



TRANSESTERIFICATION OF VEGETABLES OIL USING ALUMINA SUPPORTED HETEROGENEOUS CATALYST

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ABSTRACT

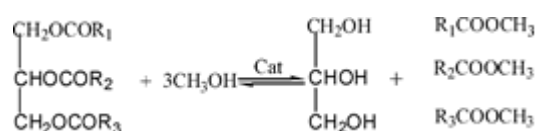
Alumina supported heterogeneous catalyst have been synthesized and used to transesterification of vegetable oil. Calcium oxide solid base catalyst includes single promoted catalyst $\text{CaO}/\gamma\text{-Al}_2\text{O}_3$ and double promoted catalyst $\text{CaO}/\text{KI}/\gamma\text{-Al}_2\text{O}_3$ were synthesized by precipitation process and the combination of precipitation and impregnation process, respectively. Whereas, alumina supported zinc oxide $\text{ZnO}/\gamma\text{-Al}_2\text{O}_3$ was synthesized by combining of precipitation and gel methods. Single promoted catalyst $\text{CaO}/\gamma\text{-Al}_2\text{O}_3$ was used to transesterification of refined palm oil (RPO) and double promoted catalyst was used to transesterification of RPO and used cooking oil (UCO). Meanwhile, the acid catalyst of $\text{ZnO}/\gamma\text{-Al}_2\text{O}_3$ was used to transesterification non-edible kesambi (*Sclleichera Oleosa* L) oil. Transesterification process was conducted in glass batch type reactor with refluxed methanol. The reaction was carried out in varies of reaction temperature (from 35-65° C) with 10° C of interval and time of reaction (from 1-7 h) with 1 h of interval. The results show that all type of catalysts used in the experiment indicated that they potentiated used for converting vegetables oil into biodiesel.

Keywords: biodiesel, heterogeneous catalysts, transesterification, vegetable oil.

1. INTRODUCTION

Nowadays, the petroleum reserve has been dwindled and the environmental problems such as global warming, greenhouse gas emission and local air pollution have been increased drastically [1, 2]. Therefore, the renewable energy was absolutely needed to substitute the conventional energy. Among all the potential alternatives energy, biodiesel is an excellent and a benign renewable fuel because of its characteristics include: good biodegradability, non-toxicity, high cetane number, sulfur-free properties, and similar properties to petrodiesel fuel [3, 4], which make it a promising alternative for fossil fuels.

Conventionally, biodiesel has been produced by transesterification of triglyceride to methyl esters using homogeneous basic catalysts, such as sodium or potassium hydroxides, carbonates or alkoxides, as represented by the Equation 1 [2]:



Actually, biodiesel can be derived from vegetable oils, animal fats and waste cooking oil. Although the conventional process offers the high yield of biodiesel, however it also has several disadvantages including: the formation of side products in the form of soap, the complexity of the separation of products from catalyst and the catalyst cannot be regenerated and reused [1, 2, 5, 6]. Those problem need additional steps include neutralization and washing process which resulted the huge quantity of

alkaline waste that require an advanced process and lead reduced the yield of biodiesel (Noiroj *et al.*, 2009). It also need large amount of energy to treat, which increase the final production cost [4, 6, 7, 8].

To overcome these problems, recently, researchers have begun focusing on heterogeneous catalyst for synthesizing of biodiesel because of their superiority compared to homogeneous catalysts. The use of solid catalysts can ease separation/purification of the product, avoid formation of soap and therefore, reduce separation cost that eventually leads to a more competitive biodiesel prices compare to diesel oil. In addition, it also could be reused and high purity glycerol (more than 98%) was produced as by-product [4]. Several solid base catalysts for transesterification have been investigated including earth alkaline oxides such as calcium oxide and calcium methoxides, Mg-Al hydro talsite [9], $\text{K}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ [10], $\text{TiO}_2\text{-MgO}$ [9], amorphous-zirconia catalysis (Ti/ZrO_2 , $\text{K}_2\text{O}/\text{ZrO}_2$, $\text{W}_2\text{O}_3/\text{ZrO}_2$, $\text{Al}_2\text{O}_3/\text{ZrO}_2$) [11], Zeolith and modified zeolith [12], etc. Even though these catalysts are found active in the transesterification of different kinds of triglycerides, the activity is generally less than that of homogeneous catalysts so that a longer reaction time is needed to reach high reaction conversion [8, 13, 14]. Possibly, the presence of heterogeneous catalysts, the reaction mixture constitutes a three-phase system, oil/methanol/catalyst, which for diffusion reasons inhibits the reaction and, resulted the reaction proceeded at a relatively slow rate. Nevertheless, heterogeneous catalysts could improve the synthesis methods for the development of an environmentally benign process and the reduction of production cost [15]. Therefore, studies to improve the



activity of heterogeneous catalysts still need to be developed continuously.

Important factors on the catalytic activity of the solid catalyst are specific surface area, pore size, pore volume and active site concentration on the surface of catalyst [16]. By a variety of methods, the high active surface areas can be obtained per cubic centimeter of the catalyst. Catalyst supports or carriers greatly increase the effective surface area of the catalyst [17]. The use of alumina or silica as catalyst supports such could improve the mass transfer limitation of the three phase's reaction system (oil/methanol/catalyst). Alumina is very good used as catalyst support compared to silica or activated carbon, owing to its highest thermal stability.

This work is focused on the comparative study of several alumina supported synthesized heterogeneous catalyst for biodiesel production of vegetable oil. We have synthesized three type alumina supported heterogeneous catalyst include: $\text{CaO}/\gamma\text{-Al}_2\text{O}_3$, $\text{CaO}/\text{KI}/\gamma\text{-Al}_2\text{O}_3$, $\text{ZnO}/\gamma\text{-Al}_2\text{O}_3$. Those catalyst were synthesized by precipitation, precipitation and impregnation and, sol and gel methods, respectively. The vegetable oils (VOs) used in this study include: refined palm oil (RPO), used cooking oil (UCO) and kesambi (*Schleiera oleosa* L) oil (SOO). Several factors which may influence the yield of biodiesel including, reaction temperature, reaction time, molar ratio of oil to methanol and amount of catalyst were investigate.

2. MATERIAL AND METHOD

2.1 Materials

The refined palm oil (RPO) as the raw material was purchased from local market. The palm oil consisted of 0.26% lauric acid, 1.01% myristic acid, 10.93 (%) linoleic acid, 45.96% oleic acid, 3.64% stearic acid, and 38.20% palmitic acid (wt. %) and was used without further purification. Used cooking oil (UCO) was obtained from California Fried Chicken restaurant located in Surabaya. The composition of the UCO was determined by gas chromatography (GC-HP 6890 Varian), which consist of 53.01% glyceryl three palmitic and 46.99% glyceryl three oleic. The physical and chemical characteristics of CFC's WFO were analyzed using several methods. The FFA content of 2.82% was analyzed based on American Oil Chemist (AOCS) official Method (Ca 5a-71, 1993). Meanwhile, the density of CFC's UCO was 0.92 g/cm^3 and its water content was 0.69% which was analyzed based on ISO 662 - 1089 (E). Meanwhile, kesambi (*Schleiera oleosa* L) oil (SOO) that used as feedstock for biodiesel production in this work was purchased from local market.

Coconut coir, a cheap adsorbent for treating UCO was obtained from local coconut processing mill in Lamongan city, East Java. FAME standards and internal standards of chromatographic grade were obtained from Sigma-Aldrich (Switzerland). Analytical grade γ -alumina (BET surface area of $120\text{-}190 \text{ m}^2/\text{g}$) and, analytical grade potassium iodide were purchased from Merck, Germany. Commercial grade of calcium oxide, acetic acid and

methanol were purchased from the local supplier. Technical grade of methanol was purchased from local supplier Bratacho-Chem.

2.2 Methods

2.2.1 Preparation of alumina supported heterogeneous catalyst

The single promoted $\text{CaO}/\gamma\text{-Al}_2\text{O}_3$ catalyst was prepared by precipitation method using procedure described below: Calcium acetate with a mass ratio of 1:1 to the alumina support was dissolved in 50 ml of distilled water and then added with 40 gram of $\gamma\text{-Al}_2\text{O}_3$ under stirring at room temperature for four hours. The performed slurry was heated up at $100\text{-}105^\circ\text{C}$ in an oven over night in order to remove the water content. Finally, the catalyst was calcinated in nitrogen flow at 718°C for 5 hours using muffle furnace. This procedure has been described in the previous work [18].

Double promoted catalyst $\text{CaO}/\text{KI}/\gamma\text{-Al}_2\text{O}_3$ with optimum composition which consists of 30% loading of CaO and 30% loading of KI (wt. % to γ -alumina) was used in this study. The catalyst was synthesized by precipitation and impregnation methods. The procedure of preparation and characterization of this catalyst has been completely described in the previous work [7, 13].

Whereas, Alumina supported zinc oxide (AZO) catalyst was prepared by precipitation of analytical grade zinc methoxide with analytical grade $\gamma\text{-Al}_2\text{O}_3$ and gel methods. Zinc methoxide was synthesized by reacting 3 grams of sodium hydroxide in 100 ml of methanol (90%) and 1 molar zinc chloride (98%) in 80 ml of distilled water and stirred for 3 hours. The solution was centrifuged for 5 minutes to separate the solids from the liquid and wash twice with distillate water. The solid was then introduced into the dispersion of 10 gram of Al_2O_3 in 50 ml of water and stirred for 3 h. The mixture was added with 1 mole of oxalic acid in 50 ml of methanol, and then it was evaporated at 70°C until it was turned into gel form. The formed gel was dried at 80°C in oven for 12 hours. The dried synthesized catalyst was crushed, milled into powder and then calcinated at 500°C in a muffle furnace with flowing air for 6 h [17].

After calcinating process, those catalysts were kept in desicators in the presence of silica gel in order to prevent water and CO_2 contacting with the catalysts. The characterizations of catalysts were performed by X-Ray Diffraction (XRD), Brunauer-Emmett-Teller (BET), Scanning Electron Microscope (SEM) and x-ray fractionation (XRF) analyses. XRD gives information on the crystallization structure. The specific surface area, pore volume and pore diameter of the prepared catalysts were measured using the BET method. SEM (Jeol, JSM-6390LV, Japan) was used to identify the morphology and size of $\text{CaO}/\text{KI}/\gamma\text{-Al}_2\text{O}_3$ catalyst particle. Meanwhile, XRF method was done for giving the information associated with the composition of catalyst [2, 13, 15].



2.2.2 Preparation of vegetable oils (VOs)

There are three type of VOs used in this study including: RPO, UCO and SOO. There was no pretreatment subjected to the RPO, due to it nature was feasible being transesterified into biodiesel using heterogeneous base catalyst. However, it was need the serious pretreatment step for UCO before transesterifying process. The collected UCO was pre-treated based on the procedure described elsewhere [2, 8]. First, the collected UCO was filtered to remove the food residues or the suspended particulate matters, and then it was heated at 100-105°C for 30 minutes to remove the excess of water content. Further, UCO was treated by adsorption process using coconut coir powdered (CCP) (wt.% to the UCO) to reduce the FFA content of the UCO. It has been stated in the last work [2] that the optimum amount of CCP is 7% (wt.% to the UCO), therefore it was used for treating UCO in this work. The treated UCO was analyzed to determine its final FFA content, and then it was ready subjected for transesterification process using ES-CaO catalyst. Whereas, kesambi oil (SOO) that was obtained from local market was treated using phosphoric acid and heating at 100° C to reduce gum, free fatty acid (FFA) and water content of the oil. The treated SOO was ready for transesterifying into biodiesel.

2.2 Transesterification Process

Transesterification process was conducted in batch type reactor system which consists of 250 ml three-neck glass flask fitted with reflux condenser and magnetic hot plate stirrer. A known amount of methanol and catalyst were added into the batch reactor and heated at a certain reaction temperature. Preheated oil with a certain molar ratio of oil to methanol was also added into the reactor. After the temperature in the system reached the desire value (35-75 °C), the mixture was agitated using a magnetic stirrer at constant desired speed. After predetermined time (1-7 h), the reaction was stopped by cooling the reactor to room temperature, and the catalyst was separated from the mixture using a vacuum filtering flask. The excess methanol removed by vacuum evaporation. The liquid mixture was discharged into a separator funnel leave it overnight to ensure that the mixture was completely separated into two layers. The top layer is the excess of methanol, the middle is biodiesel and the bottom layer is glycerol. Biodiesel product was analyzed with GC, using a GC HP 5890 with HP's first column with carrier gas flow of 28 ml/min, initial temperature of the column was 125 °C with the temperature increment of 15° C per minute and the final temperature was set at 275 °C.

The same procedure for GC analyses has been used in the previous work [4]. The yield of biodiesel was calculated from the content of methyl ester that analyzed by GC as shown at the Equation 1 [2, 4, 17]:

$$\text{Yield of biodiesel (\%)} = \frac{\text{weight of biodiesel produced} \times \text{biodiesel concentration (wt.\%)}}{\text{weight of SOO}} \quad (1)$$

3. RESULT AND DISCUSSIONS

3.1 Catalyst Characterization

The crystalline structure, the specific surface area, the morphology, and the composition of the prepared catalysts were measured using X-RD, Breneuer-Emmet-Teller (BET), SEM and XRF methods, respectively.

The XRD pattern of pure CaO, γ -Al₂O₃, and the synthesized catalysts (CaO/ γ -Al₂O₃, CaO/KI/ γ -Al₂O₃ and, ZnO/ γ -Al₂O₃) were presented in Figure-1. The XRD patterns of pure Al₂O₃ show the typical diffraction peaks at $2\theta=20, 32, 37, 46$ and 67° . When Al₂O₃ was promoted by 50% loading of CaO (wt.% to alumina) the new diffraction peaks of CaO can be observed at $2\theta=18, 23, 28, 31, 34$ and 51° . The same results were stated by Ilgen and Akin (2008). However, when the double promotor of 30% (wt.% to alumina) of CaO and 35% (wt. % to alumina) of KI were subjected on Al₂O₃, beside the two peaks of Al₂O₃ and CaO, the new diffraction peaks of K₂O were observed. The diffraction peaks of CaO/KI/ γ -Al₂O₃ were shown at $2\theta=17^\circ, 18^\circ, 19^\circ, 21^\circ, 23^\circ, 25^\circ, 29^\circ, 31^\circ, 32^\circ, 34^\circ, 35^\circ, 39^\circ, 42^\circ, 45^\circ, 51^\circ, 55^\circ, 59^\circ$ and 65° . Whereas, for ZnO/ γ -Al₂O₃ (AZO) catalyst the wide peaks with low intensity at $2\theta=37^\circ, 47^\circ, 56^\circ$ still appear indicating the alumina retained its amorphous structure. The new peaks

of ZnO were appeared at $2\theta=32^\circ, 34^\circ, 36^\circ, 46^\circ$ and 63° . The BET specific surface area, cumulative pore volume, and mean pore diameter the catalysts are summarized in Table-1.

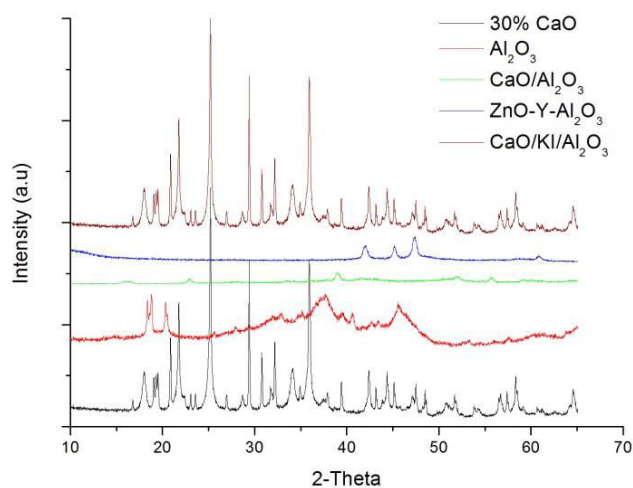


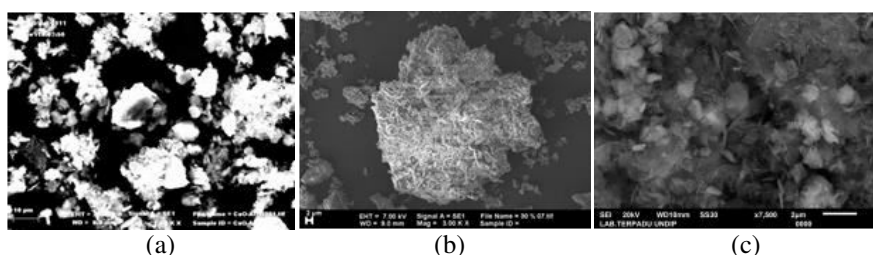
Figure-1. X-RD patter of synthesized Alumina supported catalyst.

**Table-1.** BET surface area, pore volume and pore diameter of the prepared catalyst.

Type of catalyst	BET Area (m^2g^{-1})	Pore volume (m^3g^{-1})	Pore Diameter (\AA)
γ - Al_2O_3	120-200	0.481	134.3
CaO/γ - Al_2O_3	83.77	0.145	35.218
$\text{CaO}/\text{KI}/\gamma$ - Al_2O_3	16.508	0.049	77.904
ZnO/γ - Al_2O_3	71.561	0.137	8.149

As shown in Table-1, the surface area of double promoted catalyst $\text{CaO}/\text{KI}/\gamma$ - Al_2O_3 was smallest ($16.508 \text{ m}^2\text{g}^{-1}$) when compared with two others (CaO/γ - Al_2O_3 and $\text{ZnO}/\text{Al}_2\text{O}_3$) of 83.77 and $71.561 \text{ m}^2\text{g}^{-1}$, respectively. Meanwhile, the surface area of analytical grade γ - Al_2O_3 provided by Merck is 120-198 m^2g^{-1} . Typically, the

surface areas of those catalysts (CaO/γ - Al_2O_3 , $\text{CaO}/\text{KI}/\gamma$ - Al_2O_3 , ZnO/γ - Al_2O_3) were smaller than that of γ - Al_2O_3 , possibly due to partly of the porous surface of γ - Al_2O_3 of each catalyst is covered by metal oxide compound include: CaO , $\text{CaO}\&\text{K}_2\text{O}$ and ZnO , respectively. The similar result was reported by Asri *et al.* [4] and Xi and Li [14].

**Figure-2.** SEM images of synthesized catalyst. a) CaO/γ - Al_2O_3 catalyst, b) $\text{CaO}/\text{KI}/\gamma$ - Al_2O_3 and c) ZnO/γ - Al_2O_3 catalyst.

SEM analyses are shown in Figure-2. Figure-2a) shows SEM images of CaO/γ - Al_2O_3 that presented irregular shapes with 10 μm in size. Meanwhile, Figure-2b) shows the images of $\text{CaO}/\text{KI}/\gamma$ - Al_2O_3 with 30% of CaO loading. The SEM image shows crystallites of 10 μm in size with similar irregular coral shapes. Whereas, Figure-2c) shows the SEM image of ZnO/γ - Al_2O_3 catalyst.

The XRF analyses are presented in Table-2. The compositions of double promoted catalyst $\text{CaO}/\text{KI}/\gamma$ - Al_2O_3 is as follows: CaO with the highest order of 51.2%, followed by I_2 , Al_2O_3 and K_2O with the concentrations of 30.6; 12 and 5.32% (wt.%), respectively. Whereas, the remaining of 0.88% (wt.%) called trace element/impurities. There are two main compositions composed the ZnO/γ - Al_2O_3 catalyst include: ZnO (53.303%) and Al_2O_3 (44.421%). Meanwhile, the rest of 2.276% were impurities consists of SO_3 (1.905%), SiO_2 (1.173%), and CaO (0.198%).

3.2 The Effect of Reaction Temperature on Yield of Biodiesel

Those three of synthesized catalysts (CaO/γ - Al_2O_3 , $\text{CaO}/\text{KI}/\gamma$ - Al_2O_3 and ZnO/γ - Al_2O_3) have been introduced to transesterification process of vegetable oils. CaO/γ - Al_2O_3 was used for transesterification RPO. Meanwhile, $\text{CaO}/\text{KI}/\gamma$ - Al_2O_3 was used for transesterifying RPO and UCO, whereas, ZnO/γ - Al_2O_3 was used for transesterifying of SOO.

The reaction temperature played the important role in the transesterification process. The influenced of reaction temperature on yield of biodiesel was investigated

by carrying out the reaction in the temperature ranging from 35 to 75 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}$ interval with a constant 5h of reaction time. Meanwhile, the other conditions include: the molar ratio of oil to methanol and the amount of catalyst were taken based on the optimum condition according to the previous works. The molar ratio of 1:42 and the catalyst amount of 6% (wt% to oil) were used for transesterifying of RPO using CaO/γ - Al_2O_3 and $\text{CaO}/\text{KI}/\gamma$ - Al_2O_3 . Transesterification of UCO with $\text{CaO}/\text{KI}/\gamma$ - Al_2O_3 used molar ratio oil to methanol 1:12 and catalyst amount of 6%. Meanwhile, molar ratio of 1:12 and catalyst amount of 4% were being used for transesterifying of SOO with ZnO/γ - Al_2O_3 catalyst. The results shown in Figure-3, indicate that the yield of biodiesel increases significantly by increasing the reaction temperature for all catalyst used. Double promoted catalyst $\text{CaO}/\text{KI}/\gamma$ - Al_2O_3 has the highest activity compared with the two others. However, the activity of the catalyst is also strongly influenced by the type of oil used as the raw material. The temperature of 65 $^{\circ}\text{C}$ was shown as the optimum temperature for all of the catalyst used, as well as the oils used.

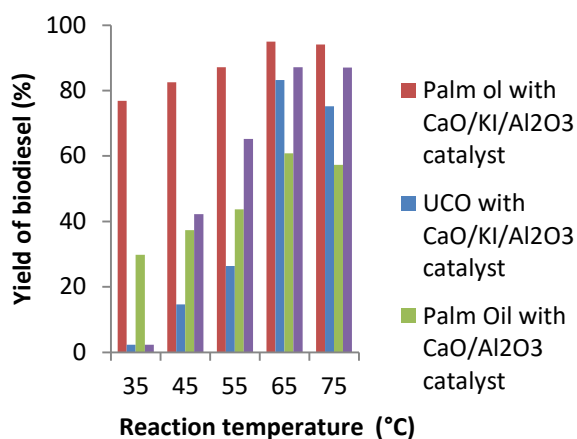


Figure-3. The influence of reaction temperature on yield of biodiesel (%).

3.3 The Effect of Reaction Time on Yield of Biodiesel

The influence of reaction time on yield of biodiesel was studied using 4% of catalyst amount, 65°C of reaction temperature and molar ratio oil to methanol of 1:12 under constant stirring speed. The reaction was carried out at 7 different reaction times ranging from 1 up to 7 h with 1 h of interval. Effect of reaction time on yield of biodiesel was shown in Figure-4. The results indicate that yield of biodiesel elevate along with the increase of reaction time. At the beginning (at 1 h of reaction time) the reaction was slow due to the limitation of diffusion among the three phases of oil, methanol and AZO catalyst, which made the biodiesel yields low (28%). After a while, reaction was faster than before and the yield gradually increased to approach 40%. Yield of biodiesel sharply increase into 65% at reaction time of 3 h, afterward it was gradually increase into 73.0, 87.0, and 92.29% at reaction time of 4, 5 and 6 h, respectively. Conversely, beyond 6 h there is no a significant increase on yield of biodiesel. It means the reaction reached the equilibrium state after 6 h with yield of 92.29%. Maximum yield of 92.31% was achieved at 7 h. However, for the efficiency and the economic consideration the reaction time of 6 h was chosen as the optimum reaction time in this work. Compared with previous work, Xie and Li [15] obtain 87% yield of biodiesel on transesterification of soybean oil using 6.5% of KNO₃/Al₂O₃ solid base catalyst at 65° C, 1:15 and 7 h of reaction time, molar ratio oil to methanol, and reaction time, respectively.

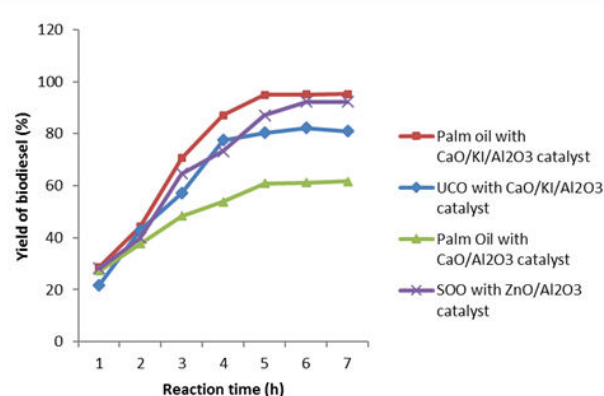


Figure-4. The influence of Reaction time (h) on yield of biodiesel (%).

4. CONCLUSIONS

The three type of alumina supported catalyst included: CaO/ γ -Al₂O₃, CaO/KI/ γ -Al₂O₃ and ZnO/ γ -Al₂O₃) has been synthesized through the various methods. The single promoted catalyst CaO/ γ -Al₂O₃ was synthesized by precipitation method. The double promoted catalyst CaO/KI/ γ -Al₂O₃ was done through the combination of precipitation and impregnation method. Whereas, ZnO/ γ -Al₂O₃) was synthesized by co-precipitation, impregnation and gel methods. Each catalyst has different characteristics and different activities. Both of them are strongly influenced by the promoters and the methods' used on preparation of the catalysts. Different catalysts were need different conditions on transesterification of different vegetables oil. So it can be concluded that transesterification process is highly depended on the conditions of the reaction (reaction temperature, reaction time, molar ratio of oil to methanol, amount of catalyst), type of catalyst and the characteristics of vegetables oil.

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REFERENCE

- [1] N.P. Asri, S. Machmudah, W. Wahyudiono, S. Suprpto, K. Budikarjono, A. Roesyadi, M. Goto. 2013. Non Catalytic Transesterification of Vegetables Oil to Biodiesel in Sub-and Supercritical Methanol: A kinetic's study. Bulletin of Chemical Reaction Engineering & Catalysis. 7(3): 215-223.
- [2] N.P. Asri, B. Poejojono, D.A. Puspitasari, S. Suprpto, A. Roesyadi. 2015. Biodiesel production



- using double promoted catalyst $\text{CaO/KI}/\gamma\text{-Al}_2\text{O}_3$ in batch reactor with refluxed methanol. Springer Proceeding in Energy, Energy System And Management 2015: Germany, Springer Verlag, ch 15
- [3] N. P. Asri, S. Machmudah, W. Wahyudiono, S. Suprpto, K. Budikarjono, A. Roesyadi, M. Goto. 2013. Non Catalytic Transesterification of Vegetables Oil to Biodiesel in Sub-and Supercritical Methanol: A kinetic's study. Bulletin of Chemical Reaction Engineering & Catalysis. 7(3): 215-223.
- [4] N. P. Asri, S. Machmudah, W. Wahyudiono, S. Suprpto, K. Budikarjono, A. Roesyadi, M. Goto. 2013. Palm oil transesterification in sub and supercritical methanol with heterogeneous base catalyst. Chemical Engineering and Processing: Process Intensification. 72, 63-67.
- [5] O. Ilgen, A.N, Akin. 2008. Development of alumina supported alkaline catalyst used for biodiesel production. J Turkey. 33, 281-287.
- [6] M. Zabeti, W.H.A.M. Daud, M.K, Aroua. 2009. Activity of solid catalysts for biodiesel production: A review. Fuel Processing Technology. 90, 770-777.
- [7] N.P. Asri, D.A. Puspitasari, B Poedjojono & Suprpto. 2015. Pre-treatment of waste frying oils for biodiesel production. Mod Appl Sci. 9(7): 99-106. doi:10.5539/mas.v9n7p99
- [8] N.P, Asri, S. Suprpto, K, Budikarjono, A. Roesyadi. 2015. Kinetics of Palm Oil Transesterification Using Double Promoted Catalyst $\text{CaO/KI}/\gamma\text{-Al}_2\text{O}_3$. Journal of Engineering and Technological Sciences. 47(4): 353-363.
- [9] Z. Wen, X. Yu, S.T, Tu, J. Yan, E. Dahlquist E. 2010. Biodiesel production from waste cooking oil catalyzed by $\text{TiO}_2\text{-MgO}$ mixed oxides Bioresource Technology. 101(24): 9570-9576.
- [10] M.K. Lam, K.T. Lee, A.R. Mohamed. 2010. Homogeneous, Heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: A review. Biotechnology advances. 28, 500-518. doi: 10.1016/j.biotechadv.2010.03.002
- [11] S. Furuta, H. Matsushashi, K. Rata. 2006. Biodiesel diesel fuel production with solid amorphous-zirconia catalyst in fixed bed reactor. J. Biomass and Bioenergy. 30, 870-873.
- [12] K.H. Chung, D.R. Chang, B.G. Park. 2008. Removal of free fatty acid in waste frying oil by esterification with methanol on zeolite catalysts. Bioresource Technology. 99, 123-130.
- [13] N.P. Asri, S. Machmudah, W. Wahyudiono, S. Suprpto, K. Budikarjono, A. Roesyadi, M. Goto. 2013. Palm oil transesterification in sub and supercritical methanol with heterogeneous base catalyst. Chemical Engineering and Processing: Process Intensification. 72, 63-67.
- [14] I Perdana, N Nugrahanti, Sofiyah and I M Bendiyasa. 2017. Transesterification of palm oil using sodium silicate base catalyst from geothermal sludge. IOP Conf. Series: Materials Science and Engineering. 162: (2017) 012024 doi:10.1088/1757-899X/162/1/012024
- [15] W. Xie, H. Li. 2006. Alumina supported potassium iodide as a heterogeneous catalyst for biodiesel production from soybean oil. J Molecular Catalysis A: Chemical. 255, 1-9.
- [16] M. Mukenga. 2012. Biodiesel production over supported zinc oxide nanoparticles. Thesis Book, Chemical Engineering Department, University of Johannesburg, South Africa.
- [17] N. P. Asri, S. Siswanti, P. Bambang, S. Suprpto. 2018. Alumina supported zinc oxide catalyst for production of biodiesel from kesambi oil and optimization to achieve highest yields of biodiesel. Euro-Mediterr J Environ Integr. 3: 3:1-7
- [18] N.P. Asri, A. Anisa, F. Rizqi, I. Gunardi, K. Budikarjono, Suprpto., A. Roesyadi. 2010. Biodiesel production from palm oil Using $\text{CaO/Al}_2\text{O}_3$ as a solid base catalyst. The 1st International Seminar on Fundamental & application of Chemical Engineering. Kuta- Bali.