Functionalization of Multiwall Carbon Nano-Tube Supported Zinc Oxide Solid Acid Catalyst Using Sulfonate Compound for Transesterification of *Schleichera Oleosa* L Oil

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Abstract. Biodiesel is an alternative energy obtained through the transesterification of vegetable oil in the presence of a catalyst. The catalyst plays a very important role in the success of the transesterification process. One way to increase the activity of the catalyst is through chemical modification called functionalization, which generally using SO₃ group as a sulfonating agent is known as the sulfonation process. However, the disadvantage of this process is that it uses strong acids which are corrosive, require high temperatures and are not environmentally friendly. This study aims to increase the activity of zinc oxide catalyst supported by multi-wall carbon nano tube (Z/MWCNTs) sulfonated using (NH₄)₂SO₄ as sulfonating agent. The synthesis route includes co-precipitation, sulfonation and precipitation time. The effect of concentration of ammonium sulfate, co-precipitation time, and sulfonation time on yield of biodiesels of kesambi (*Schleichera oleosa* L) oil (OSOBD) was investigated. The result showed that the activity functionalized Z/MWCNTs catalyst (Zs-MWCCNTs) could enhance significantly. The results of the catalyst activity test on transesterification of OSO into biodiesel showed that Zs-MWCNTs gave a high yield of 91% for the functionalized catalyst using ammonium sulfate with a concentration of 35%, co-precipitation time 12 hours and sulfonation time 4 hours. The functionalization of MWCNTs with the sulfonation process using ammonium sulfate has the potential to increase catalyst activity and can increase the efficiency of the transesterification process for non-edible oils, especially kesambi oil.

1. Introduction

Currently, about 80% of the world's energy needs are supplied by fossil fuels [1, 2]. Crude oil which is a fossil fuel when used continuously will not only have an impact on the depletion of its reserves, but also lead to a decrease in environmental quality [3]. Many researchers have made efforts to explore the potential of renewable fuels to overcome this problem. Biodiesel (BD) has proven to be very potential
to replace fossil fuels, because it is environmentally friendly, easily biodegradable, low greenhouse gas emissions, non-toxic, and many other advantages [1].

Generally, BD is easily produced through the transesterification of refined edible oil (REO) with short-chain alcohol (methanol is most preferable) in the presence of a homogeneous alkaline catalyst. In fact, the price of high-quality REO is expensive, hence its usage caused the high cost of BD production. Several previous references stated that raw materials is the highest contributor about 70-90% to the BD production cost [2, 3]. Therefore, the preferred feedstock currently used is low-quality vegetables oil (LQVOs) include non-edible oil (Jatropha curcas oil, cottonseed oil, rubber seed oil, Schleichera oleosa L oil, etc.), palm free fatty acid distillated (PFAD) and waste cooking oil, which is the price is much cheaper than REO. Oil of Schleichera oleosa L (OSO), known as kesambi oil, has the potential to be used as raw material for BD, due to its high oil content, abundance, and currently being cultivated by the Ministry of Forestry of the Republic of Indonesia [3].

The development of (LQVOs) as a raw material for BD production is a very effective strategy to reduce the total production cost of BD [2, 4, 5, 6]. In addition, it can also avoid competition with the needs of the food industry's feedstock. However, it is known that all LQVOs contain very high FFA, so the use of homogeneous alkaline catalysts on its transesterification process is very unprofitable, due to it takes a large amount of catalyst dosage, high purification cost, and declined in BD yield [2, 7]. Instead, an acid heterogeneous catalyst is the most suitable for converting LQVOs into BD because its insensitivity properties to FFA better than that of alkaline heterogeneous catalysts [1, 5].

Research on acid heterogeneous catalysts has been carried out by many previous researchers including: sulfated zinc oxide catalyst on transesterification of soybean oil [8], sulfonated MWCNTs on converting of PFAD [9, 10] nano zinc oxide composite catalyst doped in copper metal (CZO) for transesterification used fraying oil (UFO) [11]. The synthesis of Co-doped ZnO nanocatalyst and its application on biodiesel production from non-edible oil was reported by Borah et al. [12]. Meanwhile, mesoporous SO\textsubscript{3}H–ZnAl\textsubscript{2}O\textsubscript{4} solid acid catalyst for PFAD transesterification was investigated by Soltani et al [13]. However, none of them discussed the application of heterogeneous acid catalysts for transesterification of OSO.

Asri et al. (2020c) [14, 15, 16], have synthesized zinc oxide acid catalyst supported by MWCNTs (Z/MWCNTs) via Stober-like process that was proposed by Mukenga et al.[17] followed by precipitation method. The catalyst has been applied for transesterifying OSO with observe some parameter of transesterification process namely ZnO loading, catalyst dosage, and reaction time [14, 15, 16]. However, the result is not worthy and very unsatisfying. The highest BD yield of 42% was obtained at 20% of ZnO loading (wt.% to MWCNTs), within 5 h of reaction time , and 4% of catalyst dosage [16]. This is possible because the MWCNTs as catalyst support is not treated before the ZnO promoter was added, so the ZnO couldn't be well distributed in the pores and didn't properly adhere to its surface. Therefore, the activity of Z/MWCNTs should be enhanced to gain an efficient transesterification process with a high yield of BD. One easy way to increase catalyst activity is by chemical modification, namely functionalization of MWCNTs [2].

This study aims to increase the activity of the Z/MWCNTs catalyst by modifying the route of the catalyst synthesis process via functionalizing prior against MWCNTs support then followed by the precipitation method. Generally, the functionalization process was done using some acid groups include sulfonate (–SO\textsubscript{3}H) or carboxilate (–COOH) groups [10]. The activities of the sulfonated carbon-based catalysts are better than most other acid catalysts [2]. MWCNTs are trusted to be the most potential as catalyst support for the sulfonic group (–SO\textsubscript{3}H) due to their specific properties such as high surface area, high purity, very good conductivity, and good stability [10]. The strong acids such as sulfuric and nitric acid are the common used for sulfonating process. However, these acids include hazardous materials and are highly corrosive as the sulfonating agent. This method could be produced a large amount of wastewater from the washing process that should be conducted after the sulfonation process.

Therefore, this work focuses on the functionalization of Z/MWCNTs using ammonium sulfate ((NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}) to obtain nano-zinc oxide catalyst supported by sulfonated MWCNTs which further
coded by Z/s-MWCNTs). The activity of the Z/s-MWCNTs catalyst should be better than that of Z/MWCNTs and can be enhancing the BD yield of the transesterification of OSO. In addition, some parameter includes the concentration of sulfonating agent ((NH$_4$)$_2$SO$_4$), the oxalate impregnating time and reaction temperature were investigated. The synthesized Z/s-MWCNTs was used to covert OSO into BD of schleichera oleosa L oil (OSOBD).

2. Material and method

2.1. Materials.
Analytical grade of Ammonium sulfate, oxalic acid (H$_2$C$_2$O$_4$·2H$_2$O), zinc acetate (Zn(CH$_3$COO)$_2$·2H$_2$O), acetone and methanol for synthesized of Z/s-MWCNTs were provided by Mreck, Germany. Other materials both analytical and commercial grade are the same as the previous work [16]. All those material are used directly without pretreatment. Commercial grade of OSO as the feed-stock was purchased from local market at Probolinggo city. Although the city is different from the OSO source in the previous study (Pasuruan city), it is located next to Pasuruan City and is in the same province (East Java). Likewise, the chemical and physical properties of the OSO are almost the same, namely: FFA as linolelaidic acid (w/w %), Iodine value (g I$_2$/100 gr), moisture content (w/w%), saponification value (mg/gr), viscosity (cSt), and density (mg/mL) of 9.26, 77.50, 0.01, 526.61, 2.14, and 0.91, respectively

2.2. Methods
2.2.1. Preparation of Z/s-MWCNTs

The different route was used for synthesizing of Z/s-MWCNTs compare to Z/MWCNTs. The new route consists of co-precipitation, sulphonation of MWCNTs followed by precipitation process. First, dissolve 2.84 g of zinc acetate into 50 mL of demineralized water while stirring until it dissolves completely. Add the oxalic acid solution (2.835 g oxalic acid in 50 mL demineralized water) dropwise while stirring for 12 hours until a white precipitate of zinc oxalate is formed. The precipitate was separated followed by washing 3-5 times using distilled water, then finally washed with 10 mL of acetone. The precipitate was dried in the oven for 24 hours. Furthermore, the dry solids are calcined in the muffle furnace at 500◦C for 4 hours. After calcining process the ZnO catalyst was kept in desiccator while waiting the sulphonation of MWCNT process. Sulphonation procedures were modified according to previous reference [10, 18, 19]. In this process, 5 gram of MWCNTs was mixed with 375 ml of different concentration of ammonium sulfate solution (20, 5, 30 and 35 w.%). The mixture was stirred by magnetic stirrer in room temperature for 3 h. Then the mixture was continued stirring under reflux condenser, and oil bath system at 120◦C for 4 h. The sulphonated MWCNTs precipitate (MWCNTs-SO3H) was separated from the mixture, washed with distilled water 3-5 times, and then coded as s-MWCNTs. To prepare zinc oxide nano catalyst supported by s-MWCNTs, the calcined ZnO was mixed with 50 ml demineralized water and poured into the dispersion of 50ml s-MWCNTs in demineralized water. The mixture was stirred using magnetic stirrer 4 h at room temperature. To prepare zinc oxide nanocatalyst supported by s-MWCNTs, the calcined ZnO was mixed with 50 ml demineralized water and poured into the dispersion of 50ml s-MWCNTs in demineralized water. The precipitate of ZNO/s-MWCNTs was separated from the mixture and put it into the crucible dish for drying overnight in the oven at 120 C. After the drying process the catalysts were put in a small plastic bag coded by Z/s-MWCNTs then stored in a desiccator until further used for catalyst characterizing and testing of the activity. The catalyst carachterization was done by XR-D, FTIR, SEM-EDX and BET methods.

2.2.2. Pretreatment of kesambi oil (OSO)

Pretreatment of OSO include degumming and reducing of the FFA content. The FFA content of OSO is quite high as much as 9.26% as has been shown in the material sub-chapter, it’s necessary to
reduce the FFA level before the transesterification process. Besides that, OSO also contains impurities in the form of gum, so it’s need to remove before the FFA reduction process is carried out. The purpose of degumming is to separate oil from gum which is an impurity consisting of phosphates, proteins, carbohydrates, water residues and resins, so the oxidation stability of the final product can be improved. The degumming procedure is simple using 0.1% (v/w.% to oil) analytical grade Phosphoric acid, which has been fully described at previous work [1, 16]. After the degumming process, the oil was treated to reduce FFA levels using dry coconut coir powder as an adsorbent. The procedure has been explained in detail at previous studies [5]. Furthermore, the treated OSO is ready to be used for the transesterification process.

2.2.3. Catalytic activity test

The activities of Z/s-M WCNTs synthesized catalysts were done through transesterification process to convert OSO as starting feedstock into biodiesel of kesambi oil (OSOBD). The experiments were carried out in a laboratory-scale glass type reactor coupled with other equipment such as a reflux condenser, a thermometer, an electric stove with a magnetic stirrer, and a water bath to regulate the reaction temperature. Enter the oil, methanol and catalyst Z/s-MWCNTs into the three necks round bottom flask according to the desired ratio, then heated to the desired temperature while stirring with a magnetic stirrer. The reaction was stopped after the desired time was reached. Leave for a while at room temperature, after which the mixture is filtered to separate the catalyst and liquid. The liquid is poured into a separating funnel, allowed to stand until 3 layers are formed consisting of methanol, BD and glycerol in order from the top layer to the bottom layer. BD is separated from the mixture for analysis, volume measurement, and characterization. Furthermore, the OSOBD yield (%) was calculated by the following equation:

\[
\text{Yield of OSOBD (\%) = } \frac{w \text{ of OSOBD product}}{w \text{ of OSO}} \times 100\%
\]  

Where \( w \text{ of OSOBD product} \) was calculated from volume of product (ml) multiplied by density of OSOBD. Meanwhile, \( w \text{ of OSO} \) was weight used in the experiment (g).

3. Results and Discussion

3.1. Physicochemical properties of OSO

Table 1 shows the physicochemical properties of collected OSO before and after treatment. The FFA content decreased from 9.26 into 0.07%, water content reduces from 0.12 into 0.01%, and the other components showed significant improvements. It’s well known that FFA and the water content of vegetable oil are the two main components that influence the success of the transesterification process [20]. The value of those two components could be safe and believed wouldn't interfere with the transesterification process because it is already below the allowable threshold (the maximum level of them is 3 and 0.5%, respectively) [21, 22]. The other components also showed significant improvements. Degumming and coconut coir treatment proved reducing the FFA content of OSO significantly.
Table 1. The comparison of physicochemical properties of OSO before and after treatment

| Parameter                   | OSO before treatment | OSO After treatment |
|-----------------------------|----------------------|---------------------|
| FFA as Linolelaidic (%w/w)  | 9.26                 | 0.07                |
| Density (g/ml)              | 0.91                 | 0.88                |
| Iodine Value (g I² / 100 g) | 77.50                | 79.10               |
| Moisture Content (% w/w)    | 0.12                 | 0.01                |
| Saponification Value (mg/g) | 525.61               | 531.02              |
| Viscosity(cSt)              | 2.14                 | 2.25                |

Meanwhile, the fatty acid composition of OSO used in this work is the almost same as the previous work [15]. OSO was dominated by more than 90% unsaturated fatty acid mainly linolelaidic acid, eicosenoic acid, linoleic acid, and oleic acid namely about 50%, 29%, 5%, and 3%, respectively. The saturated fatty acids are palmitic acid around 7% and miristic acid 0.01%. While 6% remaining is consists of a small amount of other unsaturated fatty acids.

3.2. Characteristics of synthesized ZnO/s-MWCNTS

3.2.1. SEM analysis

SEM analysis was done to identify the surface condition and morphology of the particle. Figure 1 shows the SEM image comparison of the MWCNTs it selves (Figure (a), non-sulfonated catalysts (Z/MWCNTs) (Figure (b)), and sulfonated catalysts (Z/s-MWCNTs) (Figure (c)). Figure (a) shows the morphology of the pure MWCNTs in the form of randomized array carbon tubes. In figures (b) and (c) seen that MWCNTs are still in the form of carbon tubes which attributed that there is no change in the shape of the MWCNTs after the ZnO particle is anchored on its surface. Furthermore, ZnO particles were clearly visible in the form of white flower-like spots attached to both the surface of Z/MWCNTs and Z/s-MWCNTs. However in Figure c, white flower-like spots appear smooth, and homogeneous on the surface of s-MWCNT. This indicates that ZnO is well distributed on the mouth of the catalyst pore and properly adhered to its surface.

Figure 1. SEM image of MWCNTs (a), Z/MWCNT (b) and Z/s-MWCN

3.2.2. X-ray diffraction

XRD was used to identification the structure of the catalyst (crystalline or amorphous), and it’s also used to calculate the crystal size. The XRD pattern of Z/s-MWCNTs (Figure 2 (a) has more diffraction peaks appearing at 2θ compare to pure ZnO (Figure 2 (b) and pure MWCNTs (Figure 2 (c). There are some types of diffraction peaks on its pattern. A broad beak low peak indicates amorphous of carboneous material. The graphite form which is stacking to interlayer of graphene sheet was shown by a strong and sharp peak at 27.06° [23]. The diffraction peaks registered at 2θ=37.0°, 46.0° and 66.7° assigned to amorphous Al₂O₃ as an impurities of MWCNTs.
X-ray diffraction (XRD) was used to identification the structure of the catalyst it’s used to identify the structure of the catalyst (crystalline or amorphous), and it’s also used to calculate the crystal size. The XRD pattern of Zs-MWCNTs (Figure 2 (a) has more diffraction peaks appearing at 2θ compare to pure ZnO (Figure 2 (b) and pure MWCNTs (Figure 2 (c). There are some types of diffraction peaks on its pattern. A broad beak low peak indicates amorphous of carboneous material. The graphite form which is stacking to interlayer of graphene sheet was shown by a strong and sharp peak at 27.06° [22]. The registered diffraction peaks at 37.0°, 46.0° and 66.7° assigned to amorphous Al2O3 which is an impurities of MWCNTs. Meanwhile, the most sharp and highest diffraction peak of ZnO appears in a good agreement with the patent standard of hexagonal wurtzite ZnO according to Joint Committee of Powder Diffraction Standard (JCPDS) card no. 00-036-1451[24].

![X-ray diffraction pattern](image)

**Figure 2.** X-ray diffraction pattern; (a) Z/s-MWNTs; (b) ZnO; (c) MWCNTs based on JCPDS #01-0646

3.2.3. FT-IR analysis

In this work, the FT-IR spectroscopy (Perkin-Elmer Spectrophotometer Spectrum one) was used to investigate the functional group of substances. The FT-IR spectrum of Zs-MWCNTs was shown in Figure 3. Figure 3 (a) shows a graph of the FT-IR spectrum of pure ZnO. This spectrum shows an absorption band at a wave number of 450 cm⁻¹ which indicates the stretching vibration of ZnO. The Z/s-MWCNTs catalyst (Figure (b) and (c)) also shows stretching vibrations indicated by the absorption band at 450 cm⁻1. However, the vibration peaks are not sharp, which indicates that the ZnO fed to the buffer MWCNTs is not all distributed and adheres well to the surface of the MWCNTs. This fact is supported by the results of the composition analysis of the catalyst through the sem-edx analysis. From some of ZnO loading (20-60% to the MWCNTs) only the 6-25% of them is well dispersed and adhered in the pore and surface of MWCNTs. Furthermore, the functional groups O=S=O and S−O were seen in the adsorption bands 1061 and 668 cm⁻1, but their presence was not very clear.
3.3. The effect of the catalyst synthesized parameters

The test of the effect of catalyst synthesis parameters on the activity of the synthesized Z/s-MWCNTs was carried out through a transesterification process, which Z/s-MWCNTs was used to convert OSO into OSOBD via one variable at the time (OVAT) approach. The factors studied included the effect of ammonium sulfate concentration (ASC) (wt%), co-precipitation time (CT) (h) and sulfonation time (ST) on the yield of OSOBD.

3.3.1. Effect of CT (h) and ST (h) on yield of OSOBD

The time of co-precipitation of oxalic acid on zinc acetate (CT) and sulfonation of MWCNT were also investigated using OVAT approach, with varying of CT from 6-12 h with 2h interval, and ST varies at 3 and 4 h. Furthermore, the others condition were kept constant. Figure 5 shows the effect of CT and ST on the yield of OSOBD. It seen that both of them significantly affected the yield of OSOBD. At ST 3 h, yield gradually increases with the raise of CT from 6-8-10, 12 h. A different performance was seen at ST 4h. Initially, the low yield of 20% was achieved at 6h of CT. Yield increased sharply at 8 h CT, then yield slowly increased again with increasing CT from 8 to 10, and 12 h.

3.3.2. Effect of ammonium sulfate ((NH₄)₂SO₄) concentration

To investigate the influence of ASC on the yield of OSOBD, the experiments were conducted by varying the ASC from 20% to 35% with a 5% of interval. The other synthesized conditions were kept constant at 20% loading ZnO, calcination temperature 500°C, and 4 h of ST time. Meanwhile, the transesterification process was conducted at 65°C, 3% of loading catalyst, and ratio molar oil to methanol of 1:15. Figure 4 shows the ASC significantly influence the OSOBD yield. It seen that OSOBD increases gradually from 46.01 to 54.63% with the increasing of ASC from 20% to 25%. Conversely, the yield sharply rises to 85.7% at ACS 30%, and then gradually rises to highest of 91%
at 35% ACS. Shuit et al. (2015) found different results, where at low concentrations of (NH4)2SO4 (1, 5, and 10%) there was an increase in biodiesel yield with increasing concentration of ammonium sulfate solution. However, at a high concentration solution of (NH4)2SO4 (15-20%) the performance of the catalyst is lower than that the catalyst synthesized with a low concentration of ammonium sulfate. This is possible, because they use a sulfonation process with a different route, namely the sonication process and followed by thermal decomposition at high temperatures (235 C). So that in the catalyst synthesized using a high concentration of ammonium sulfate solution there is an interaction effect between high temperature and long sonication time which causes agglomeration of the catalyst (Shuit et al., 2015). Meanwhile, preparation of Z/s-MWCNT was conducted at mild temperature (120°C) without sonication, so that logically it requires a higher concentration of Ammonium sulfate and a longer co-precipitation time.

![Figure 5](image_url)

**Figure 5.** Effect of ammonium sulfate concentration (ASC) (wt. %) on OASOBD yield (%)

4. Conclusion

Functionalization of Z/MWCNTs has been done to increasing its activity by co-precipitation, sulfonation, and impregnation methods. Sulfonation was done using ammonium sulfate as the sulfonating agent. From the activity catalyst test via transesterification process of OSO using the synthesized catalyst of Z/s-MWCNTs, found that the parameters of the route of catalyst synthesis include Concentration of ammonium sulfate (ASC), Co-precipitation time (CT) and sulfonation time (ST) has a significant effect on the yield of OSO BD. It was concluded that the functionalized of Z/MWCNTs to Z/s-MWCNTs catalyst can enhance the catalytic activity, proved by yielding the high of 91% of OASOBD.

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