Reaktor

p-ISSN 0852 – 0798
e-ISSN 2407 – 5973

Acredited: SK No.: 60/E/KPT/2016
Website : http://ejournal.undip.ac.id/index.php/reaktor/

Reaktor, Vol. 18 No. 3, September Year 2018, pp. 149-154

Biodiesel Production from Waste Cooking Oil Purified with Activated Charcoal of Salak Peel

Luqman Buchori[*)], Dinda Labibah Ubay, and Khonsa Syahidah

Department of Chemical Engineering, Faculty of Engineering, Diponegoro University
Jl. Prof. Soedarto, SH, Tembalang, Semarang
Telp./Fax: +62247460058 / +622476480675

[*)]Coresponding author: luqman.buchori@che.undip.ac.id

(Received: Juni 15, 2018 ; Accepted: September 5, 2018)

Abstract

Biodiesel is one of diesel fuel alternative made from renewable resources such as vegetable oils and animal fats. One of the natural ingredients that can be used as a material in the production of biodiesel is waste cooking oil (WCO). Biodiesel from WCO can be made through a transesterification reaction using a CaO catalyst. Free fatty acid (FFA) content in WCO needs to be reduced by activated charcoal adsorption. This research aims to determine the optimum time of adsorption by activated charcoal that made from salak peel and to determine the effect of transesterification temperature on biodiesel yield. The results showed that the FFA content of WCO decrease from 6.16% to 0.224% with adsorption time is 80 minutes and 10 gram of activated charcoal. Biodiesel yield increase by increasing transesterification temperature. The appropriate temperature is 50^{o}C with 86.40% of yield, 887.2 kg/m^{3} of density, 5.174 mm^{2}/s of kinematic viscosity and acid number 0.421 mg KOH/gram sample. The composition of alkyl ester was obtained 65.54% with a fatty acid alkyl ester (FAAE) yield of 56.63%.

Keywords: *activated charcoal; biodiesel; salak peel; transesterification temperature; waste cooking oil*

How to Cite This Article: Buchori, L., Ubay, D.L., and Syahidah, K., (2018), Biodiesel Production from Waste Cooking Oil Purified with Activated Charcoal of Salak Peel, Reaktor, 18(3), 149-154, http://dx.doi.org/10.14710/reaktor.18.3.149-154

INTRODUCTION

Energy consumption is something that cannot be released in various fields such as transportation, power generation, industrial processes, and households. Oil fuel is still the most consumed energy compared to others. In 2014, the average fuel oil consumption was around 1.01 billion barrels per day and is estimated to increase by 4% per year. Meanwhile, national crude oil production in 2014 was only 795.5 thousand barrels per day (ESDM, 2014). As we know, fuel oil is very limited and non-renewable so that alternative energy is required to overcome the energy crisis.

Currently, alternative energy developed in Indonesia is biofuels. The development of biofuel as an energy alternative is driven by President Instruction or Instruksi Presiden (Inpres) number 1 the year of 2006 concerning the Provision and Utilization of biofuel as other fuels. In the national energy policy, the government targets the use of biofuels to reach 5% of national energy consumption (Murtiningrum and Firdaus, 2015). One of the biofuels developed in Indonesia is biodiesel.

Biodiesel is a mono alkyl ester which contains a chain of long fatty acids produced from the transesterification reaction of vegetable oils or animal

fats with alcohol and catalyst (Abdullah *et al.*, 2013; Buchori *et al.*, 2017). The catalyst used can be homogeneous or heterogeneous. Heterogeneous catalysts are better than homogeneous catalysts due to biodiesel products and catalysts can be easily separated at the end of the process. Heterogeneous catalysts have different phases of reactants and products (Buchori *et al.*, 2016). Heterogeneous base catalysts that can be used in the transesterification reaction are MgO, CaO, SrO, zeolite, Al_2O_3, ZnO, TiO_2 dan ZrO_3. The catalyst that has high activity in the transesterification process and is easily found in the environment is CaO (Wendi *et al.*, 2015). One source of calcium for preparing CaO catalysts is chicken bone waste. Calcium in chicken bones is in the form of calcium and phosphorus, deposited in soft matrix tissue consisting of organic material containing collagen fibers and mucopolysaccharide gels (Mohadi *et al.*, 2013). Research conducted by Rutto and Enweremadu (2013) using waste cooking oil (WCO) and CaO catalyst obtained biodiesel yield of 85.96 %.

Biodiesel can be made from vegetable oil. One of the raw materials that can be used to produce biodiesel is WCO. Waste cooking oil is waste vegetable oil that is not suitable for use and reuse can be harmful to health. Waste cooking oil can pollute the environment due to its presence in water can inhibit oxygen exchange and damage ecosystems (Carlos *et al.*, 2011). The application of WCO as raw material for biodiesel can reduce pollution of water and reduce the cost of biodiesel production.

The utilization of oil repeatedly and at high temperatures (160-180^{o}C) accompanied by contact with air and water can accelerate the hydrolysis of triglycerides and increase the content of free fatty acids (FFA). The FFA content has a negative impact on the transesterification process because it is difficult to separate mono alkyl ester compounds and glycerol (Sharma *et al.*, 2011). For this reason, WCO for biodiesel production needs to be purified to reduce the free fatty acid content. Purification of WCO can be done using an adsorbent which is active charcoal. Activated charcoal is a porous solid containing 85-95% charcoal, produced by heating at high temperatures.

'Salak' peel is one of the raw materials that can be used as an activated charcoal adsorbent. Salak peel is a natural waste material that is not used. The nutrient content is low and has an abundance of cellulose, hemicellulose and lignin so that the salak peel is very good if used as an adsorbent in the form of activated charcoal (Pakpahan *et al.*, 2013; Buasri *et al.*, 2013). Another raw material that can be used as activated charcoal adsorbent is coconut shell which can reduce the free fatty acid of WCO by 33.71% (Paputungan *et al.*, 2018). Meanwhile, the activated charcoal adsorbent from banana peel was able to reduce free fatty acids from WCO by 52.73% (Nasir *et al.*, 2014).

This research aims to study the effect of adsorption time and weight of activated charcoal from salak peel on the FFA content in WCO. In addition, this study also investigates the effect of operating temperature on the transesterification reaction of WCO using CaO catalyst from chicken bone.

MATERIALS AND METHODS

Materials

The raw material used in this study is WCO obtained from Fried Chicken at Tembalang, Semarang. Chicken bones are obtained from restaurant waste around Tembalang. Salak peel is obtained from fruit market waste in Ungaran. The chemicals used include potassium hydroxide (KOH), methanol (98%) and hydrogen chloride (HCl 37%) from Merck.

Procedure

The experiment was carried out through several steps, i.e. free fatty acid (FFA) analysis, preparing and activating activated charcoal, adsorption of WCO, and transesterification process.

Free Fatty Acid (FFA) analysis

The FFA analysis was carried out to determine the content of FFA in WCO before and after adsorption with activated charcoal from salak peel. The FFA analysis was done by titration using KOH 0.1 N. Free fatty acid was calculated by equation (1).

$$FFA(\%) = \frac{V_{titran} \times N_{KOH} \times MW_{fatty\ acid}}{1000 \times m_{sample}} \qquad (1)$$

Where V_{KOH} is volume of titrant (mL), N_{KOH} is normality of KOH (mmol/mL), $MW_{fatty\ acid}$ is molecular weight of fatty acid (mg/mmol), and m_{sample} is weight of WCO sample (mg).

Preparing and activating activated charcoal

Activated charcoal is made from salak peel. Salak peel was put into the furnace and heated at 600^{o}C for 1 hour. Furthermore, charcoal from salak peel was impregnated with 20% KOH solution. The weight ratio of salak peel charcoal : KOH is 1 : 4. The impregnation results are then shaken with shaker bottle for 20 hours, then dried in an oven at 105^{o}C. The result is then activated in the furnace at 800^{o}C for 1 hour. The activated charcoal produced is then washed using demin water and dilute HCl solution until the pH reaches 6-7. Furthermore, the activated charcoal is dried in an oven at 105^{o}C overnight.

Adsorption of WCO

Waste cooking oil which has been analyzed for the content of FFA is adsorbed using activated charcoal from salak peel at a temperature of 80^{o}C. The adsorption time and activated charcoal weight were varied at 10-80 minutes and 5-10 gram, respectively.

Transesterification process

Waste cooking oil whose FFA content has been reduced, then used as raw material in the transesterification process. The transesterification process is carried out using CaO catalyst from activated chicken bones. Waste cooking oil is reacted with methanol at the molar ratio of methanol:WCO is 15:1. Transesterification is carried out in three-neck flask.

Waste cooking oil is first put in a three-neck flask. CaO catalyst as much as 5% by weight of oil is mixed with methanol in a beaker glass, then heated to reach the reaction temperature according to the variable. A mixture of methanol and CaO catalyst was put into a three-neck flask filled with WCO. Furthermore, the transesterification reaction was carried out according to the temperature variable for 2 hours with a stirring speed of 400 rpm. The transesterification results were filtered with Whatman 42 filter paper to separate the catalyst. The solution is then put into a separating funnel and allowed to stand overnight. Three layers will form inside the separating funnel, the upper layer is residual methanol, the middle is biodiesel and the bottom is glycerol. The resulting biodiesel is analyzed by GCMS. The yield of biodiesel and FAAE can be calculated by equations (2) dan (3).

$$Yield_{Biodiesel}\ (\%) = \frac{\text{weight of biodiesel product (g)}}{\text{weight of waste cooking oil (g)}} \text{ x } 100\% \quad (2)$$

$$Yield_{FAAE}(\%) = \frac{\%_{GC\ area\ FAAE} \text{ x weight of biodiesel produk (g)}}{\text{weight of waste cooking oil (g)}} \text{ x } 100\% \quad (3)$$

RESULTS AND DISCUSSION

Effect of Adsorption Time on FFA Content in WCO

The transesterification process in biodiesel production is influenced by the content of free fatty acids (FFA). Waste cooking oil has a high FFA content so it needs to be refined. One method of purifying WCO is by adsorption using activated charcoal from salak peel. In this study, the weight of activated charcoal from salak peel and adsorption time was varied at 5 and 10 grams and 0, 10, 20, 30, 40, 50, 60, 70, 80 minutes, respectively. The results of this study are shown in Figure 1.

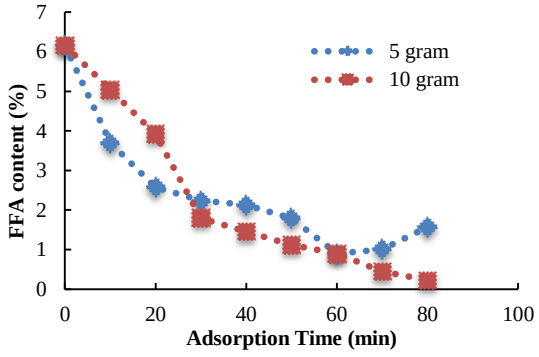

Figure 1. Effect of activated charcoal weight and adsorption time on FFA content in WCO

Based on Figure 1, the FFA content in WCO before adsorption is 6.16% and decreases with the length of adsorption time. The lowest FFA content was obtained at 80 minutes adsorption time with 10 grams of activated charcoal which was equal to 0.224%. The research conducted by Mangalo *et al.* (2014) used 5 grams of activated charcoal from salak peel with an adsorption temperature of 80ºC, obtained the adsorption optimum time is 80 minutes with FFA content of 0.64%.

Figure 1 shows that the FFA content decreases with increasing adsorption time. Activated charcoal contains cellulose in which the molecular structure contains a hydroxyl group. This hydroxyl group will adsorb FFA in WCO. The longer the adsorption time, the more adsorbed FFA will be before reaching the saturation point (Pakpahan *et al.*, 2013). However, on adsorption with 5 grams of activated charcoal at 60-80 minutes, the FFA content looks constant. This is due to the adsorbent has reached saturation. The adsorbent pores are no longer able to adsorp FFA so that the FFA content tends to be constant (Mangallo *et al.*, 2014).

The weight of the adsorbent is one of the factors that affect the adsorption of FFA in WCO. At 10 grams of activated charcoal, the adsorbed FFA content is greater than the use of 5 grams of activated charcoal adsorbent. This shows that the increasing weight of the adsorbent causes the surface area of the adsorbent to be greater so that contact between adsorbent particles and solute molecules will occur frequently. Thus, more free fatty acids will be adsorbed (Okeola *et al.*, 2012).

Effect of Temperature of Transesterification Reaction on Yield of Biodiesel

The best result of adsorption of WCO with activated charcoal from salak peel, namely with 10 grams of activated charcoal weight and 80 minutes adsorption time then reacted with methanol. The molar ratio of methanol to WCO is 15:1. The temperature of transesterification was varied at 30, 35, 40, 45, 50, 55, 60, and 65ºC. The transesterification reaction was carried out using a 5% wt CaO catalyst from chicken bones with a reaction time of 2 hours. The effect of the temperature of the transesterification reaction on the yield of biodiesel is presented in Figure 2.

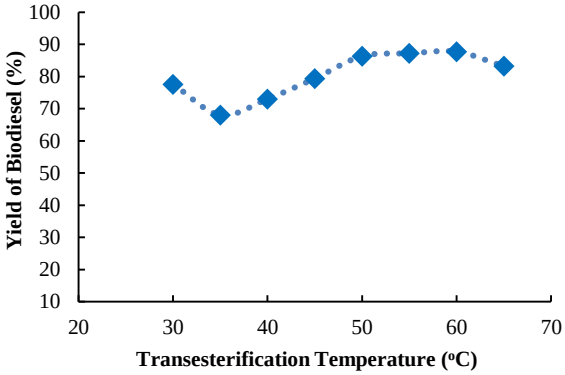

Figure 2. Effect of transesterification temperature on yield of biodiesel

Figure 2 shows that biodiesel yield increases with increasing reaction temperature. The higher the reaction temperature, the higher the reaction rate constants. This fact has resulted in a greater yield of biodiesel. Increasing the product formation reaction rate constant is greater than the reverse reaction rate constant (Sofyan *et al.*, 2014). The results of this study are in accordance with the results of research conducted

by Farooq and Ramli (2014). Based on this study it was found that the yield of biodiesel increases with increasing reaction temperature, but then decreases above the temperature of 60ºC because it has passed the boiling temperature of methanol.

Test of Biodiesel Product Parameter

The biodiesel product is then tested for density, kinematic viscosity, and acid number. The biodiesel test results can be seen in Table 1.

Table 1. Biodiesel test results for density, kinematic viscosity and acid number

No	Reaction temperature (ºC)	Analysis results		
		Density (kg/m^3)	Kinematic viscosity (mm^2/s)	Acid number (mg KOH/g sampel)
1	30	897.6	5.119	2.704
2	35	895.2	5.336	2.711
3	40	890.8	4.916	1.467
4	45	887.2	4.941	1.052
5	50	887.2	5.174	0.421
6	55	889.8	4.949	0.842
7	60	894.4	4.425	0.626
8	65	897.6	4.808	1.472

Based on the biodiesel quality standard (SNI No. 04-7182-2012), the density of biodiesel at 40ºC is permitted between 850-890 kg/m^3, kinematic viscosity at 40ºC between 2,3-6,0 mm^2/s, and maximum acid number is 0.6 mg KOH/g sample. Based on Table 1, biodiesel product that fulfill quality standards when viewed from their density, kinematic viscosity, and and acid number are biodiesel produced at 50ºC transesterification reaction temperature. This shows that the optimal temperature for the production of biodiesel from WCO with CaO catalyst from chicken bones is 50ºC with yield of biodiesel is 86.40%. Rahkadima and Abdi (2016) also conducted an investigate on the production of biodiesel from WCO using a CaO catalyst with a molar ratio of methanol to oil is 48:1 for 6 hours of reaction time. The optimal temperature of the transesterification reaction is 50ºC. Some studies state that the optimal temperature for biodiesel production from WCO is between 50-70ºC (Yakoob *et al.*, 2012).

Results of Fatty Acid Alkyl Ester (FAAE) Identification in Biodiesel Product

The composition of compounds in biodiesel can be known based on the analysis of Gas Chromatography-Mass Spectrometry (GCMS). GCMS analysis was carried out on biodiesel obtained at its optimum temperature at a reaction temperature of 50ºC. The results of GCMS analysis is shown in Figure 4 and Table 2.

The percentage of FAAE area obtained from GCMS analysis was 65.54% with the composition: Hexadecanoic acid, 2-hydroxy-1,3-propanediyl ester with %area 16.55 (peak no 1), Cyclopropaneoctanoic acid, 2-[[2-[(2-ethylcyclopropyl)methyl] cyclopropyl]methyl]-,methyl ester with %area 30.95 (peak no 2) dan Octadecanoic acid, 2-hydroxy-1,3-propanediyl ester with %area 18.04 (peak no 7). Yield of FAAE is calculated by Equation (2) obtained 56.63%.

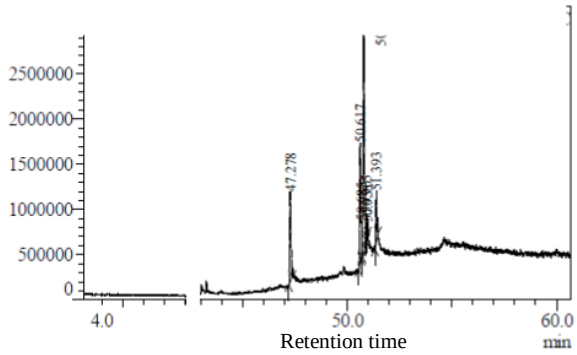

Figure 4. The result of GCMS analysis on biodiesel product

Table 2. The result of compound identification in biodiesel product

Peak	R. Time	%Area	Name
1	47.278	16.55	Hexadecanoic acid, 2-hydroxy-1,3-propanediyl ester (CAS)
2	50.617	30.95	Cyclopropaneoctanoic acid, 2-[[2-[(2-ethylcyclopropyl)methyl]cyclopropyl]methyl]-, methyl ester (CAS)
3	50.685	2.54	3-Hydroxy-7,8-dihydro-.beta.-ionol
4	50.785	29.02	DI-(9-OCTADECENOYL)-GLYCEROL
5	50.905	1.99	Patchouli alcohol
6	50.935	0.91	3-Chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone
7	51.393	18.04	Octadecanoic acid, 2-hydroxy-1,3-propanediyl ester (CAS)

The study conducted by Farooq and Ramli (2014) using WCO as raw material obtained biodiesel yield of 89.33% with an FAAE composition of 97.91%. The catalyst used of CaO from the chicken bone with a reaction time of 4 hours, temperature of transesterification reaction is 65ºC, and the molar ratio

of methanol to oil is 15:1. Meanwhile, Rahkadima and Abdi (2015) obtained biodiesel yield of 81.83% from transesterification reaction between WCO and methanol with CaO catalyst for 6 hours reaction time, 50^{o}C reaction temperature, and 48:1 molar ratio of methanol:oil.

The composition of alkyl ester in this study is still low due to the transesterification reaction has not reached its optimum reaction time. According to Lee *et al*. (2015), the optimum reaction time for CaO heterogeneous catalyst is 4-6 hours. Maximum conversion is achieved after reaching 6 hours and decreases at the 7th hour. In the first 3 hours, the transfer mass of heterogeneous catalyst runs slowly so that the conversion of the obtained biodiesel is low. Furthermore, the reaction runs fast and reaches its peak at a reaction time between 4-6 hours.

The results of GCMS analysis showed that the composition of glycerol obtained was rather high at 49.02%. The high composition of glycerol is due to the large molar ratio of methanol:oil. To get the maximum conversion, molar ratio of methanol:oil is 12:1. At a higher molar ratio, glycerin will dissolve in excess methanol so that it will reduce the amount of methanol and inhibit the reaction between reactants and catalysts. The reaction polarity increases and the solubility of glycerol in biodiesel also increases. This fact makes biodiesel difficult to separated from glycerol. As a result, the conversion of biodiesel product is small.

CONCLUSION

Salak peel is a potential adsorbent to reduce FFA content in WCO. Based on the results of this study, it can be concluded that the optimum time for adsorption of FFA in WCO with activated charcoal from salak peel is 80 minutes with a weight of an active charcoal is 10 grams. The FFA content of WCO decreased from 6.16% to 0.224%. In the transesterification reaction, the yield of biodiesel increases with increasing temperature of the transesterification reaction. The best transesterification temperature on the production of biodiesel from WCO with CaO catalyst from chicken bone is 50^{o}C with 86.40% yield of biodiesel. Under these conditions, density, kinematic viscosity, and acid number were 887.2 kg/m^3, 5.174 mm^2/s, and 0.421 mg KOH/gr sample, respectively. Based on GCMS analysis, the biodiesel produced contain 65.54% alkyl ester with yield of FAAE of 56.63%.

ACKNOWLEDGEMENT

We would like to thank the Faculty of Engineering, Diponegoro University, the Republic of Indonesia for funding assistance in this study.

REFERENCES

Abdullah, N.H., Hasan, S.H., and Yusoff, N.R.M., (2013), Biodiesel Production Based on Waste Cooking Oil (WCO), *International Journal of Material Science and Engineering*, 1(2), pp. 94-99.

Buasri, A., Chaiyut, N., Loryuenyong, V., Phakdeepataraphan, E., Watpathomsub, S., and Kunakemakorn, V., (2013), Synthesis of Activated Carbon Using Agricultural Wastes from Biodiesel Production, *International Journal of Materials and Metallurgical Engineering*, 7(1), pp. 106-110.

Buchori, L., Istadi, I., and Purwanto, P., (2016), Advanced Chemical Reactor Technologies for Biodiesel Production from Vegetable Oils - A Review, *Bulletin of Chemical Reaction Engineering & Catalysis*, 11(3), pp. 406-429.

Buchori, L., Istadi, I., and Purwanto, P., (2017), Synthesis of Biodiesel on a Hybrid Catalytic Plasma Reactor over K_2O/CaO-ZnO Catalyst, *Scientific Study & Research, Chemistry & Chemical Engineering, Biotechnology, Food Industry*, 18(3), pp. 303-318.

Carlos, A.G.F., Andrés Guerrero-Romero, A., and Sierra, F.E., (2011). Biodiesel Production from Waste Cooking Oil, *Biodiesel - Feedstocks and Processing Technologies*, Dr. Margarita Stoytcheva (Ed.), ISBN: 978-953-307-713-0, InTech.

ESDM, (2014), *Analysis and Data Evaluation of JODI Oil Semester I-2014*, Pusdatin ESDM.

Farooq, M. and Ramli, A., (2014). Biodiesel Production from Low FFA Waste Cooking Oil using Heterogeneous Catalyst Derived from Chicken Bones. *Renewable Energy*, 76, pp. 362-368.

Instruksi Presiden No. 1 (1996), *Penyediaan dan Pemanfaatan Bahan Bakar Nabati (Biofuel) sebagai Bahan Bakar Lain*.

Lee, S.H., Wong, Y.C., Tan, Y.P. and Yew, S.Y., (2015), Transesterification of Palm Oil to Biodiesel by Using Waste Obtuse Horn Shell-derived CaO Catalyst, *Energy Conversion and Management*, 93, pp. 282-288.

Mangallo, B., Susilowati, and Wati, S.I., (2014), Effectiveness of Salak Peel Activated Charcoal at Purification of Waste Cooking Oil, *Chemistry Progress*, 7(2), pp. 58-65.

Mohadi, R., Lesbani, A., and Susie, Y., (2013), Preparation and Characterization of Calcium Oxide (CaO) from Chicken Bone, *Chemistry Progress*, 6(2), pp. 76-80.

Murtiningrum and Firdaus, A., (2015), Development of Biodiesel in Indonesia: Overview of Current Condition, Production Technology and Prospective Analysis, *Jurnal PASTI*, 9(1), pp. 35-45.

Nasir, N.S.W., Nurhaeni, and Musafira, (2014), Utilization of Kepok Banana Peel (Musa Normalis) Activated Charcoal as an Adsorbent to Reduce Peroxide Number and Free Fatty Acid of Used Cooking Oil, *Jurnal of Natural Science*, 3(1), pp. 18-30.

Okeola, O.F., Odebunmi E.O., and Ameen, O.M., (2012), Comparison of Sorption Capacity and Surface Area of Activated Carbon Prepared from Jatropha Curcas Fruit Pericarp and Seed Coat, *Bulletin of the Chemical Society of Ethiopia*, 26(2), pp. 171-180.

Pakpahan, J.F., Tambunan, T., Harimby, A., and Ritonga, M.Y., (2013), Reduction of FFA and Color of Waste Cooking Oil with Adsorbents of Coconut Fiber and Rice Straw, *Jurnal Teknik Kimia USU*, 2(1), pp. 31-36.

Paputungan, R., Nikmatin, S., Maddu, A., and Pari G., (2018), Microstructure of Activated Charcoal from Coconut Shell as Consumables Oil Refining, *Jurnal Keteknikan Pertanian*, 6(1), pp. 69-74.

Rahkadima, Y.T. and Abdi, P., (2016), Production of Biodiesel from Waste Oil Using Calcium Oxide Catalyst, *Journal of Research and Technology*, 2(1), pp. 44-48.

Rutto, H. and Enweremadu, C., (2013), Optimization of Production Variables of Biodiesel Using Calcium Oxide as A Heterogeneous Catalyst: An Optimized Process, *Material and Processes for Energy: Communicating Current Research and Technological Developments*, FORMATEX.

Sharma, Y.C., Singh, B., and Korstad, J., (2011), Latest Development on Application of Heterogenous Basic Catalysts for an Efficient and Eco Friendly Synthesis of Biodiesel: A Review, *Fuel*, 90, pp. 1309-1324.

Sofyan, M., Tanjung, I., and Santosa, H., (2014), The Most Influential Variables Optimization in Biodiesel Production from Randu Seed Oil with Transesterification Process, *Teknik*, 35(1), pp. 42-28.

Wendi, Cuaca, V., and Taslim, (2015), The Effect of Reaction Temperature and Catalyst Amount on Biodiesel Production from Cattle Fat Waste Using CaO Heterogeneous Catalyst from Chicken Eggshell, *Jurnal Teknik Kimia USU*, 4(1), pp. 35-41.

Yakoob, Z., Mohammad, M., Alherbawi, M., Alam, Z., and Sopian, K., (2013). Overview of the Production of Biodiessel from Waste Cooking Oil, *Renewable and Sustainable Energy Reviews*, 18, pp. 184-193.