

Alumina supported zinc oxide catalyst for production of biodiesel from kesambi oil and optimization to achieve highest yields of biodiesel

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Received: 30 January 2017 / Accepted: 16 August 2017
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Abstract Biodiesel is one of the promising alternative energy substitutes for fossil fuel. In this work kesambi (*Schleichera Oleosa* L.) oil (SOO) is converted into biodiesel with clean technology using alumina supported zinc oxide solid catalysts. The alumina supported zinc oxide (AZO) catalyst was prepared by the precipitation and gel method and calcined at a temperature of 500 °C. The synthesized catalyst was characterized by Breneuer-Emmet-Teller (BET) and X-ray fluorescence (XRF) methods. The surface area, total pore volume and mean pore diameter of the catalyst powder obtained were 71.561 m² g⁻¹, 0.137 cm³ g⁻¹, and 8.149 nm, respectively. The effects of catalyst amount, the molar ratio of oil to methanol and time of reaction on the yield of biodiesel were investigated. The results showed that those three variables significantly influenced the yield of biodiesel. The highest biodiesel yield of 92.29% was obtained at a catalyst loading of 4% (wt% to oil), a molar ratio of oil to methanol of 1:12, a reaction time of 6 h and a reaction temperature of 65 °C.

Keywords Biodiesel · Kesambi oil · Solid catalyst · Transesterification · Zinc oxide

Introduction

The conventional energy resources on which the world has relied for many years are insufficient to meet today's demands (Asri et al. 2013a, 2015c). Additionally, the continuous use of fossil energy has impacts on the environment such as increased global warming, greenhouse gas emission and local air pollution (Asri et al. 2013b). The three key themes for securing sustainable energy are improving fossil fuel technologies to reduce environmental and social impact, applying renewable technologies on a wider scale and introducing energy efficiency measures in the fields of energy conservation, distribution and consumption (Brnabic and Turkovica 2015). In the future, renewable energy will play a major role in competing, securing and sustaining energy systems, because the global energy demand is steadily increasing from year to year.

Among the renewable energy resources, biomass energy seems very strategic to be developed in Indonesia. Biodiesel shows excellent potential as a substitute for fossil based diesel fuels (Asri et al. 2013b, 2015c). Biodiesel is one of the renewable energies that derives from vegetable oils, animal fats and waste cooking oil. Vegetable oils are particularly strategic resources to be developed because Indonesia is abundant in vegetable oils such as palm, coconut, rubber, *nyamplung* oil (*Calophyllum inophyllum*), kesambi (*Schleichera oleosa* L.), jatropha oil, hazelnut oil and many others. The main problem of the commercialization of biodiesel in Indonesia is the high cost of production and, as a result, the price of biodiesel cannot compete with the price of diesel oil. There are two causes.

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First, biodiesel was produced through the transesterification process using homogeneous acid/alkaline catalyst (Asri et al. 2010). This conventional process has many disadvantages, including the formation of side products such as soaps (Ilgen and Akin 2008; Zabeti et al. 2009; Asri et al. 2015a), complexity of separating the product from the catalyst, and production of large quantities of alkaline waste. The waste products require treatment processes and consume much energy and results in increased cost of production (Zabeti et al. 2009; Asri et al. 2015b, c). Second, the raw material used for biodiesel production is refined palm oil (RPO), a group which includes some edible oils. Because some RPOs are edible, the price is very high for fuel use, and RPO-based biodiesel competes with the food industry for resources, so that it can destabilize national food security. Some of these challenges could be addressed by substituting the homogeneous catalyst with a heterogeneous catalyst and substituting alternative raw materials for edible vegetable oils. Therefore, more development and intensive research are still needed to achieve an efficient process of biodiesel production.

Solid catalysts present a promising method in biodiesel production that could reduce its production cost, so its price could compete with diesel oil. A heterogeneous catalyst has many advantages over a homogeneous catalyst, such the relative ease with which it can be separated from the reaction product so it can be reused. Glycerol is directly produced with high purity (more than 98%), it does not produce soap during transesterification and it does not need a washing process, so no liquid waste is produced. Therefore, transesterification using a solid catalyst is generally identified as a green and clean process. Various types of heterogeneous catalysts, both base and acid, have been investigated by previous researchers. The solid base catalysts researched include CaO base oxide (Huaping et al. 2006; Kouzu et al. 2008; Lam et al. 2010; Zabeti et al. 2010; Asri et al. 2013a, 2015a), amorphous-zirconia catalysis (Ti/ZrO_2 , $\text{K}_2\text{O/ZrO}_2$, WO_3/ZrO_2 , $\text{Al}_2\text{O}_3/\text{ZrO}_2$) (Furuta et al. 2006), zeolite and modified zeolite, (Chung et al. 2008; Wu et al. 2013). Many studies showed that calcium oxide, CaO, is a potential catalyst in the transesterification process. It has shown promising results with 94% yield at a reaction temperature of 60 °C and a 1:13 methanol:oil molar ratio in the transesterification of sunflower oil (Istadi et al. 2015). Meanwhile, Asri et al. (2013b), (2015b) introduced double promoted catalyst $\text{CaO/KI/Al}_2\text{O}_3$ on transesterification of refined palm oil (RPO) with refluxed methanol and sub-supercritical methanol. The high yield biodiesel of 94.94 and 94.85% are achieved for refluxed methanol conditions (at 5 h of reaction time), and sub-supercritical conditions (at 1 h of reaction time), respectively. To reduce biodiesel production cost, Asri et al. (2015a) also introduced the same

catalyst ($\text{CaO/KI/Al}_2\text{O}_3$) into transesterification of waste cooking oil. It has shown quite a good result with 83.26% yield of biodiesel, but not as good as the result of refined palm oil transesterification. Possibly, due to the high free fatty acid (FFA) content of waste cooking oil (more than 1%), a small amount of soap was still found along with the product. It has been shown that the solid base catalyst $\text{CaO/KI/Al}_2\text{O}_3$ is less suitable for waste cooking oil, as well as non-edible oil and other low-grade oil. More intensive research is needed to identify the appropriate catalyst for low-grade oil.

Metal oxides from the group of transition metals as well as some from the group of earth metals could be successfully applied as an acid catalyst for biodiesel synthesis. Many studies have been directed to the analysis of Zn, which also belongs to the group of transition metals, as a suitable catalyst for biodiesel synthesis. The catalyst activity was attributed to the probable active Lewis acid sites of Zn^{2+} on the catalyst surface. Since acid catalysts can simultaneously do esterification of FFA and transesterification of triglyceride into methyl ester, they could process low-grade feedstock, thereby reducing overall production cost. Istadi et al. (2015) stated that $\text{SO}_4^{2-}\text{-ZnO}$ is a promising catalyst for transesterification of soybean oil into biodiesel, with 80.19% yield obtained under mild conditions. Other researchers developed copper doped zinc oxide nano composite (CZO) as a heterogeneous catalyst for transesterification of waste cooking oil (Baskar and Aiswarya 2015). They reported that CZO catalyst was potentially used as a heterogeneous catalyst for biodiesel production from waste cooking oil.

Modified ZnO was reported as a suitable catalyst for the transesterification of rapeseed oil due to its high activity and minimal weight loss (Istadi et al. 2015; Yoo et al. 2010). 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 the catalyst (Mukenga 2012). By a variety of methods, a high number of 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. The use of alumina or silica as such catalyst supports could improve the mass transfer limitation of the three-phase reaction. Alumina is a very good catalyst support compared to silica, owing to its high thermal stability and porosity. However, there are no previous studies focused on the development of alumina supported zinc oxide (AZO) catalyst as a solid acid catalyst. Therefore, the development of AZO, either prepared by precipitation, coprecipitation, impregnation or gel method, needs to be further studied for enhancing the yield of biodiesel production of vegetable oil, particularly non-edible oil and used cooking oil.

In this work, the authors focus on utilization of kesambi (*Schleichera oleosa* L.) oil (SOO) for biodiesel production. Non-edible kesambi oil (SOO) shows good potential as biodiesel feedstock due to its high oil content, low price, abundant availability, and the fact that it will not compete with the food industry. Clean technology to convert kesambi oil into biodiesel is a transesterification process using an alumina supported zinc oxide (AZO) solid catalyst. In this study, we observed and characterized synthesized AZO catalyst. For testing the activity of the catalyst the influence of catalyst amount (wt% to SOO), the molar ratio of oil to methanol and time of reaction on the yield of biodiesel were investigated.

Materials and methods

Materials

Kesambi (*Schleichera oleosa* L.) oil (SOO) used as feedstock for biodiesel production in this work was purchased from a local market. A commercial grade of methanol used as a reactant for the transesterification process was also purchased from the domestic market. The analytical grade reagents used for AZO catalyst preparation including sodium hydroxide, methanol, zinc chloride, oxalic acid, and gamma alumina, were provided by Merck, Germany. They were used directly without any further purification. All standard reagents for gas chromatography analyses were also supplied by Merck, Germany.

Preparation of alumina supported zinc oxide (ZnO/ γ -Al₂O₃) catalyst

Alumina supported zinc oxide (AZO) catalyst was prepared by precipitation methods of analytical grade zinc methoxide and analytical grade γ -Al₂O₃. Zinc methoxide was synthesized by reacting 3 g of sodium hydroxide in 100 mL of methanol (90%) and 1 M zinc chloride (98%) in 80 mL of distilled and stirred for 3 h. The solution was centrifuged for 5 min to separate the solids from the liquid and washed twice with distilled water. The solid was then introduced into the dispersion of 10 g of γ -Al₂O₃ in 50 mL of water and stirred for 3 h. To this mixture was added 1 mol of oxalic acid in 50 mL of methanol, and then the mixture was evaporated at 70 °C until it was turned into gel form.

The formed gel was dried at 80 °C in an oven for 12 h. The dried synthesized catalyst was crushed, milled into powder and then calcined at 500 °C in a muffle furnace with flowing air for 6 h. After calcination was completed, the catalyst powder was stored in a desiccator equipped with silica gel to avoid contact with the catalyst, water, and

carbon dioxide. The characterizations of catalysts were performed by Brunauer–Emmett–Teller (BET) and X-ray fluorescence (XRF) analysis. The total specific surface area, pore volume and average pore diameter of the prepared catalysts were measured using the BET method. The XRF method was used to obtain information regarding the composition of the catalyst.

Transesterification process

Kesambi oil (SOO) that was obtained from the local market was treated using phosphoric acid and heated at 100 °C to reduce gum, free fatty acid (FFA) and water content of the oil. The treated SOO was ready for converting into biodiesel. Transesterification process was conducted in 250 mL glass batch type reactors that consists of a three-necked round bottom flask equipped with a reflux condenser, thermometer, hot plate, thermostat-controlled water-bath and magnetic stirrer.

Oil and methanol with the different molar ratios from 1:6 to 1:18 were poured into a three necked flask, and then added with the various amounts of AZO catalyst from 1 to 6% (w/w% of SOO). The flask was immersed in a water bath, and subsequently, the mixture was refluxed at 65°C under vigorous stirring at a constant speed with a magnetic stirrer. The reaction was carried out until it reached the desired reaction time (reaction time varied between 1 and 7 h with intervals of 1 h). After the reaction was completed, the hot plate and magnetic stirrer were turned off, and the reactor was allowed to cool down naturally to room temperature. After cooling, the mixture was withdrawn and filtered using filter paper to separate the solid catalyst from the liquid mixture (methanol–biodiesel–glycerol). The excess methanol was removed by vacuum evaporation. The liquid mixture was poured into a separatory funnel, leave it overnight at room temperature until forming two layers; the top layer being fatty acid methyl ester/FAMES or biodiesel, and the bottom layer being glycerin.

Biodiesel product was analyzed with a gas chromatography flame ionization detector (GC-FID), using a GC HP 5890 equipped with 20 m Carbowax Column. The carrier gas was nitrogen with a flow of 28 mL min⁻¹, the initial temperature was 150 °C, and the initial time was 3 min, while the temperature increment was 7.5 °C per minute with a final temperature of 275 °C. The same procedure for GC analyses has been used in the previous work (Asri et al. 2013b). The yield of biodiesel was calculated from the content of methyl ester analyzed by GC as shown in the Eq. (1).

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

Results and discussion

Catalyst characterization

The specific surface area of prepared AZO catalyst was measured using Breneuer-Emmet-Teller (BET) and the composition of catalyst was measured by XRF methods. The BET surface area, pore volume and mean pore size were $71.561 \text{ m}^2 \text{ g}^{-1}$, $0.137 \text{ cm}^3 \text{ g}^{-1}$ and 8.149 nm , respectively. The surface area of analytical grade $\gamma\text{-Al}_2\text{O}_3$ provided by Merck was $120\text{--}198 \text{ m}^2 \text{ g}^{-1}$. Total surface area of AZO catalyst was smaller than that of $\gamma\text{-Al}_2\text{O}_3$ due to some parts of the zinc oxide compounds being well dispersed on the surface of the pores of $\gamma\text{-Al}_2\text{O}_3$, and part of them remained on the surface of the support as active sites. The presence of those substances increases the activity of the catalyst. The result was confirmed by X-ray diffraction pattern of AZO catalyst (the figure is not shown). The XRD pattern of AZO has diffraction peaks of ZnO appearing at 2θ (31.67° , 34.31° , 36.14° , 47.40° , 56.52° , 62.73° , 66.28°). Meanwhile, the diffraction peak of 2θ (at 37° , 46.0° and 66.7°) are still registered on the XRD pattern assigned to the amorphous of Al_2O_3 . A similar result was reported by Asri et al. (2013b) on the preparation of doubled-promoted catalyst $\text{CaO}/\text{KI}/\gamma\text{-Al}_2\text{O}_3$, while Xie and Li (2006) also stated the same thing in their work of alumina supported potassium iodide heterogeneous catalyst. XRF analysis was used to determine the ZnO content of the AZO catalyst. The result shows that there are two main compositions of the catalyst, including ZnO (53.303%) and Al_2O_3 (44.421%). Meanwhile, the remaining 2.276% is impurities, which consist of SO_3 (1.905%), SiO_2 (1.173%), and CaO (0.198%). As expected, ZnO was the highest component, followed by Al_2O_3 and impurities, respectively. This result shows that the prepared catalyst has high purity, approaching 98%.

The effect of catalyst amount on yield of biodiesel

The amount of catalyst played an important role in the transesterification process. The effect of catalyst amount on the yield of biodiesel was investigated by carrying out the reaction with varied catalyst amounts of 1–6% (wt% to SOO) with a range of 1%. Meanwhile, the other conditions, including the reaction temperature, molar ratio of oil to methanol and reaction time, were kept constant at 65°C , 1:12 and 6 h, respectively. The influence of catalyst amount on yield of biodiesel is depicted on Fig. 1.

The results shown in Fig. 1 indicate that yield of biodiesel increases significantly by increasing the catalyst amount. Without the presence of a catalyst, it seems that biodiesel was not formed. In contrast, by using a catalyst

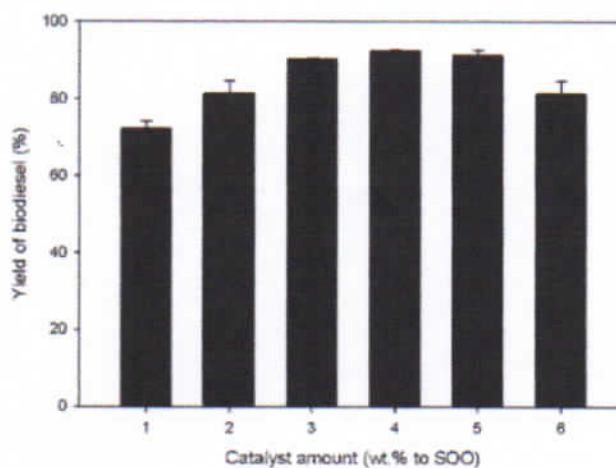


Fig. 1 The influence of catalyst amount (wt% to SOO) on yield of biodiesel (%) (reaction temperature = 65°C , molar ratio = 1:12 and reaction time = 6 h)

amount of 1%, the yield of biodiesel drastically increased by 70.12%. It was strongly proved that the presence of a catalyst in transesterification process significantly influenced the rate of reaction (Levenspiel 1999). Biodiesel yield was increased linearly from 70.12 to 81.40% and from 81.40 into 90.20% by increasing the catalyst amount from 1 to 2% and 2 to 3%, respectively. However, the yield of biodiesel was increased only slightly to 92.29 with a catalyst amount of 4%. The use of catalyst amounts over 4% (5 and 6%) led to decreases in biodiesel yield to 91.07 and 85.77%, respectively. Possibly, the mixture of oil, methanol and catalyst is too viscous, giving rise to a problem of mixing, resulted in the limitation of the diffusion. The higher-percentage catalysts mixtures also require higher power consumption for adequate stirring.

The maximum yield of 92.29% achieved in this work was higher than that of 65% acquired by Asri et al. (2010) on transesterification of palm oil using $\text{CaO}/\text{Al}_2\text{O}_3$ as catalyst at the same reaction temperature (65°C). Moreover, the other conditions (such as reaction time, the amount of catalyst, and the molar ratio of oil to methanol of 7 h, 6% and 1:42, respectively) were worse than the conditions of this work (6 h, 4% and 1:12, respectively). Another research team, Xie et al. (2006), studied the transesterification of soybean oil with $\text{KNO}_3/\text{Al}_2\text{O}_3$ and their highest yield of 87% was achieved at 7 h, 6.5% and 15:1, respectively. The result proved that kesambi (SOO) oil has good potential for producing biodiesel using alumina supported zinc oxide (AZO) solid as catalyst. In the present work, we have found the highest yield of 92.29% was achieved at a catalyst amount of 4%. Therefore, the 4% catalyst amount was adopted as the optimum condition and selected for continuing the experiment.

The effect of molar ratio oil to methanol on yield of biodiesel

The molar ratio of oil to methanol is one of the important factors of the transesterification reaction. Theoretically, the stoichiometric molar ratio of oil to methanol is 1:3. Since transesterification is an equilibrium reaction, to shift the reaction to the right side, a large excess of methanol is required (Asri et al. 2013b). In the literature review, it is stated that the molar ratio of 1:6 is used on transesterification of low free fatty acid using a homogeneous sodium hydroxide alkaline catalyst (Asri et al. 2015c). However, on transesterification using heterogeneous catalyst, most of the researchers have used a higher molar ratio (within range 1:9–1:42) compared to homogeneous alkaline catalyst (Asri et al. 2015c; Kouzu et al. 2008; Petchmala et al. 2010), possibly, owing to the mass transfer being limited in the heterogeneous catalyst system. However, too much excess methanol leads to some problems, such as recovering it and the high amount of energy needed, which increased production cost (Asri et al. 2013b; Huaping et al. 2006).

In this work the effect of the molar ratio of oil to methanol on the yield of biodiesel was investigated by varying the ratio from 1:6 to 1:18 at a reaction temperature of 65 °C, a reaction time of 6 h and a catalyst amount of 4%. Figure 2 depicts the influence of the molar ratio of oil to methanol on the yield of methyl ester (biodiesel) of SOO. It shows that the molar ratio of methanol to SOO significantly affected the yield of biodiesel. It was observed that yield of biodiesel increased along with the increase of molar ratio from 1:6 to 1:12. The highest yield of 92.29% was achieved at molar ratio 1:12. However, at a molar ratio of 1:15 it was slightly decreased to 91.27% and finally

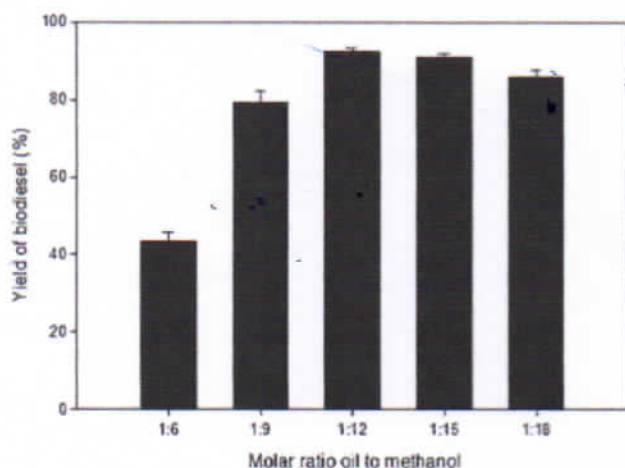


Fig. 2 The influence of molar ratio oil to methanol on yield of biodiesel at reaction temperature 65 °C, reaction time 6 h and amount of catalyst 4%

decreased to 85.77% at a molar ratio of 1:18. Possibly, the ratio of catalyst amount to the reactant (oil and methanol) was decreased with increasing the methanol content. Moreover, when the amount of methanol was over 1:15, glycerol separation became more difficult, which led the reduction of the yield of biodiesel. Also, more energy is needed to recover the significant amount of un-reacted methanol (Asri et al. 2013b; Huaping et al. 2006). A similar result was stated by previous researchers (Kim et al. 2004; Noiroj et al. 2009). This proved that the yield of biodiesel was increased up to a certain molar ratio of oil to methanol. Therefore, the optimum ratio should be determined to eliminate excess of methanol usage for economic reasons. The optimum molar ratio of oil to methanol in transesterification of kesambi oil using AZO catalyst was 1:12.

The effect of reaction time on yield of biodiesel (%)

The influence of reaction time on the yield of biodiesel was studied using a catalyst amount of 4%, reaction temperature of 65 °C and molar ratio of oil to methanol of 1:12 under constant stirring speed. The reaction was carried out at seven different reaction times ranging from 1 to 7 h with 1 h intervals. Effect of reaction time on the yield of biodiesel is shown in Fig. 3. The results indicate that yield of biodiesel elevates 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, the reaction was faster than before, and the yield gradually increased to approach 40%. The yield of biodiesel sharply increased to 65% at a reaction time of 3 h. Afterward, it gradually

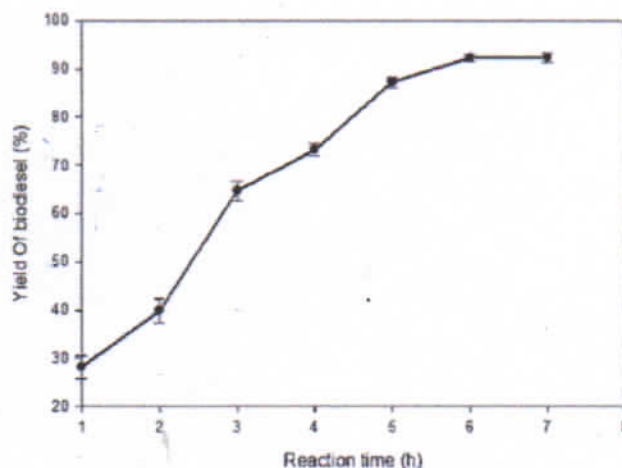


Fig. 3 Effect of reaction time (h) on yield of biodiesel with reaction temperature 65 °C, molar ratio of oil to methanol 1:12 and catalyst amount 4% (wt% to oil)

increased to 73.0, 87.0, and 92.29% at a reaction time of 4, 5 and 6 h, respectively. Beyond 6 h there was no significant increase in yield of biodiesel. It means the reaction reached the equilibrium state after 6 h with a yield of 92.29%. Maximum yield of 92.31% was achieved at 7 h. However, for efficiency and economic considerations, the reaction time of 6 h was chosen as the optimum reaction time for this work. Compared with previous work, Xie et al. (2006) obtained 87% yield of biodiesel on transesterification of soybean oil using 6.5% of $\text{KNO}_3/\text{Al}_2\text{O}_3$ solid base catalyst at 65 °C, 1:15 and 7 h of reaction time, molar ratio of oil to methanol, and reaction time, respectively.

Conclusion

The alumina supported zinc oxide (AZO) catalyst with a high surface area of $71.561 \text{ m}^2 \text{ g}^{-1}$ has successfully been synthesized with the combination of precipitation process, impregnation and gel methods. The transesterification process of kesambi oil (*Schleichera oleosa* L. oil), called SOO in this work, was significantly influenced by the amount of AZO catalyst (wt% to oil) used. The catalytic activity test that was conducted at 65 °C, with a molar ratio of oil to methanol 1:12 and reaction time of 6 h showed that the maximum biodiesel yield of 92.29% was achieved at a catalyst amount of 4%. It can be concluded that the local Kesambi oil (SOO) has great potential for use as an alternative feedstock for biodiesel production. Similarly, the AZO catalyst is very promising for use as a catalyst for converting non-edible oils of kesambi into biodiesel. Therefore, in the next project, we will develop the fundamental aspects and industrial applications. In the fundamental aspects, we will develop the kinetics model of transesterification of kesambi oil using AZO as catalyst.

Acknowledgements The authors would like to express their gratitude to Directorate of Research and Community Services, Directorate General of higher education, the Ministry of Research Technology and Higher Education of Republic Indonesia, for the financial support through the research grant in the fiscal year of 2017 by Contract No. 06/LPPM/UNIPRA/IV/2016 and 05/LPPM/UNIPRA/IV/2017.

Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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