Synthesis of biodiesel from kesambi (Schleichera oleosa L.) oil using carbon nanotube-supported zinc oxide heterogeneous catalyst

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Abstract. Multiwall carbon nanotubes (MWCNTs)-supported zinc oxide (ZnO/MWCNTs) heterogeneous catalyst has been prepared using impregnation and gel process. This catalyst has been utilized to synthesize biodiesel via transesterification process from Kesambi (Schleichera oleosa L.) oil (SOO) and methanol. The prepared ZnO/MWCNTs catalyst prior was characterized using the X-ray diffraction (X-RD), Brunauer-Emmett Teller (BET), and Scanning Electron Microscopy with energy dispersive X-Ray microscopy (SEM-EDX) methods. The transesterification process was performed in a three necks round bottom flask batch type reactor. The influence of several parameters includes reaction time (h) and the amount of catalyst (w/w% of SOO) on biodiesel's yield, were studied. It was found that ZnO/MWCNTs were potentially used as a heterogeneous catalyst for transesterification of kesambi oil. The highest biodiesel yield of 41.9% was achieved at 65 °C, 5 h of reaction time, 4% of catalyst amount, and 1:15 of molar ratio SOO to methanol.

1. Introduction

The increasing growth of the world’s population has an impact on the increasing energy needs and ultimately has caused a drastic decline in oil reserves. The scarcity of fossil fuels and the increasing awareness of environmental problems has led to the development of alternative fuels from renewable sources [1]. There are three main ways to overcome the sustainability of the energy problem, namely: the enhancement of petroleum technology, the development of renewable energy, and the increasing efficiency of energy conservation [2]. In the future, it seems that the development of renewable energy plays a vital role, especially in Indonesia, because of its huge renewable energy sources [3]. Vegetable oil is one of the potential sources to be developed because of its abundant presence. Even today, Indonesia is known as the world's largest producer of palm oil. The fact vegetable oil is one of an excellent biodiesel feedstock [4]. Currently, raw materials for producing biodiesel are preferably using low-grade oil (LGO) and non-edible oil (NEO) such as jatropha oil, kesambi (Schleichera oleosa L.)
oil (SOO), kapok seed oil, and many others. Those oils were abundantly available and cheap price. Moreover, its use as feedstock might reduce biodiesel production costs and not interfere with the national food industry [1].

Biodiesel, with another name, fatty acid methyl ester (FAME), is generally produced by converting oils/fats through the transesterification process using methanol as a reactant with a catalyst. It has been believed, it offers many advantages such as non-toxic, low carbon dioxide emissions, renewable, and biodegradable, so it has the potential to replace diesel oil [4,5]. The use of heterogeneous (solids) catalysts has proven to be very effective in replacing homogeneous catalysts because it offers many advantages, including being easily separated with products, can be regenerated (reused), and environmentally friendly [6,7].

Many types of solid catalysts for biodiesel synthesis, whether acidic or basic catalysts, have been developed by previous researchers [7]. Alkaline catalysts that have been widely developed for transesterification include calcium oxide [8,5], magnesium oxide [9], alumina-based [10,3], amorphous-zirconia based (Ti/ZrO2, K2O/ZrO2, and WO3/ZrO2) [5], zeolite-based catalyst [11], and hydroalumina catalyst [12]. Calcium mixed oxide catalysts are one of those catalysts that have been proven to be used in the transesterification process. Asri et al. [1] developed double promoted catalyst CaO/Al2O3 for transesterification of refined oil (RPO) at mild temperature (65 °C), resulting in 94.94% yield of biodiesel [4].

However, those base catalysts are not suitable for transesterification of LGO or NEO that the fact contains a high level of free fatty acid (FFA) [1]. Many researchers are recently interested in exploring heterogeneous acid catalysts for transesterification of LGO/NEO due to their excellent characteristics. The important characteristics of heterogeneous acid catalysts include large pores, strong active sides, and hydrophobic surface properties [13, 14]. Those characteristics provide many advantages, including insensitivity to FFA content, promoting esterification and transesterification reactions simultaneously, and it does not need the washing process of FAME products [13]. Generally, acid catalysts are sourced from transition metal or metal oxides. There are many transition metal oxides include ZrO2 [15], WO3 [16], TiO2 [17], ZnO [18], and SnO2 [19], have been developed to address the conversion of many kinds of triglyceride (TG). However, all those catalysts have some limitations, like a slow reaction rate and appearing undesirable parallel reactions [13].

The heterogeneous catalyst's physical properties, including specific surface area, pore size, pore-volume, crystallinity, and the number of active sites on its surface, highly influenced solid catalyst activity [20]. To increase the physical properties of a solid catalyst can be done by adding catalyst support, which could reduce the three-phase reaction's resistance, subsequently increasing the mass transfer rate. Asri et al. [3] investigated alumina-supported heterogeneous acid catalysts of ZnO/γ-Al2O3 (ZA) and ZnO-CuO-SO4γ/Al2O3 (ZCSA) for transesterification of SOO. However, the result is not satisfying with a low biodiesel yield of 35% [3], due to its active site is easily reduced by hydration of acid hydroxyl (OH) group in the presence of water [21]. A carbon-based acid catalyst with a hydrophobic property might be a solution to this problem [21].

Some of the catalyst supports are commonly used include γ- alumina, silica, bentonite, and various kinds of carbon. Multi-walled carbon nanotubes (MWCNTs) seem to be promising to be used as catalyst support for the transesterification process due to the beneficial intrinsic properties such as high surface area, high purity, and well-developed surface morphology and porosity [22]. Shuif et al. [22] studied MWCNTs that were functionalized by a sulphuric acid group as an active site used on esterification of palm fatty acid distillate (PFAD), obtaining a 93.5% yield of biodiesel [22]. Asri et al. have developed a zinc oxide catalyst supported by MWCNTs with various variables such as ZnO loading, calcination temperature, and calcination time [23]. The activities of the synthesized catalysts have been tested through the transesterification reaction of kesambi oil. It turns out that the catalyst with a ZnO loading of 20% (MWCNTsZ20), a calcination temperature of 500 °C, and a calcination time of 5 h gives the highest biodiesel yield. However, those tests were carried out under a constant transesterification parameter, which included the amount of catalyst (w/w% of oil), reaction temperature, and reaction time of 3%, 65 °C, and 3 h, respectively. It is necessary to optimize the


parameters that affect SOO's transesterification process using MSCNTsZ catalyst to get the best FAME yield. With the lack of information related to the development of MWCNT supported zinc oxide (MWCNTZ) solid catalysts and their limited use in biodiesel synthesis, it is necessary to conduct more intensive research. So far, no studies are discussing the application of WCNTZ for transesterification of kesambi oil.

Therefore, an in-depth examination addressing the influence of transesterification parameters on the yield of biodiesel was needed. Among those parameters that influenced the transesterification process, in this study, we focus on two parameters, namely the effect of the amount of MWCTsZ20 catalyst (w/w% of oil) and reaction time (h) on yield (%) of biodiesel of kesambi oil (BKO).

2. Materials and Methods

2.1 Materials

As the previous work [23], the starting material, namely multi-walled carbon nanotubes (MWCNTs), was purchased from Advanced Material Esoterica, China. Merck, Germany, provided all the analytical grade materials needed for synthesizing the MWCTsZ20 (methanol, sodium hydroxide, zinc chloride, ammonia, and ethanol). Likewise, all standard reagents used for gas chromatography (GC) analysis were also provided from Merck, Germany. Those substances were directly used without prior purification. Technical grade methanol as a reagent in the transesterification process was obtained from a local chemical supplier. Meanwhile, kesambi oil (SOO) as feedstock for biodiesel synthesis was supplied by local suppliers in the city of Pasuruan, East Java.

2.2. Methods

2.2.1. The preparation of (MWCNTsZ20) catalyst

MWCNTsZ20 was a synthesis using modified Stober methods [20] combined with the precipitation method. The procedure has been explained in previous studies [23]. First, zinc methoxide precursor was synthesized by reacting 50 ml of 3% (weight %) sodium hydroxide solution, and 35 ml of zinc chloride solution with 20% of ZnO loading (w/w of MWCNTs), both of those solvents are methanol. The mixture was stirred well for 3 hours at room temperature; a white precipitate of zinc methoxide would be formed and subsequently was centrifuged for 5 minutes to separate zinc methoxide with the solution. The white precipitate of zinc methoxide was then dried in the oven at 45 °C. Furthermore, the dried zinc methoxide was dissolved in 50 ml of alcohol, then added by dropwise technique through the burette into 50 ml of dispersion of MWCNTs in ammonia and distilled water while stirring for 3 hours to direct ZnO solids to disperse in the pore of catalyst and part of them stick to the surface of MWCNTs. The mixture was filtered to separate black solid with the solution and washed using methanol, then dried in the oven overnight at 80 °C. The dried black solid product was crushed in a porcelain mortar into a fine black powder and calcined at 500 °C for 5 h in a muffle furnace.

The calcined MWCNTsZ20 catalyst was stored in a desiccator containing silica gel, then ready to be characterized to determine its physical properties using several methods, including x-ray diffraction (X-RD), Brunauer Emmet-Teller (BET), and scanning electron microscopy (SEM_EDX). X-RD method was used to identify the structure of the catalyst. BET analysis was performed to determine the average surface area, pore volume, and diameter of the pores, while SEM-EDX to show the morphology and determine the composition of the catalyst.

2.2.2. Synthesis of biodiesel from kesambi (Schleichera oleosa) oil

Biodiesel synthesis was carried out through the transesterification process of kesambi oil using a synthesized MWCTsZ20 catalyst. However, before synthesized into biodiesel, SOO must be treated prior because it is one of the NEO groups, which is including low-quality oil with high levels of free fatty acids and contains impurities such as water and gum. To eliminate the water content, SOO was heated at 105 up to110 °C in a 11 beaker glass. The degumming process was then performed by adding analytical grade H3PO4 as much as 0.1% (v / v to oil) heated at 70 °C while stirring well for 3 minutes, followed by washing with distilled water by slow stirring for 5 minutes. The mixture was
centrifuged for 5 minutes and then poured into a separating funnel, allowed one night at room temperature until it forms 3 layers. SOO was separated from the mixture subsequently; it was heated at 110 °C in the oven overnight for removing the remaining water content. After that, SOO was ready to synthesize into biodiesel.

The transesterification process of SOO using the MWCNTsZ20 catalyst was carried out in a laboratory-scale reactor as the procedure described in previous studies [1,23,24]. The treated SOO and methanol with a molar ratio of 1:15 were poured into a 250 ml three necks flask equipped with auxiliaries such as a reflux condenser, heating stove with a magnetic stirrer, water bath, and thermometer. Next, the MWCNTsZ20 catalyst was added to the mixture while stirring during the reaction. The experiments were carried out at 65 °C, 1:15 of the molar ratio of SOO/methanol, and 150 rpm of stirring speed, while the catalyst loading varied from 2 to 4.5% at 0.5% interval, and the reaction time varied from 1 to 7 h with 1 h interval. After reaching a predetermined time, the reaction was stopped and the mixture filtered to separate the catalyst. Furthermore, the liquid product was inserted into a separating funnel, then allowed to form three layers: the lowest layer of glycerol, the middle of biodiesel from kesambi oil (BKO), and methanol was at the top layer. BKO was separated from the mixture to analyze its FAME content using gas chromatography (GC) analysis. FAME content in the product was used to determine BKO yield (%), calculated using equation (1).

\[
\text{Yield of BKO} \, (\%) = \frac{W_{\text{of product}} \times \% \text{FAME in the sample}}{W_{\text{of SOO}}} \times 100\%
\]  

(1)

Where \(W_{\text{of product}}\) and \(W_{\text{of SOO}}\) are the amount of biodiesel in the product (mg) and amount of SOO used in the experiment (mg).

3. Results and discussion

3.1. Characteristic of WCNTsZ20

X-ray diffraction (X-RD) was used to investigate the crystal structure of the WCNTsZ20 catalyst. Furthermore, it can also identify the ZnO compound present in the pore and on the surface of MWCNTs. Figure 1 (a) shows the diffractogram of MWCNTs, meanwhile figure 1 (b) shows the diffractogram of MWCNTsZ20. Figure 1 (a) shows wide and low peaks; this shows that MWCNTs have an amorphous structure. However, the unknown peaks were seen at 20 = 38°; 44°; 64°; 77° shows there are some impurities substances in the catalyst. Those unidentified peaks seem a similar pattern with the synthesized aluminum that is given by JCPDS card no. 00-04-0787 [26].

Meanwhile, for MWCNTsZ20 the new peaks emerge at an angle of 2 \( \theta = \) 31.4; 33.8; 35.8; 46.8; 55.9; 61.7; 65.5; 66.9; 68.2; 71.5; 71.5; 75.8; 79.7° (figure 1b). This shows that ZnO was successfully fed into the surface of MWCNTs in accordance with Joint Committee of Powder Diffraction Standard (JCPDS) card no. 00-036-1451. A similar result was found in the previous study [21,22]. This XRD pattern had been indexed to the ZnO wurtzile structure [1,25].
The SEM image of MWCNTs and MWCNTsZ_{20} were shown in Figures 2 (a) and (b). The random array of carbon nanotubes with a small amount of Al_{2}O_{3} appeared on the image of MWCNTs (figure 2 (a)). This morphological surface was slightly different from nanotubes synthesizing with the CVD method with a well-alignment of nanotubes shape [27]. Meanwhile, ZnO was successfully anchored on the nanotubes' surface, shown by flower-like white spotting dispersed on the nanotubes' entire surface (figure 2 (b)). It was also confirmed by EDX analysis that the MWCNTs Z_{20} catalyst contains 5.77 \%wt of ZnO, as shown in Table 1.

Also, MWCNT has a large surface area of 316.026 m\(^2\)/g (Table 2), which could be a great potential for catalyst support. It is larger than that other compounds, which are usually used as catalyst supports such as silica, \(\gamma\)-Al2O3, zeolite, bentonite, and hydrotalcite [1,7,12]. The surface area of MWCNTsZ_{20} was smaller than MWCNTs themselves, which reduced about 50\% (Table 2); this is possible because ZnO covers part of the pore of MWCNTs. Although the dispersion of ZnO in the MWCNTs pore results in a reduction in the catalyst surface area, its presence on the catalyst surface is an active site that can increase catalyst activity. Both of them can increase contact between reactants (kesambi oil and methanol) and overcome the limitations of mass transfer, ultimately increasing the reaction rate.

Figure 1. Diffractogram of (a) MWCNTs; (b) MWCNTsZ_{20}

Figure 2. SEM image of the catalyst, (a) MWCNTs; (b) MWCNTsZ_{20}. 
Table 1. Composition of the solid catalyst using EDX analysis.

| Compound | Composition (% mass) |
|----------|----------------------|
|          | MWCNTsZ20 | MWCNTs |
| C        | 89.43      | 99.4   |
| Al₂O₃    | 0.44       | 0.6    |
| ZnO      | 5.77       | -      |
| Other impurities | 4.36 | -      |

Table 2. BET surface area analysis of the solid catalyst.

| Analysis | MWCNTs | MWCNTsZ20 |
|----------|--------|-----------|
| Surface Area (m²/g) | 673.242 | 316.026 |

3.2 The influence of transesterification parameter on the yield of BKO

Many factors influence vegetable oil's transesterification process, including oil/ methanol molar ratio, catalyst loading, the catalyst's nature, reaction temperature, and reaction time. In this work, we focused on studying the effect of reaction time (h) and catalyst loading % (w/w of SOO) on biodiesel yield (%) for transesterification of SOO using synthesized catalysts MWCNTsZ20. Moreover, the type of feedstock also affects the transesterification process because its different types have different characteristics. As described in the introduction and method section, SOO in non-edible oil with high FFA levels and impurities includes gum and water content. The FFA and water content of SOO used in this work was 7.47 and 0.95%, respectively. After the purification process, it was reduced to 5.87 and 0.09%, respectively. Although the FFA and water content were still slightly higher than that allowed for the transesterification process (generally FFA and water content <= 2 and 0.05%, respectively), the transesterification process might be possible due to the catalyst of MWCNTZ20 used in this process acid catalyst that theoretically more insensitive to FFA content of the feedstock.

The reaction time's optimization study was investigated at 1 to 7 h with 1 h of interval. Meanwhile, catalyst loading varied from 2 to 4.5% (w/w to SOO) with a 0.5% interval. Other conditions were kept constant at 65 °C, 1:15 of the molar ratio of SOO/methanol, and 150 rpm of stirring speed. In any reaction, including the transesterification process, contact time has an important factor affecting the product's yield. Meanwhile, the presence of catalyst has been known to reduce the activation energy so that each reaction can take place properly.

Figure 3 shows the effect of reaction time simultaneously with catalyst loading on the yield of BKO (%). In the beginning (1 h of reaction time) yield % of BKO is low (30-36%) for the entire catalyst loading (CL) (2-4.5%), which may be attributed it was not enough to well mixing and dispersion of methanol into the SOO properly and the slow mass transfer has occurred. However, the yield of BKO (%) is increasing significantly with increasing reaction time. The highest yield was obtained after the reaction reached 5 h for all CL (the obtained BKO yield was 30.88%, 38.6%, 39.3%, 39.7%, 41.9% and 37.72% for CL of 2%, 2.5%, 3%, 3.5%, 4% and 4.5%, respectively).
The yield of BKO was decreased for reaction time beyond 5 h; this might happen probably due to the occurrence of reverse transesterification leading to ester loss and more soap formation by the FFA content (it should be noted that SOO used in this work has a high content of FFA of 5.87%). A similar result was found by previous researchers [28,29]. To determine the best amount of catalyst, plotting catalyst loading versus the yield (%) of BKO was carried out for the best reaction time (5 hours) (Figure 4). It shows that the yield (%) of BKO increases with the increase of catalyst loading. This might be attributed to the fact that an increase in the catalyst increases the total surface area and the amount of active site in the catalyst surface [29]. The transesterification could not occur without catalyst, and biodiesel could not form (the data are not shown in the figure).

The highest BKO yield (%) of 41.9% was achieved at 4% of catalyst loading. On the contrary, beyond 4% of catalyst loading, the yield of BKO was decreased (%), proved by catalyst loading of 4.5%, only 37.72% of BKO yield was achieved. This could be possible because the mixture is too viscous so that it inhibits the stirring process and eventually inhibit the mass transfer process. The obtained results are not encouraging; due to the metal oxide of ZnO is not well dispersed in the pores of the catalyst and less of the active site that attaches to the catalyst surface. This is supported by the SEM image where the morphology of Wurzite- crystal structure and a flower-like shape. This result was also confirmed by SEM- EDX analysis, as shown in Table 1. The composition of ZnO in the crystal is much lower (is only 5.77%) than C content (89.43%). This problem can be overcome by controlling the surface chemistry of MWCNTs to increase catalyst activity. The modification used is the functionalization of pure MWCNTs with acid groups such as –SO3H or –COOH [22,30].
4. Conclusion
The synthesized catalyst of 20% zinc oxide (w/w of MWCNTs) supported by multi-wall carbon nanotubes (MWCNTsZS0) with a large surface area of 326.026 m²/g has introduced into transesterification of kesambi oil (SOO). The effects of transesterification conditions include reaction time and catalyst loading, on biodiesel yield was deeply studied. The optimization study revealed that the highest 41.9% yield of biodiesel of kesambi oil was achieved at 4% catalyst loading (w/w of kesambi oil) and 5 h of reaction time. Although the results are not very encouraging, in the next work, some modifications on the synthesized catalyst, such as functionalization of MWCNTs by some acid group (–SO₃H or –COOH), will be done. It could be increasing the dispersion of ZnO in the pores of MWCNTs and enhancing the active site of the MWCNTsZ. Also, with the optimization of other transesterification parameters, a promising result might be obtained.

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