification [25]. Other impurities appeared inside the pore of MWCNTs after loaded with an amount of ZnO at the Z15 catalyst. This other impurity might be entrained during the preparation of the solid catalyst and formed other compounds in addition to the desired ZnO particle.

![Figure 2. SEM image of the catalyst surface, (a) MWCNTs; (b) ZT5.](image)

The morphological appearance of the catalyst was shown in the SEM image (figure 2). It is showed that MWCNTs material has randomly nanotubes arrays filling with the little amount of Al2O3 inside the nanotubes. This morphological surface was different from other nanotubes synthesizing with the CVD method that has typical well-alignment of nanotubes [25]. On the other hand, ZnO was successfully filled inside the nanotubes that are shown by dispersed white spotting on the entire surface of the nanotubes (figure 2b). It was also clarified from EDX analysis that the Z15 catalyst contains 4.53 %wt of ZnO.

**Table 1.** Composition of solid catalyst from EDX analysis.

| Compound     | % mass | Z15  | MWCNTs |
|--------------|--------|------|--------|
| C            | 93.45  | 99.4 |        |
| Al2O3        | 0.49   | 0.6  |        |
| ZnO          | 4.53   | -    |        |
| Other impurities | 1.53  | -    |        |

Moreover, MWCNTs have great potential to be used as catalyst support because of its large surface area (table 2). Its surface area was larger than other compounds that usually utilized as catalyst support like γ-Al2O3, zeolite, bentonite, and hydrotalcite [1][7][12]. Generally, dispersing ZnO particle inside the pores of MWCNTs could reduce its total surface area. After ZnO was dispersed inside the nanotubes of MWCNTs, the surface area of the catalyst decreased to nearly 40% (table 2). However, its reducing area due to ZnO loading is still not significant with the total surface area of catalyst exceed to 400 m²/gram. This large total surface area provides great potential to attract reactants while reducing the mass transfer and enhancing the reaction rate.
Table 2. BET surface area analysis of the solid catalyst.

| Analysis | MWCNTs  | Z10  | Z15  | Z20  | Z25  | Z35  |
|----------|---------|------|------|------|------|------|
| Surface Area (m$^2$/g) | 673.242 | 296.991 | 409.043 | 316.026 | 228.824 | 136.918 |

3.2. Transesterification of *kesambi* (*Schleichera oleosa*) oil

The biodiesel product from the transesterification of kesambi oil was measured by Gas Chromatography (GC) analysis method. The activity of catalyst is determined by the active site concentration which in this case is zinc oxide (ZnO) loading into catalyst support. The amount of ZnO as an acid active site played an important role in this transesterification process. The effect of ZnO loading on this process was studied during the reaction by varying ZnO loading from 10 %wt until 35 %wt inside the catalyst. Meanwhile, the other process conditions were kept constant such as 65 °C of reaction temperature, 3 h of reaction time, and 1:15 of oil to methanol molar ratio.

![Figure 3. The yield of biodiesel product from transesterification of kesambil oil using a various catalyst.](image)

The yield of biodiesel is depicted in figure 3 and generally increases while % loading of ZnO is raised. It is presumed that transesterification would not take place without the presence of catalyst and biodiesel would not form. The highest yield of biodiesel is achieved while using the Z20 catalyst in the reaction. And, increasing % loading of ZnO above 20 %wt precisely decreases the yield of biodiesel.

However, the yield of biodiesel product is somehow having low value under 15% (figure 3). This is in contrast with the previous study that resulted above 70% yield of biodiesel during the addition of a few amounts (1% w/w of oil) of ZnO based catalyst [3]. It might have occurred because in the previous study ZnO was dispersed over 50 %wt inside the pore of catalyst support that means there is 0.5% (w/w oil) of ZnO in the entire of oil reactant [3]. This huge amount of ZnO active acid site would increase the rate of reaction. It was different from the result of this research that is disappearing under 5 %wt of ZnO. With 3% (w/w oil) of solid catalyst in the reaction, it would be only 0.136 %wt of ZnO in the entire process feedstock.

Theoretically, Zn$^{2+}$ probably has active Lewis acid sites giving an effect to trigger both esterification and transesterification reaction simultaneously [3]. Because of that, ZnO would be appropriate to catalyze these reactions and could process low-grade oil that contains high FFA. But, the result was not satisfied yielding a low concentration of FAME in the product. This result indicates that the preparation
of catalysts using a modified Stober-like process with impregnation and precipitation simultaneously did not give much more dispersed ZnO on the surface of the catalyst support. It was different from the previous study while used modified Stober-like synthesis with the sol-gel method.

4. Conclusion
The multi-walled carbon nanotubes supported zinc oxide (MWCNTsZ) catalyst with a large surface area had been successfully prepared with the modified Stober-like process with simultaneously impregnation and precipitation method. Zinc Oxide (ZnO) was successfully dispersed inside the nanotubes of MWCNTs via this modified technique. However, due to only a few amount of ZnO was dispersed inside the pores, biodiesel could not be produced with satisfactory results. This result encourages us to develop multi-walled carbon nanotubes supported zinc oxide (MWCNTsZ) catalyst using another routing process in order to gain high FAME content in biodiesel products.

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