Malaysian Journal of Analytical Sciences
(MJAS)
Published by Malaysian Analytical Sciences Society
ANALIS
Persatuan Sains Analisis Malaysia

# PRODUCTION OF BIODIESEL FROM WASTE COOKING OIL USING POTASSIUM HYDROXIDE SUPPORTED ON ALUMINA CATALYST

## (Penghasilan Biodiesel daripada Minyak Masak Terpakai Menggunakan Kalium Hidroksida Disokong oleh Mangkin Alumina)

Shahida Hanum Kamarullah*, Zainal Kifli Abdul Razak, Norshahidatul Akmar Mohd Shohaimi,
Nailul Amal Zakariah

*Faculty of Applied Sciences,*
*Universiti Teknologi MARA Pahang, Jengka Campus, 26400 Bandar Tun Abdul Razak Jengka, Pahang, Malaysia*

**Corresponding author: shahidahanum@uitm.edu.my*

Received: 19 May 2021; Accepted: 26 July 2021; Published: 29 August 2021

### Abstract

In this study, waste cooking oil (WCO) was used to produce biodiesel using KOH supported on alumina (KOH/$Al_2O_3$) as the catalyst. Three parameters were studied to find the optimum conditions which are catalyst loading, reaction time and the reusability of the catalyst. $Al_2O_3$ was impregnated with KOH and characterized using thermogravimetric analyzer (TGA) before the catalyst was calcined at 700 ˚C for 3 hours. The reaction was refluxed with constant conditions at the temperature of 65 ˚C, 10% of KOH-$Al_2O_3$, and methanol to oil ratio of 12:1 for 3 hours. The reaction time was studied using optimum catalyst loading which was 7 wt.% of catalyst amount and the reaction varied from 1-hour to 4-hour reaction. The highest yield of biodiesel obtained was 73.7% in 2 hours of reaction. At the end of the study, the reusability of the catalyst was studied. Three cycles of reaction were done using the used catalyst from the previous 2-hours reaction of yield determination and the result found a decreasing pattern of yield after 4 cycles of reaction. Hence, the optimal conditions for this catalyst were reaction temperature of 65 ˚C, 10% of KOH-$Al_2O_3$, methanol to oil ratio of 12:1, and 7 wt.% of catalyst loading at 2 hours of reaction. The highest yield of biodiesel was 73.7%.

**Keywords:** potassium hydroxide supported on alumina, biodiesel, waste cooking oil, transesterification

### Abstrak

Dalam kajian ini, sisa minyak masak (WCO) digunakan untuk menghasilkan biodiesel menggunakan kalium hidroksida yang disalutkan atas sokongan alumina (KOH/$Al_2O_3$) sebagai mangkin. Tiga parameter telah dikaji untuk mencari keadaan optimum iaitu berat mangkin digunakan, masa tindak balas dan kebolehgunaan semula mangkin. KOH telah diintegrasikan dengan $Al_2O_3$ dan diuji menggunakan penganalisis termogravimetrik (TGA) sebelum mangkin itu dibakar pada suhu 700 ˚C selama 3 jam. Tindak balas itu di refluks dalam keadaan malar pada suhu 65 ± 2 ˚C, 10% KOH-$Al_2O_3$, nisbah metanol kepada minyak 12:1 selama 3 jam. Waktu tindak balas dikaji menggunakan mangkin optimum iaitu 7 wt.% dan tindak balasnya di ubah dari 1-4 jam dan hasil tertinggi diperolehi adalah 73.3% pada tindak balas 2 jam. Pada akhir kajian ini, kebolehgunaan semula mangkin telah dikaji. 3 kitaran tindak balas telah dilakukan menggunakan mangkin yang telah digunakan untuk tindak balas sebelumnya semasa penentuan hasil untuk 2 jam dan hasil kajian mendapati corak hasil biodiesel menurun selepas 4 kitaran tindak balas.

Oleh itu, keadaan optimum untuk mangkin ini ialah suhu tindak balas pada suhu 65 ˚C, 10% KOH-$Al_2O_3$, nisbah metanol kepada minyak 12:1, 7 wt.% jumlah mangkin pada masa tindak balas jam dan hasil tertinggi biodiesel ialah 73.7%.

**Kata kunci:** kalium hidroksida, biodiesel, minyak masak terpakai, transesterifikasi

## Introduction

Biodiesel is one of the alternatives for petroleum which has the potential to replace the fossil fuels which are produced partially from parts of dead organisms such as plants and animals. It is defined as the mono alkyl esters of long chain fatty acids [1, 2] formed from biolipids through transesterification of vegetable oils such as palm oil [3, 4] canola oil [5], castor oil [6] and waste oil from the food industry [7, 8] in reaction with methanol under either acidic or basic conditions. Waste Cooking Oil (WCO) has been used in studies since it is available in the lowest price because it is 2-3 times cheaper than virgin vegetable oil and the supply of vegetable oil is abundant in the Malaysian market [9].

There are some studies [10, 11, 12, 13] which investigated the production of biodiesel using homogeneous base catalysts such as potassium hydroxide and sodium hydroxide as well as homogeneous acid catalyst using sulfuric acid. However, such processes have many disadvantages such as they could reduce the yield of biodiesel production, homogeneous base could not be reused or regenerated after a reaction and toxic wastewater might also be produced [14]. Besides, the production cost due to the separation of catalyst from products in hydrolysis and saponification reactions of transesterification is also higher because the elimination of the catalysts from the biodiesel product requires a large amount of water which could contaminate the products [15], thus resulting in the loss of useful material [16]. Moreover, the separation between the catalysts and glycerol is difficult [17]. In the same case, even if the separation process succeeds, a huge amount of wastewater is still produced [3] which is not economically and environmentally friendly [2]. In addition, some soap would be produced with the presence of too much FFAs in the process that would reduce the yield of FAME production [3]. A high content of FFAs (>1% w/w) would lead to these phenomena which increase the viscosity of the solution and difficulty to separate the glycerol [18].

In that case, heterogeneous catalysts were thus used in this study as they were separable and produce high quality methyl ester and glycerol, resulting in a lowered cost of processing operations. Hence, the use of heterogeneous base catalysts was proven to be effective due to their reusability, widespread availability, easy separation process from the product and longer lifetime [14]. Furthermore, for active species like potassium hydroxide (KOH), attaching catalysts to support such as alumina increases the contact area and number of pores [19]. Alumina had been investigated as the most frequently used catalyst support to produce biodiesel due to its high thermal and mechanical stability, high contact area (can exceed to 300 $m^2$ /g), large pore diameter (5-15 nm), bigger pore volume (1.07 $cm^3$ /g) and the ability to form and extrude the pellets. The aim of this study was to investigate the effect of catalyst loading and reaction time on biodiesel production from waste cooking oil (WCO) using potassium hydroxide supported on alumina as a heterogeneous catalyst. The reusability of the catalyst was also investigated over several consecutive runs as it is a major advantage for industrial biodiesel development.

## Materials and Methods

### Materials

Waste cooking oil was collected from a household in Jengka. Aluminium oxide, $Al_2O_3$, was obtained from Sigma-Aldrich (commercial grade). Potassium hydroxide ($K_2CO_3$, 99%) was obtained from Merck and methanol ($CH_3OH$, 99%) was that of analytical grade (AR). The chromatographic standards were methyl heptadecanoate as the internal standard and the FAME standard mixture GLC-10 from Sigma-Aldrich. GLC-10 consists of methyl palmitate, methyl stearate, methyl oleate, as well as methyl linoleate and methyl linolenate.

### Pre-treatment of waste cooking oil

The waste cooking oil was first filtered to remove traces of suspended particles followed by heating at 100 ℃ for 1 hour to remove moisture. The pre-treated waste cooking oil was then stored in a closed container before proceeding with the transesterification reaction.

### Catalyst preparation

A 5 g of alumina powder was dissolved in 10 mL of distilled water and stirred until it became a suspended mixture. The alumina suspended solution was heated and stirred using a magnetic stirrer and 2.15 g of KOH solution was then added to the mixture dropwise. The paste was then dried in an oven at 90 ˚C for 24 hours to remove excess water [20, 21]. Next, this impregnated catalyst was calcined in a muffle furnace at 700 ˚C for 3 hours with a ramp rate of 5 ˚C/min. The catalyst was characterized using thermogravimetric analysis (TGA) to determine the thermal transition and the decomposition of the catalyst [2].

### Transesterification reaction

WCO, methanol and catalyst were the main components in this process. The selected parameter in this study was catalyst loading on the percentage yield of biodiesel. The transesterification reaction was conducted in a 500 mL round bottom flask equipped with a reflux condenser, thermometer, and magnetic stirrer [22] submerged in a steel basin with paraffin oil and the reaction was done at the boiling point of methanol (65˚C). Then, 10 g of WCO was mixed with 4.3 g of methanol together with a series of catalyst loading (1 wt.%, 3wt.%, 5 wt.%, 7 wt.% and 9 wt.%) added into the flask. A magnetic stirrer was used to mix the oil, catalyst, and methanol together [3] and the reaction was carried out for 3 hours while the external temperature (temperature of paraffin oil) was maintained at 75 ˚C. After the reaction completed, the mixture was poured into a centrifuge tube and then was centrifuged at 4000 rpm in 5 minutes. The mixture formed two layers by which the methyl ester obtained was on the top layer while the glycerol was at the lower layer. The glycerol was discarded and the removal of excess methanol on the upper part and catalyst at the bottom layer was done by washing the methyl ester using warm distilled water (80-100 ˚C) in a separatory funnel. The mixture was then shaken gently and left for about 3 minutes until two layers were formed by which the lower layer was then removed again [8]. After that, the washed methyl ester was transferred into a 100 mL beaker and heated to remove any existing moisture/methanol for about half an hour while being stirred. All these procedures were repeated for other reaction mixtures at different reaction time (1 hour, 2 hour and 4 hour).

### Reusability test

This test was conducted only for the catalyst with the highest yield of biodiesel using the same reaction conditions stated previously. The catalyst was isolated from the reaction product after the first reaction. To eliminate the non-polar compounds attached to the catalyst, it was washed with methanol three times and filtered using filter paper. The catalyst was then dried for 1 hour in the oven and used in the transesterification reaction. With the same optimum condition, the procedures were repeated three times and the composition of the biodiesel was tested with gas chromatography (GC) analysis.

### Gas chromatography analysis

The GC-MS is a library-built instrument that offers a complete list of elements in the sample [21]. The purity of methyl ester produced was determined by using gas chromatography. The analysis was done by Agilent 7890B gas chromatographer equipped with 5977A MSD and Zebron ZB-FAME capillary column (60 m x 0.20 mm x 0.25 µm). The instrument was set up as the following: Split ratio of 100:1 and initial oven temperature of 60˚C to 240˚C at 14˚C/min. The temperature of the injection was set at 250˚C while the MS transfer line temperature was 280˚C. The sample was injected to reach reproducible peaks where methyl heptadecanoate was used as an internal standard. After the ester content was obtained, the percentage of pure biodiesel was then calculated.

## Results and Discussion

### Characterization of KOH/$Al_2O_3$ catalyst

Figure 1 shows the thermal degradation pattern of KOH/$Al_2O_3$ catalyst. From the figure, it was observed that there were three stages of weight loss process within the temperature range of 32.50˚C to 926.39˚C. The first level of weight loss was about 7.9% which took place at the temperature of 32.50˚C to 135.42˚C pointing that water had evaporated and was removed from the catalyst surface. Meanwhile, the second level of weight loss was about 1.18% at the temperature of 201.20˚C to 314.76˚C which indicated a complete removal of water surface on the catalyst. The amount of mixture content and slight weight loss were observed below 200˚C due to the catalyst being subjected to oven drying at 80˚C overnight before the analysis was conducted. At the end of the analysis, about 2.57% of catalyst became decomposed at 767.41˚C to 926.39˚C. This shows that the removal of hydroxyl group (-OH) and formation of $K_2O$ phase was due to the decomposition at the end of the analysis. It can be concluded that water and impurities were removed after the thermal treatment at the temperature of 700˚C.

**Effect of catalyst loading**

The effect of wt.% of catalyst loading on the yield of biodiesel produced is summarized in Figure 2. In this study, the catalyst loading varied within the range of 1 wt.% to 9 wt.% to catalyze the reaction. Referring to the figure, the yield of each loading did not show a significant difference except for 1 wt.% and 3 wt.%. For the first two catalyst loading (1 wt.% and 3 wt.%), there was no biodiesel produced on both due to the formation of emulsions. The production of FAME could not be achieved in an insufficient catalyst loading amount [6]. This might be due to a slow reaction rate resulting from a low amount of catalyst in a short reaction time. The highest pure biodiesel obtained was 9 wt.% which is 58.52% while at catalyst loading of 7 wt.% and 5 wt.%, they are 58.38% and 51.5% respectively. Since there were no obvious differences between 7 wt.% and 9 wt.%, the 7 wt.% was considered as the optimum catalyst loading.

Larger catalyst loading triggered high resistance to mass transfer because of the viscous mixture [23]. When the excess catalyst was used, the reaction mixture became more viscous, resulting in poor dispersion of reactants in the three phase systems. This brought about reduced yield and conversion, thus consuming more costs and time [24].

**Effect of reaction time**

The effect of reaction time was studied as it had a significant impact on the transesterification of waste cooking oil. The reaction time varied from 1 to 4 hours in 7 wt.% of catalyst loading. As summarized in Figure 3, the FAME yield increased from 58.35% to 73.7% in the first two hours. However, the yield declined as the reaction continued further than 2-hour reaction. It is concluded that when the temperature increased during the 2 hours of reaction, the rate of reaction increased, and the yield of biodiesel became optimal (73.7%) before the yield decreased due to methanol evaporation [25] as well as the loss of solvent and by-product formation such as olefins and fatty alcohol [9]. The methyl ester favored a backward reaction in a longer reaction time, producing more glycerol than methyl ester [11]. In addition, high molar ratio required a shorter time as it had enough methanol to produce high yield reaction. Hence, 2-hour reaction time was selected as the optimum reaction time as it provided the highest biodiesel yield. In a previous work [26], WCO was converted to biodiesel and it achieved a higher yield of 95% after 2 hours of reaction with methanol to oil ratio of 9:1 and catalyst loading of 5%. The catalyst used was also KOH/alumina, but it was calcined at 700ºC for 7 hours, compared to the catalyst in this research which was calcined for only 3 hours at the same temperature. Therefore, it could be regarded that increasing the calcination time would increase the catalytic activity of the catalyst.

**Reusability test**

Catalyst reusability is an important aspect in the development of biodiesel. The reusability of $KOH/Al_2O_3$ was determined at the optimum state of the conditions for 3 cycles as shown in Figure 4. It was noticed that after cycle 1 with yield of 73.7%, the cycle demonstrated a declining pattern of yield of pure biodiesel which was 72.12%, 70.86% and 68.75% for cycle 2, 3 and 4 respectively. This decreasing trend caused by the deactivation of the catalyst due to the loss of almost half of the original weight after the third cycle. The loss of catalyst due to the partial solubility of the catalyst in methanol (leaching) eventually affected the glycerol recovery [2] and disrupted the reaction mixture.

**Qualitative analysis of gas chromatography**

Figure 5 shows the GC-MS chromatogram of biodiesel for 2-hour reaction. Four peaks of methyl esters were observed in Table 1 which consisted of methyl palmitate, methyl stearate, methyl oleate and methyl linoleate. The main components of biodiesel were methyl palmitate and methyl oleate which showed high peak of GC. This GC-MS chromatogram was comparable to the fatty acid profile of palm oil. Thus, it indicated the formation of biodiesel from the oil used [2]

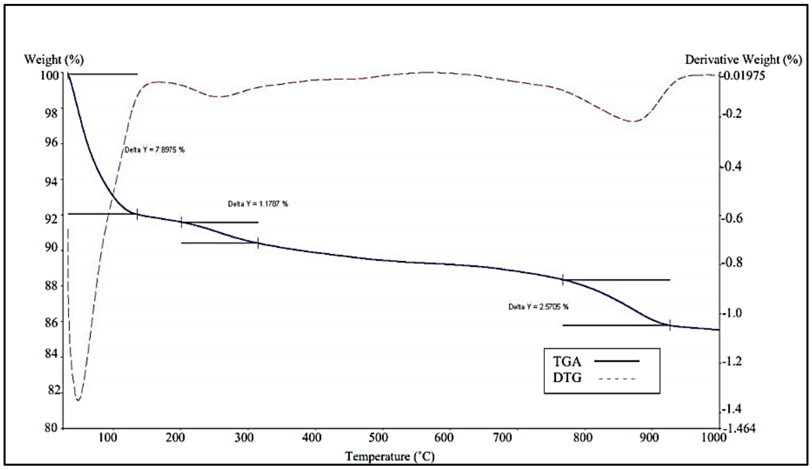

Figure 1. TGA and DTG curve for $KOH/Al_2O_3$ catalyst

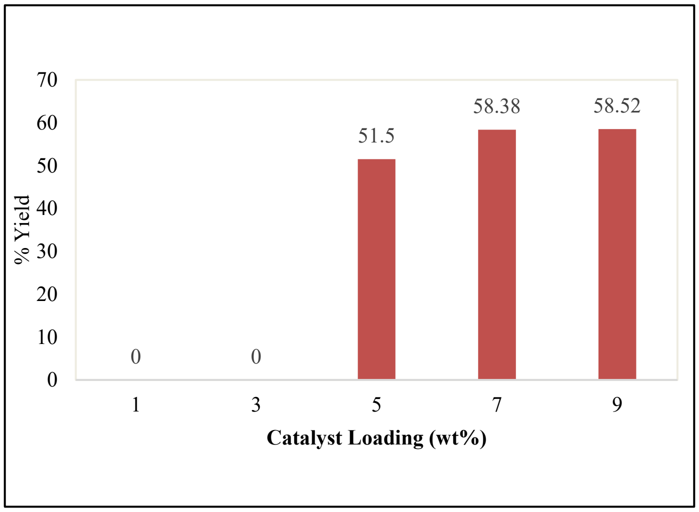

Figure 2. The effect of the catalyst loading on the yield (10% of $KOH-Al_2O_3$, 12:1 MeOH: oil, 65 ˚C temperature and 3-hour reaction.

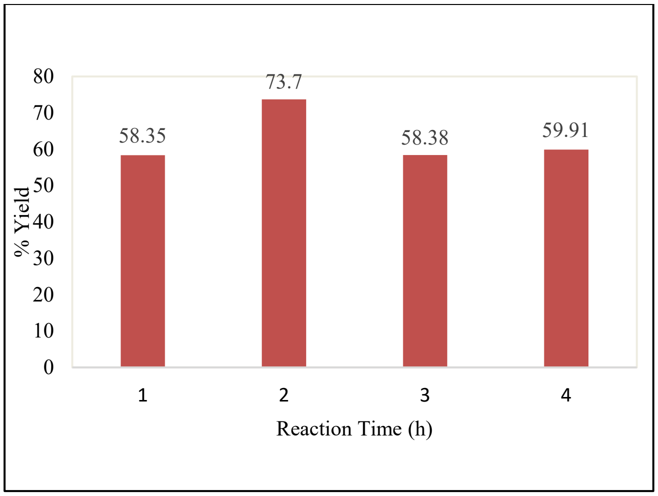

Figure 3. Effect of reaction time on the yield (12:1 MeOH: oil, 65˚C temperature and 7 wt.% catalyst)

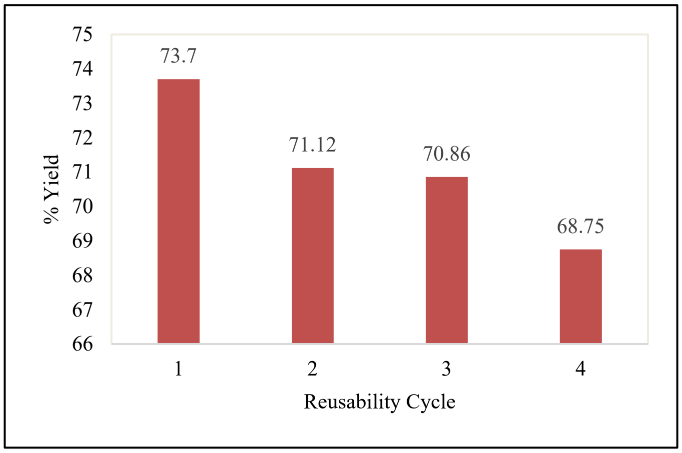

Figure 4. The reusability of the catalyst

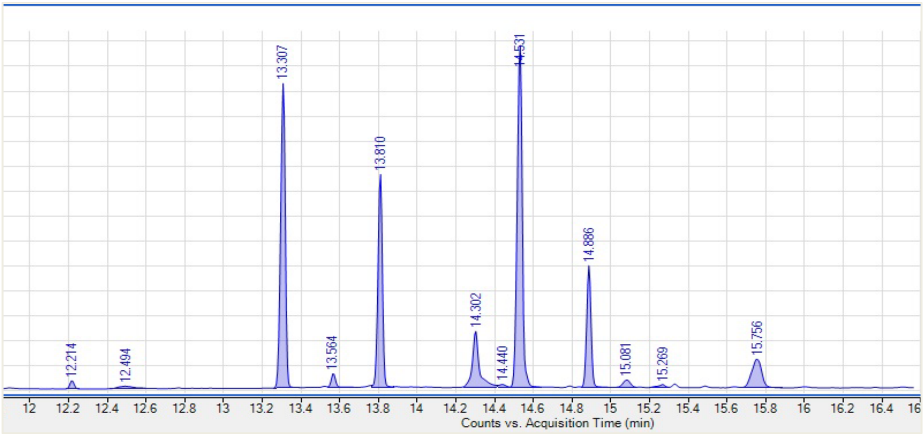

Figure 5. GC-MS chromatogram of biodiesel for 2-hour reaction (10% KOH-$Al_2O_3$, 12:1 MeOH: oil, 65˚C temperature and 7 wt.% catalyst)

Table 1. Retention time and FAME of biodiesel obtained using 7 wt.% catalyst

| **Retention Time (min)** | **Common Name** |
|---|---|
| 13.307 | Methyl palmitate |
| 13.810 | Methyl heptadecanoate (Internal standard) |
| 14.302 | Methyl stearate |
| 14.531 | Methyl oleate |
| 14.886 | Methyl linoleate |

## Conclusion

In this study, the maximum biodiesel yield achieved was 73.7% with the reaction temperature of 65 ˚C, 10% of KOH-$Al_2O_3$, catalyst loading of 7 wt.%, reaction time of 2 hours and methanol to oil ratio of 12:1. After the reaction was done in 4 cycles, the yield of biodiesel became reduced to 68.75% as the catalyst was deactivated because almost half of the weight was lost. The GC-MS chromatogram confirmed the presence of two main components of methyl ester which were methyl palmitate and methyl oleate. For future research, it is suggested that the preparation of the catalyst is to be studied in more detail, for example, optimizing the ratio of KOH: alumina, the calcination temperature, and the calcination time for preparing the catalyst, as these might improve the catalytic activity.

## Acknowledgement

Authors would like to express gratitude to all staff of the chemistry laboratory of UiTM Jengka Pahang, Malaysia, for their assistance in the completion of this research.

## References

1. Alkabbashi, A. N., Alam, M. Z., Mirghani, M. E. S. and Al-Fusaiel, A. M. A. (2009). Biodiesel production from crude palm oil by transesterification process. *Journal of Applied Sciences*, 9: 3166-3170.
2. Aqliliriana, C. M., Ernee, N., M. and Irmawati, R. (2016). Preparation and characterization of modified calcium oxide from natural sources and their application in the transesterification of palm oil. International *Journal of Scientific & Technology Research*, 4(11): 168-175.

3. Noiroj, K., Intarapong, P., Luengnaruemitchai, A. and Jai-In, S. (2009). A comparative study of KOH/$Al_2O_3$ and KOH/NaY catalysts for biodiesel production via transesterification from palm oil. *Renewable Energy*, 34, 1145-1150.
4. Sulaiman, S. and Ramli, N. S. (2017). Biodiesel production from palm oil using KOH supported polyvinyl alcohol as the catalyst. *Energy Sources*, 39(18): 1948-1953.
5. Ilgen, O. G. and Akin, A. S. N. U. (2009). Development of alumina supported alkaline catalysts used for biodiesel production. *Turkish Journal Chemistry*, 33: 281-287.
6. Keera, S. T., Sabagh, S. M. E. and Taman, A. R. (2018). Castor oil biodiesel production and optimization. *Egyptian Journal of Petrol*, 27: 979-984.
7. Ghasemi, M. and Molaei Dehkordi, A. (2014). Transesterification of waste cooking oil to biodiesel using KOH/$\gamma$-$Al_2O_3$ catalyst in a new two-impinging-jets reactor. *Industrial & Engineering Chemistry Research*, 53(31): 12238-12248.
8. Taslim, Andika Sinaga, B., Nathalia Sihaloho, M., Iriany, and Bani, O. (2019). Biodiesel synthesis from waste cooking oil using heterogeneous catalyst from corncob ash impregnated with KOH. *Journal of Physics: Conference Series*, 1175: 012281.
9. Ma, G., Hu, W., Pei, H., Jiang, L., Ji, Y. and Mu, R. (2015). Study of KOH/$Al_2O_3$ as heterogeneous catalyst for biodiesel production via in situ transesterification from microalgae. *Environmental Technology*, 36:5, 622-627.
10. Jitputti, J., Kitiyanan, B. and Rangsunvigit, P. (2006). Transesterification of crude palm kernel oil and crude coconut oil by different solid catalysts. *Chemical Engineering Journal*, 116: 61–6.
11. Renganathan, S. V., Narashimhan, S. L., and Muthukumar, K. (2008). An overview of enzymatic production of biodiesel. *Bioresource Technology*, 99: 3975-3981.
12. Zhang, J., Liu, J. and Ma, H. (2012). Esterification of free fatty acids in *Zanthoxylum bungeanum* seed oil for biodiesel production by stannic chloride. *Journal American Oil Chemical Society*, 89:1647-1653.
13. Zhang, L., Wu, H. T. and Yang, F. X. (2015). Evaluation of Soxhlet extractor for one-step biodiesel production from *Zanthoxylum bungeanum* seeds. *Fuel Process Technology*, 131: 452–457.
14. Modiba, E., Enweremadu, C., and Rutto, H. (2014). Production of biodiesel from waste vegetable oil using impregnated diatomite as heterogeneous catalyst. *Chinese Journal of Chemical Engineering*, 2014: 1-9.
15. Roschat, W., Siritanon, T., Yoosuk, B., and Promarak, V. (2016). Biodiesel production from palm oil using hydrated lime-derived CaO as a low-cost basic heterogeneous catalyst. *Energy Conversion and Management*, 108: 459-467.
16. Kansedo, J., Lee, K. T. and Bhatia, S. (2009). Biodiesel production from palm oil via heterogeneous transesterification. *Biomass and Bioenergy*, 33: 271-276.
17. Buasri, A., Chaiyut, N., Loryuenyong, V., Rodklum, C., Chaikwan, T. and Kumphan, N. (2012). Continuous process for biodiesel production in packed bed reactor from waste frying oil using potassium hydroxide supported on *Jatropha curcas* fruit shell as solid catalyst. *Applied Science*, 2: 641-653.
18. Refaat, A. A. (2010). Different techniques for the production of biodiesel from waste vegetable oil. *International Journal of Environment, Science & Technology*, 7(1): 183-213.
19. Uprety, B. K., Chaiwong, W., Ewelike, C. and Rakshit, S. K. (2016). Biodiesel production using heterogeneous catalysts including wood ash and the importance of enhancing byproduct glycerol purity. *Energy Conversion and Management,* 115: 191-199.
20. Shohaimi, N. A. M., Bakar, W. A. W. A. and Jaafar, J. (2014). Catalytic neutralization of acidic crude oil utilizing ammonia in ethylene glycol basic solution. *Journal of Industrial and Engineering Chemistry*, 20(4): 2086-2094.

21. Shohaimi, N. A. M., and Marodzi, F. N. S. (2018). Transesterification of waste cooking oil in biodiesel production utilizing $CaO/Al_2O_3$ heterogeneous catalyst. *Malaysian Journal of Analytical Sciences*, 22(1): 157-165.
22. May, C. Y. (2004). Transesterification of palm oil: Effect of reaction parameters. *Journal of Oil Palm Research,* 16(2): 1-11.
23. Mahesh, S. E., Ramanathan, A., S.Begum, K. M. M., and Narayanan, A. (2015). Biodiesel production from waste cooking oil using KBr impregnated CaO as catalyst. *Energy Conversion and Management*, 91: 442-450.
24. Maneerung, T., Kawi, S., Dai, Y. and Wang, C.-H. (2016). Sustainable biodiesel production via transesterification of waste cooking oil by using CaO catalysts prepared from chicken manure. *Energy Conversion and Management*, 123: 487-497.
25. Daniyan, A., Adeodu, A. O., Dada, O. M., and Adewumi, D. F. (2015). Effect of reaction time on biodiesel yield. *Journal of Bioprocessing and Chemical Engineering*, 3(2): 1-4.
26. Madhu, A., Garima, C., Chaurasia, S. P. and Kailash, S. (2012). Study of catalytic behavior of KOH as homogeneous and heterogeneous catalyst for biodiesel production. *Journal of the Taiwan Institute of Chemical Engineers,* 43: 89-94.