Study of catalyst support utilization on ZnO-based solid catalyst to its activity at transesterification of Kesambi (Schleichera oleosa) oil

Nyoman Puspa Asri\textsuperscript{1,}\textsuperscript{*}, Rahaju Saraswati\textsuperscript{2}, Herman Hindarso\textsuperscript{3}, Suprapto\textsuperscript{4}, Yustia Wulandari Mirzayanti\textsuperscript{5}, Rachmad Ramadhan Yogaswara\textsuperscript{6}

1 Chemical Engineering Department, Universitas W. R. Supratman
Arief Rahman Hakim 14, Sukolilo, Surabaya, Indonesia
\textsuperscript{*}Email: nyoman_puspaasri@yahoo.com

2 Industrial Engineering Department, Universitas W. R. Supratman
Arief Rahman Hakim 14, Sukolilo, Surabaya, Indonesia

3 Chemical Engineering Department, Catholic University of Widya Mandala
Kalisari Selatan 1, Mulyorejo, Surabaya, Indonesia

4 Chemical Engineering Department, Institut Teknologi Sepuluh Nopember
Kampus ITS Sukolilo, Surabaya, Indonesia

5 Chemical Engineering Department, Institut Teknologi Adhi Tama Surabaya (ITATS)
Arief Rahman Hakim, Klampis Ngasem, Surabaya, Indonesia

6 Chemical Engineering Department, Universitas Pembangunan Nasional "Veteran" Jawa Timur
Raya Rungkut Madya, Gunung Anyar, Surabaya, Indonesia

Abstract. ZnO-based solid catalyst was successfully synthesized with two types of catalyst support that is gamma alumina and multi walled carbon nanotubes (MWCNTs). Those catalyst would be used to produce biodiesel from Kesambi (Schleichera oleosa) oil via transesterification reaction. The aims of this study are to compare the performance of catalyst support that are gamma alumina and multi walled carbon nanotubes (MWCNTs) for transesterification of Kesambi (Schleichera oleosa) oil. The two kinds of catalyst are gamma alumina supported zinc oxide – copper oxide (ZnO-CuO/γ-Al\textsubscript{2}O\textsubscript{3}) and multi-walled carbon nanotubes supported zinc oxide (ZnO/MWCNTs). All of the catalysts were prepared by a combination of precipitation, impregnation, and gel process that familiarly called by Stober process. All of the catalysts, then were analysed by X-ray diffraction (XRD), N\textsubscript{2} adsorption-desorption followed by Brunauer-Emmett-Teller (BET) calculation and Scanning electron microscopy (SEM). The yield of biodiesel product has significantly different value which is ZnO-CuO/γ-Al\textsubscript{2}O\textsubscript{3} catalyst can accelerate the reaction more effective than ZnO/MWCNTs catalyst. The yield of biodiesel reached above 80% while using ZnO-CuO/γ-Al\textsubscript{2}O\textsubscript{3} catalyst. Contrarily, ZnO/MWCNTs catalyst only give biodiesel yield below 15% after 3 hours reaction.

Keywords: alumina, biodiesel, CuO, kesambi, multi-walled carbon nanotube, Schleichera oleosa, ZnO.
1. Introduction

Biodiesel is one of promising alternative fuel that can replace conventional fossil fuel. Biomass is one of potential resources for biodiesel production because it is clean and environmentally friendly [1]. Then, utilization of biodiesel as main vehicle fuel in large scale from renewable natural resources will reduce fossil fuel dependencies. There are many types of vegetable oils that have a potential to be a biodiesel feedstock including edible oil and non-edible oil. But, conversion of edible oil into biodiesel will give some problems that is the food vs fuel issue resulting food security destabilization. Moreover, this issue can increase the price of edible oil affecting the economic feasibility of biodiesel industry [2]. Some non-edible oil resources have been explored as a prospective raw material for biodiesel production such as rubber, kapok seed (Ceiba pentandra), nyamplung (Calophyllum inophyllum), jatropha (Jatropha curcas), kesambi (Schleichera oleosa), and many more [3].

Schleichera oleosa had been tried in biodiesel synthesis as a raw material via transesterification using several various base catalysts. However, it still needs pre-treatment process such as degumming, bleaching, and esterification reaction. Esterification should be done using acid catalyst like sulphuric acid in order to convert free fatty acid (FFA) into ester compound [4]. Schleichera oleosa is one of species in Sapindaceae family and also known as Kesambi fruit in Indonesia. Kesambi is usually grown in the South East Asia region like Java, Timor, and Burma. Schleichera oleosa also can be found in the sub-Himalayan region along central until southern India and named by Kusum fruit [4]. Non-edible oil from kesambi can be extracted from it seeds and this oil cannot be consumed by human but usually used for skin disease treatment such as acne, skin itching, and burning [5].

Unfortunately, non-edible oil contains high FFA causing more complicated process since it cannot processed using directly conventional transesterification giving disadvantage in production cost [6]. Alcoholsysis of high FFA oil in base condition yields saponification side reaction because of FFA neutralization and forms soap products [7]. Hence, strong acid catalyst has been developed by many researchers for biodiesel production from non-edible oil with high FFA content via simultaneous transesterification and esterification reactions [8]. Metal oxide group materials can play an important role as solid catalyst for many reactions due to its strong catalytic activity. Many studies had been successfully performed to obtain the most effective acid catalyst for biodiesel synthesis from high FFA content oil e.g. zirconium oxide (ZrO2) [9], modified zirconium oxide (ZrO2) with zinc oxide (ZnO) [8], tungsten oxide (WO3) [10], titanium oxide (TiO2) [11], and tin oxide (SnO2) [12].

One of metal oxide compound performing well as solid acid catalyst is zinc oxide (ZnO) because of the strong acid active sites on its surface area. Modified sulphated zinc oxide (ZnO) was reported by Lestadi et al. as a potential solid acid catalyst for biodiesel synthesis from high FFA oil [8]. Other modified ZnO was explored by Gurnath et al. combining copper (Cu) with ZnO and preparing copper doped zinc oxide nano composite as a solid catalyst for waste cooking oil conversion into biodiesel [13]. Those modified ZnO catalysts show high catalytic activity during reaction and simultaneously convert FFA and triglycerides (TG) into fatty acid methyl ester (FAME). Meanwhile, porous material needs to be utilized as a support catalyst in order to accelerate chemical reaction because of its large surface area. Large surface area would reduce the mass transfer resistance of reactant during chemical reaction increasing chemical kinetic rate [14].

Previously, the authors have developed ZnO-based solid acid catalyst for biodiesel synthesis from Kesambi (Schleichera oleosa) using gamma alumina as a catalyst support. That catalyst namely ZnO/γ-Al2O3 was prepared via modified precipitation and gel method resulting 71.561 m2 g−1 of total surface area [2]. The last result still needs several improvement using combine active metal and other catalyst support that has larger specific surface area. In this study, the authors investigate the comparison of two types of ZnO-based catalysts that are ZnO-CuO/γ-Al2O3 and ZnO/MWCNTs for biodiesel synthesis from Kesambi (Schleichera oleosa) oil.

2. Material and method

2.1 Materials

Multi-walled carbon nanotubes (MCWNTs) used as a catalyst support material was purchased...
from Advanced Material Esoterica, China. Methanol, cupric sulphate, sodium hydroxide, sodium carbonate, gamma alumina, zinc chloride, ammonia, and ethanol with analytical grade was supplied by Merck, Germany. These all reagents were used for catalyst synthesis without any purification. Kesambi oil was supplied from domestic market in Indonesia. Furthermore, technical grade methanol as a reactant of reaction was provided from the local chemical distributor at Surabaya, East Java. Analytical standard reagents for instrumentation analysis were also purchased from Merck, Germany.

2.2 Catalyst preparation
CuO-ZnO catalyst supported by γ-Al₂O₃ (CZA) was synthesized via combination of impregnation and sol-gel method that is simultaneously occurred during preparation. The CZA catalyst was prepared by two kinds of precursors that is zinc methoxide (Zn(OCH₃)₂) and copper methoxide (Cu(OCH₃)₂) as described by our last study [15]. Finally, there are five variations of ZnO loading in catalyst, that is 15%, 20%, 25%, 30%, and 35% wt while CuO loading was kept at 15 %wt. Those synthesized catalysts were coded as CZA15, CZA20, CZA25, CZA30, and CZA35, respectively. On the other hand, another catalyst that is ZnO catalyst supported by multi-walled carbon nanotubes (CNTZ) was prepared by modified Stober gel-based process [16]. This method was already formed and proposed by Mukenga et.al as described by our latest study about the activity of CNTZ catalyst at transesterification of Kesambi oil [17]. There are several ZnO loading inside the catalyst that is 10%, 15%, 20%, 25%, and 35% wt used in this study. These catalysts were coded by CNTZ10 for 10% ZnO loading, and then CNTZ15, CNTZ20, CNTZ25, CNTZ35 respectively.

The prepared catalyst was characterized by two analysis methods to observe its physical and chemical properties. N₂ adsorption-desorption followed by Brunauer-Emmett-Teller (BET) analysis method was used to calculate the total specific area of catalyst material. Then, the appearance of catalyst surface morphology was picked up by Scanning Electron Microscopy (SEM) analysis.

2.3 Biodiesel synthesis
Kesambi (Schleichera oleosa) oil with high FFA content was utilized as a feedstock for the simultaneous reaction that is esterification and transesterification to produce biodiesel in a batch reactor. This experimental step aims to observe the catalytic activity of CZA and CNTZ catalyst at this reaction. The experimental procedure of this reaction was described at our latest work consisting of degumming process before esterification and transesterification was occurred simultaneously in a batch system [18]. In this reaction, a little amount of CZA and CNTZ catalyst (3% w/w of oil) was added and these catalysts contain varied metal oxide loading as described before in order to enhance the catalytic activity of the catalyst. And, another fixed parameter condition that was set is oil to methanol molar ratio which 1:15 ratio was used.

Fatty acid methyl ester (FAME) that called biodiesel and glycerol as by product was produced from this simultaneous reaction. FAME and glycerol created immiscible system which is FAME and the rest of oil reactant in the top layer and glycerol with methanol in the other side. Then, these two layers were separated physically using centrifuge apparatus and FAME was dried to release the rest of excess methanol. Then, FAME content in main product was analyzed using Gas Chromatography (GC) apparatus that is GC HP 5890 type equipped with carbowax column. The same detail procedure of FAME content analysis by GC equipment was conducted with the previous study [18]. The yield of FAME could be calculated according to the concentration of FAME compound in the main product from GC instrumentation analysis.

3. Result and discussion

3.1 Solid catalyst analysis
Multi-walled carbon nanotubes (MWCNTs) and γ-Al₂O₃ could be a potential catalyst support because it has large total surface area and good stability. Those good properties make them better to be used as catalyst support than other commonly catalyst support like zeolite, bentonite, hydrotalcite, and other clay group compounds [19,20]. The total specific surface area of solid catalyst was observed by N₂ adsorption – desorption followed by BET calculation method. And, it
was shown in Table 1.

Generally, dispersed metal compound inside pores of support material would decrease the total specific surface area of the catalyst. That was happened while MWCNTs was utilized as a material support on ZnO-based catalyst. It is shown that more ZnO particle was loaded into MWCNTs caused its total specific surface area reduction (Table 1). The smallest total surface area of catalyst is still above 100 m$^2$ g$^{-1}$ and arguably is still large compared to ZnO-based catalyst using other support in previous study [2].

| Catalyst  | Surface Area [m$^2$ g$^{-1}$] | Catalyst  | Surface Area [m$^2$ g$^{-1}$] |
|-----------|-------------------------------|-----------|-------------------------------|
| MWCNTs    | 673.242                       | γ-Al$_2$O$_3$ | 198                          |
| CNTZ10    | 296.991                       | CZA15     | 316.54                       |
| CNTZ15    | 409.043                       | CZA20     | 328.49                       |
| CNTZ20    | 316.026                       | CZA25     | 369.31                       |
| CNTZ25    | 228.824                       | CZA30     | 377.16                       |
| CNTZ35    | 136.918                       | CZA35     | 433.86                       |

Contrarily, CZA catalysts show different results that is enhancement of total surface area while more active metal particle was impregnated. It was happened because the catalyst active material has a dimension in nano scale and it was well dispersed inside the pore of gamma alumina as a catalyst support and the rest of them reside in the surface of material as an active site. Hence, the more amount of ZnO loading giving more ZnO nano particle were remained in the surface and resulting more active site particles [16]. However, the total specific surface area of all prepared catalyst is large and show great potential for catalysis process. The larger total specific surface area gives great possibility to attract reactant molecules while the mass transfer resistance could be reduced and the reaction kinetic rate would be more accelerated [21].

Scanning electron microscopy (SEM) analysis has been a key method and intensively utilized for determine the morphology of catalyst material or the detail of particle shape and also conform the particle size distribution. Figure 1 shows the SEM image of a synthesized CZA and CNTZ catalysts. The prepared alumina supported by mixed metal oxide catalyst (figure a) had a hierarchical 3D morphology arranged by a flower-like microstructure (ZnO) integrated with CuO in the form of rectangular-shape monoclinic structure. The particle size distribution of those catalyst material was varied between 0.2 – 1 μm and 2-10 μm, respectively. From the SEM images, it was seen that the CZA catalysts particle was formed in a nanosized scale.

![Figure 1. SEM image of the catalyst surface (a) CZA15, (b) CNTZ15](image)

On the other side, it is indicated that multi-walled carbon nanotubes (MWCNTs) material has randomly nanotubes arrays and a little amount of Al$_2$O$_3$ impurities is appearing inside the tubes. It has different morphological surface comparing with other nanotubes that synthesized via the CVD method creating a unique well-alignment of nanotubes [22]. Moreover, ZnO particle was
successfully added inside the tubes that are seen from dispersed white dot residing on the whole surface of the nanotubes.

3.2 Kesambi (Schleichera oleosa) oil characteristics
Kesambi oil (KO) is a non-edible oil that has a different characteristic than common feedstock for biodiesel production like palm oil. Its physical and chemical characteristics were given in Table 2. The collected KO used in this research has a significantly different acid value and iodine value comparing with Silitonga et al. [4] which has higher value because of diverse source of the oil. This value indicates that fatty acid molecule structure in KO has a double bond and quite large comparing with other vegetable oils, representing that KO has a high-unsaturated fatty acid. Meanwhile, the collected KO also has higher free fatty acid (FFA) and water content value than the previous study, specifically 29.56% and 0.19% respectively [4].

| KO Characteristic | Value     | Unit        |
|------------------|-----------|-------------|
| Density          | 0.8802    | gr cm⁻³     |
| Iodine value     | 149.77    | mg I₂/gr KO |
| Acid value       | 64.77     | mg KOH/gr KO|
| Saponification value | 181.62   | mg KOH/gr KO|
| Free fatty acid (FFA) | 29.56   | %           |
| Water content    | 0.19      | %           |

The enzymatic process of lipase molecules inside the seed cell of Kesambi could produce a water as a side product, so it possibly causes the raised of water content in Kesambi oil [13]. Water content is one of key parameter for vegetable oil quality determination. Water content in vegetable oil can interfere a result of the triglycerides hydrolysis into fatty acids and glycerol, besides the high level of free fatty acids (FFA) content. The high value of FFA in vegetable oil can interrupt the reaction process reducing the amount of biodiesel product. On the other side, the water content and acid value of the vegetable oil was also affected by oil storage method. FFA level in the collected KO is too high (29.56%) for transesterification process and it needs to resolve to gain high value of biodiesel yield. However, the super acid catalyst has more insensitivity to FFA comparing with base solid catalyst and it may possibly increase the rate of reaction producing high level of FAME. Furthermore, KO also contains a lot of gum and should be purified via degumming process to prevent the decreasing of FAME as a main product. After degumming process was done, the yellowish colour of KO was obtained having a 0.034% of water level.

| Fatty acid        | % wt KO (analysis) | % wt KO (other) [23] | % wt KO (other) [4] | % wt KO (other) [24] |
|-------------------|--------------------|----------------------|---------------------|----------------------|
| Myristic acid     | 0.01               | 0.1                  | 0.09                | 0.01                 |
| Palmitic acid     | 7.42               | 7.58                 | 7.83                | 7.59                 |
| Palmitoleic acid  | 1.90               | 2.83                 | 2.88                | 1.80                 |
| Stearic acid      | -                  | 5.21                 | 5.81                | -                    |
| Oleic acid        | 2.59               | 49.29                | 51.49               | 2.83                 |
| Linoleic acid     | 50.05              | -                    | -                   | 49.69                |
| Linoleic acid     | 5.35               | 5.53                 | 5.51                | 5.56                 |
| α-Linolenic acid  | 0.56               | 0.22                 | 0.27                | 0.26                 |
| Arachidic acid    | -                  | 29.24                | 27.21               | -                    |
| Eicosenoic acid   | 28.97              | -                    | -                   | 29.54                |
| Eicosadienoic acid| 0.29               | -                    | -                   | 0.24                 |
| Heneicosanoic acid| 0.06               | -                    | -                   | 0.04                 |
| Behenic acid      | 1.21               | -                    | -                   | 1.14                 |
Then, the fatty acid composition of collected KO and comparison with the others is shown at the table 3. It is shown that KO consist of unsaturated fatty acids as the major composition reaching 91.08 %wt. Moreover, the major components of collected KO are linolelaic acid and eicosenoic acid at 50.05 %wt and 28.97 %wt, respectively. Kesambi oil (KO) surely has a different composition than palm oil where palmitic acid and oleic acid content in KO are relatively quite low, that is 7.42 %wt and 2.59 %wt. These preliminary analysis results are quite similar with previous research [24], but contrast significantly from the results provided by Silitonga et al. [4] and Sudrajat [23]. The main components of Kesambi oil (KO) according to their results are oleic acid (51.49 and 49.29%) and following by Arachidic acid (27.21 and 29.24%).

3.3 Biodiesel synthesis from Kesambi oil
FAME content in the main product from transesterification of Kesambi oil (KO) was measured by Gas Chromatography (GC) equipment. The catalytic activity of zinc oxide (ZnO) loading as a metal oxide inside the catalyst was tested via the simultaneous esterification and transesterification reaction of KO. The concentration of ZnO on the entire catalyst surface as an acid active site presented a key role in this reaction process. In this study, we observed the influence of the ZnO concentration into catalyst support towards FAME content value and also yield of biodiesel. On the other hand, free fatty acid (FFA) and water content are also the two significant parameters for the hydrolysis process of vegetable oil [2].

The availability of a huge amount of moisture content in the feedstock can accelerate the kinetic of hydrolysis reaction and decrease the formation of ester product at the same time [25]. In order to achieve the highest yield of biodiesel, then moisture content inside the triglyceride that used as a feedstock in the reaction process should no more than 0.5% [23]. Furthermore, the higher value of FFA content would theoretically lead to formation of soap and water via saponification route process. If FFA content is reaching more than 3%, then the base catalyst is not appropriate for the transesterification reaction leading to saponification route [2,23]. Hence, in this research, CZA and CNTZ catalysts were utilized to substitute base catalyst for biodiesel synthesis. The catalytic activity of those catalysts would be explored through simultaneous reaction of KO, which has higher FFA value and water content.
accomplished while CNTZ20 catalyst was used during the reaction. And, increasing the concentration of ZnO above 20 %wt precisely reduce the yield of biodiesel. Unfortunately, the yield of FAME product is somehow having very low value under 15% (Figure 2). This result is very different with previous work that achieved above 70% yield of biodiesel while addition of a few amount (1% w/w of oil) of ZnO-based solid catalyst [2]. It might be occurred because the dispersion of ZnO particle in the previous study reached over 50 %wt in the entire pore of catalyst support. It is indicated there is 0.5% (w/w oil) of ZnO metal active in the whole of vegetable oil reactant [2]. This huge amount of ZnO particle on the active acid site of catalyst surely could increase the kinetic rate of reaction.

Figure 3 shows the comparison of resulting yield of biodiesel using CZA and MWCNTsZ. Two types of catalyst that compared is Z15 and CZA35 catalyst because those two catalysts have the largest total specific surface area. There is significantly different result from those two catalysts utilization. Yield of biodiesel result with CZA35 catalyst somehow nearly reaches seven times than that of Z15 catalyst. In this study, we only perform one stage reaction process even though the collected KO has a relatively higher FFA content than that of the Silitonga’s feedstock [4]. This experiment step could be possible to conduct, because the active site of Zn$^{2+}$ and Cu$^{2+}$ ions which is the Lewis acid are not sensitive against FFA molecules so that the esterification and transesterification reaction could be done simultaneously. According to the reaction mechanism, Zn$^{2+}$ ion probably has an active Lewis acid site resulting an effect to trigger both of two reactions work simultaneously [8]. Because of that, ZnO would be a suitable metal active to catalyze these reactions and also could be an alternative solution to proceed a low-grade oil (LGO) that contain high FFA level. But, this study gives unsatisfactory result producing low amount of FAME in the main product. This result shows that the preparation of ZnO-based catalyst using modified Stober-like process did not provide much more dispersed ZnO particle on the surface of the material support. It was very different with CZA35 catalyst while used combined precipitation, impregnation, and gel methods.

![Figure 3. Yield biodiesel result comparison between CZA and CNTZ catalyst use in reaction process](image)

**Figure 3.** Yield biodiesel result comparison between CZA and CNTZ catalyst use in reaction process

4. **Conclusion**

In this study, ZnO-based catalyst using multi-walled carbon nanotubes (MWCNTs) as a material support with a large total specific surface area had been successfully synthesized with the modified Stober-like process. Zinc Oxide (ZnO) particle was successfully filled inside the nanotubes of MWCNTs using this modified technique. On the other hand, bimetallic ZnO-CuO/γ-Al$_2$O$_3$ also had been successfully synthesized via combined precipitation, impregnation, and gel methods. Unfortunately, because of a few amounts of ZnO was filled inside the tubes of MWCNTs, fatty acid
methyl ester (FAME) could not be yielded with satisfactory results. From this study, it encourages the authors to develop other ZnO-based catalyst with MWCNTs as material support using other route synthesis in order to obtain the higher FAME concentration in biodiesel product.

5. Acknowledgement
The authors would like to thankful to Directorate of Research and Development, The Ministry of Research and Technology, Republic of Indonesia for financial support through The Fundamental Research Grant on fiscal year of 2020 by Contract No. 03/KP/LPPM-UNIPRA/III/2020.

6. References
[1] N. P. Asri et al., “Non-Catalytic Transesterification of Vegetable Oil to Biodiesel in Sub-and Supercritical Methanol: A Kinetic’s Study,” Bull. Chem. React. Eng. Catal., vol. 7, no. 3, pp. 215–223, Feb. 2013.
[2] N. P. Asri, S. Soe'eib, B. Poedjojono, and Suprapto, “Alumina supported zinc oxide catalyst for production of biodiesel from kesambi oil and optimization to achieve highest yields of biodiesel,” Euro-Mediterranean J. Environ. Integr., vol. 3, no. 1, p. 3, Nov. 2018.
[3] A. S. Silitonga, H. C. Ong, T. M. I. Mahlia, H. H. Masjuki, and W. T. Chong, “Biodiesel Conversion from High FFA Crude Jatropha Curcas, Calophyllum Inophyllum and Ceiba Pentandra Oil,” Energy Procedia, vol. 61, pp. 480–483, 2014.
[4] A. S. Silitonga et al., “Schleichera oleosa L oil as feedstock for biodiesel production,” Fuel, vol. 156, pp. 63–70, Sep. 2015.
[5] H. Bhatia et al., “A review on Schleichera oleosa: Pharmacological and environmental aspects,” J. Pharm. Res., vol. 6, no. 1, pp. 224–229, Jan. 2013.
[6] N. Puspa Asri and D. A. Puspita Sari, “Pre-Treatment of Waste Frying Oils for Biodiesel Production,” Mod. Appl. Sci., vol. 9, no. 7, p. 99, Jul. 2015.
[7] M. K. Lam, K. T. Lee, and A. R. Mohamed, “Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: A review,” Biotechnol. Adv., vol. 28, no. 4, pp. 500–518, Jul. 2010.
[8] I. Istadi, D. D. Anggoro, L. Buchori, D. A. Rahmawati, and D. Intaningrum, “Active Acid Catalyst of Sulphated Zinc Oxide for Transesterification of Soybean Oil with Methanol to Biodiesel,” Procedia Environ. Sci., vol. 23, no. Ictcred 2014, pp. 385–393, 2015.
[9] J. JITPUTTI, B. KITIYANAN, P. RANGSUNVIGIT, K. BUNYAKIAT, L. ATTANATHO, and P. JENVANITPANJAKUL, “Transesterification of crude palm kernel oil and crude coconut oil by different solid catalysts,” Chem. Eng. J., vol. 116, no. 1, pp. 61–66, Feb. 2006.
[10] Y. Park, D.-W. Lee, D. Kim, J.-S. Lee, and K. Lee, “The heterogeneous catalyst system for the continuous conversion of free fatty acids in used vegetable oils for the production of biodiesel,” Catal. Today, vol. 131, no. 1–4, pp. 238–243, Feb. 2008.
[11] R. M. de Almeida, L. K. Noda, N. S. Gonçalves, S. M. P. Meneghetti, and M. R. Meneghetti, “Transesterification reaction of vegetable oils, using superacid sulfated TiO2–base catalysts,” Appl. Catal. A Gen., vol. 347, no. 1, pp. 100–105, Sep. 2008.
[12] R. Gutie, P. J. Sebastian, A. Va, and I. Mexican, “Effects of the SO 4 Groups on the Textural Properties and Local Order Deformation of SnO 2 Rutile Structure,” no. 18, pp. 4265–4271, 2004.
[13] B. Gurunathan and A. Ravi, “Biodiesel production from waste cooking oil using copper doped zinc oxide nanocomposite as heterogeneous catalyst,” Bioresour. Technol., vol. 188, pp. 124–127, Jul. 2015.
[14] M. Zabeti, W. M. A. Wan Daud, and M. K. Aroua, “Activity of solid catalysts for biodiesel production: A review,” Fuel Process. Technol., vol. 90, no. 6, pp. 770–777, Jun. 2009.
[15] N. P. Asri et al., “Transesterification of kesambi oil (Schleichera oleosa l.) using nano ZnO-CuO/γ-alumina solid catalyst,” IOP Conf. Ser. Earth Environ. Sci., vol. 460, no. 1, 2020.
[16] M. Mukenga, “Biodiesel production over supported Zinc Oxide nano- particles,” University of Johannesburg, 2012.
[17] N. P. Asri, Y. Yuniati, H. Hindarso, Suprapto, and R. R. Yogaswara, “Preparation of Multi-Walled Carbon Nanotubes Supported Zinc Oxide Catalyst for Transesterification of Kesambi
(Schleichera oleosa) Oil,” *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 742, no. 1, 2020.

[18] N. P. Asri, Y. Yuniati, H. Hindarso, Suprapto, and R. R. Yogaswara, “Biodiesel production from Kesambi (Schleichera oleosa) oil using multi-walled carbon nanotubes supported zinc oxide as a solid acid catalyst,” *IOP Conf. Ser. Earth Environ. Sci.*, vol. 456, p. 012003, Apr. 2020.

[19] N. P. Asri *et al.*, “Palm oil transesterification in sub- and supercritical methanol with heterogeneous base catalyst,” *Chem. Eng. Process. Process Intensif.*, vol. 72, pp. 63–67, Oct. 2013.

[20] N. P. Asri, B. Pujojono, D. A. Puspitasari, Suprapto, and A. Roesyadi, *Energy Systems and Management*. Cham: Springer International Publishing, 2015.

[21] N. P. Asri, K. Budikarjono, S. Suprapto, and A. Roesyadi, “Kinetics of Palm Oil Transesterification Using Double Promoted Catalyst CaO/KI/γ-Al2O3,” *J. Eng. Technol. Sci.*, vol. 47, no. 4, pp. 353–363, Sep. 2015.

[22] R. Andrews, D. Jacques, D. Qian, and T. Rantell, “Multiwall carbon nanotubes: Synthesis and application,” *Acc. Chem. Res.*, vol. 35, no. 12, pp. 1008–1017, 2002.

[23] O. By, R. Sudradjat, E. Pawoko, D. Hendra, and D. Setiawan, “(Schleichera oleosa L.) (Biodiesel Manufacturing from Kesambi Seed),” pp. 358–379, 2010.

[24] N. P. Rathod, “Experimental Investigation on Use of Methyl Ester Kusum Oil and Its Blends in Direct Injection Ci Engine,” *IOSR J. Mech. Civ. Eng.*, vol. 10, no. 3, pp. 36–43, 2013.

[25] D. Y. C. Leung and Y. Guo, “Transesterification of neat and used frying oil: Optimization for biodiesel production,” *Fuel Process. Technol.*, vol. 87, no. 10, pp. 883–890, Oct. 2006.