

PRODUCTION OF BIODIESEL FROM PALM OIL USING ALUMINA SUPPORTED POTASSIUM IODIDE CATALYST WITH NICKEL DOPANT

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Abstract

Biodiesel is eco-friendly and proven to be environmentally safe compared to the conventional diesel fuel. Transesterification is the common technique used for biodiesel production in order to reduce the viscosity of triglycerides. In this study, biodiesel was produced by transesterification of palm oil utilizing potassium iodide (KI) supported on alumina beads catalyst with nickel as a dopant. The objective of this study is to investigate the effects of nickel as dopant towards the transesterification reactions. The reactions were refluxed at 65°C with 5 hours reaction time while varying the catalyst loading (0 wt%-8 wt%) and methanol to oil molar ratio at (1:15-1:55). The optimum methanol to oil ratio was 1:35 and 4 wt% catalyst loading produced FAME yield of 53.34%. Thermogravimetric analysis (TGA) results proved that the catalyst has undergone two stages of decomposition with 23.47% total weight loss. GCMS results showed six peaks of methyl esters which reveal that nickel that act as dopant has greatly affected the reactivity of the catalyst.

Keyword: Biodiesel, Dopant, Heterogeneous Catalyst, Palm Oil, Transesterification

Introduction

The conventional diesel fuel introduced some of the environmental problem such as air pollution due to exhaust emission of pollutant gases and also fossil fuel depletion (Shajaratun et al., 2014). The demand for petroleum diesel also causes the need for an alternative energy resource. Biodiesel which consists of fatty acid methyl ester (FAME) is a biofuel proposed as an alternative for conventional diesel. Besides having an advantage of easily biodegraded, biodiesel is also environmental friendly and can be produced on a greater scale (Leung et al., 2010). Biodiesel contains no sulphur content and emit less amount of carbon dioxide (CO₂), carbon monoxide (CO) and nitrogen oxides (NO_x) showing that it is a good choice as an alternative diesel.

The production of biodiesel from palm oil involves the transesterification process where the separation of glycerin from the vegetable or fat oil occurs. Both homogeneous and heterogeneous catalyst (base and acids) can be used to catalyze the transesterification reaction. Saponification process is one of the unfavorable causes that usually happened when homogenous catalysts were used especially for feedstock with high moisture and free fatty acids content (Gashaw et al., 2015). Sharma et al., (2018) reported that, homogenous acid catalysts have comparatively slower reaction rate than of basic catalyst. Normally, the use of homogeneous catalyst would lead to the difficulty in separating the catalyst from reaction medium (Shajaratun et al., 2014). For an easier separation, heterogenous catalyst was chosen since the cost of separation also can be reduced (Islam et al., 2013). However, the use of heterogenous catalyst is still subjected to leachate where a certain fraction of catalyst is dissolved in the reaction medium, thereby limiting the reusability of the catalyst. Therefore,

binding the catalyst to a solid support is recommended to defeat this problem.

Evangelista et al., (2016) also mentioned that the most suitable supporting material that can be used is alumina-supported potassium iodides (KI/Al₂O₃). It has large specific area (above 100 m²g⁻¹) as well as the conversion to triglycerides is highly active thus making it used commonly as catalyst support and adsorbents. The types of supporting material used has also greatly affected the biodiesel yield production. For example, based on a research by Islam et al., (2015), millimetric alumina spherical catalyst (Al₂O₃) beads with 1.0 mm diameter have been used in their transesterification reactions as an alternative support for the catalyst. Despite the high percentage of FAME achieved by powdered catalysts nearly 90% of yield, there are still several difficulties encountered in the process of separating the catalyst from the reaction. Small particles of catalyst also contribute to the excessive pressure decrease, poor contact efficiency and lack of mass or heat transfer. As an alternative, utilization of alumina beads as catalyst support and their application in transesterification reactions will be studied to replace alumina powder.

There are many previous studies on the effects of dopants in chemical performance. According to Dey et al., (2017), the benefit of doping a catalyst with metal dopants improved the catalytic activity. A similar finding was also made by Guo et al., (2015), which proves that doping the underlying metal substrate is a way to enhance the catalytic activity of catalyst. The aim of this study is to determine the optimum conditions for the production of biodiesel by transesterification of palm oil with methanol catalyzed by nickel doped potassium iodide supported on alumina beads. The parameters studied were methanol/oil molar ratio and catalyst loading.

Materials and Methods

Materials

The materials used were palm oil, potassium iodide, alumina bead, nickel (II) nitrate hexahydrate, methyl heptadecanoate (as internal standard), standard FAME mixture, 99.9% methanol, n-hexane.

Preparation of Catalyst

About 33.2 g of potassium iodide was dissolved in 100 mL of distilled water. Next, 5.82 g of nickel (II) nitrate hexahydrate was added to the potassium iodide solution. Then, the mixture was gently stirred by using magnetic stirrer for 10 minutes. The alumina beads were immersed in the solution of catalyst for 30 minutes. After that, the mixture was transferred onto a filter paper for filtration. The alumina beads then were heated in an oven at 80°C for 24 hours to remove the water content and to ensure the coating on the surface of the supported catalyst is sufficiently done. The calcination was carried out in the furnace at 700°C for 5 hours by using ramp rate of 5°C min.

Characterization of Catalyst

The catalyst prepared was characterized by using thermogravimetric analyzer (TGA) to observe the thermal behavior subjected to control heating and cooling inside the TGA furnace. The TGA analysis was conducted at heating flow rate 10°C/min and the temperature was set up from 0°C to 1000°C.

Transesterification Catalyzed with Potassium Iodide Support Alumina

For the transesterification reaction, 10 g of palm oil was mixed with the required mass of methanol and catalyst in a three-necked round bottom flask equipped with a thermometer, a condenser and a magnetic stirrer. The mixture was refluxed in an oil bath at 65°C for 5 hours

and stirred at 600 rpm. The parameters investigated were catalyst loading (0 wt%, 2 wt.%, 4 wt.%, 6 wt.% and 8 wt.%) and oil to methanol ratio (1:15, 1:25, 1:35, 1:45 and 1:55). After the reaction is complete, the beads were removed from the mixture using filter paper. Then, the mixture was transferred into test tubes and were placed in centrifuge at 3000 rpm for 10 minutes. Two layers were formed after the step was completed. Both layers were separated. Sodium sulphate anhydrous was added to the upper layer solution that contained FAME to remove excess moisture. The sodium sulphate anhydrous was removed by filtration and the biodiesel solution was dried overnight in an oven at 70°C to remove the methanol.

Analysis of Biodiesel Produced

The fatty acid methyl ester (FAME) or biodiesel produced were identified and quantified using Agilent 7890B gas chromatography mass spectrometry (GC-MS) equipped with 5977A MSD and Zebron ZB-FAME (60 m x 0.25 mm x 0.20 µm) capillary column. The injector and MS transfer line temperatures were set at 250°C and 280°C respectively. The initial oven temperature was 60°C, then increased at 14°C/min to 250°C and held for 3 mins. Quantification of biodiesel was done using internal standard method with methyl heptadecanoate as internal standard and GLC-10 FAME mixture (Supelco) as standards. The identification of compounds was done by comparing the retention time with these standards and further confirmed by NIST-MS database. The methyl ester yield was calculated based on the peak area of FAME (Yahya et al., 2016). The following equation is used for the calculation of the amount of FAME.

$$C = \frac{(\Sigma A)}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100\%$$

Where:

ΣA = total peak area of the FAME

A_{EI} = peak area of internal standard

C_{EI} = concentration, in mg/mL, of the internal standard solution

V_{EI} = volume, in mL of the internal standard solution

m = mass, in mg, of the sample

Results and Discussion

Characterization of Catalyst Using Thermogravimetric Analysis (TGA)

Figure 1 shows the thermogram of KI-Al₂O₃ with nickel dopant. The thermogram obtained is classified as type 2 where it exhibits mass loss region which is then followed by a constant line (Loganathan et al., 2017). The change in weight (%) of the catalyst as a function of temperature was identified by using thermogravimetry analysis (TGA). From the curve, the catalyst exhibits two stages of decomposition.

The first stage of decomposition occurred about 5.35% at approximately 41.46°C and the reaction was terminated at 167.72°C. This corresponded to the removal of the surface loosely physisorbed water (Zhen & Zaera., 2006). While for the second stage of decomposition, a broad peak in a wide temperature ranging from 194.70°C to 649°C with the percentage of weight loss at approximately about 18.12%. It was mainly attributed to the decomposition of the solid-state reaction of the added compound with the support and the dehydration of Al-OH groups of alumina (Xie & Li., 2006). Upon increasing the temperature at approximately 700°C the thermogram presented a constant line after the weight loss portion. In this region, mass of the sample was constant and unchanged in weight was observed. Thus, 700°C was considered as optimum calcination temperature from the TGA thermogram.

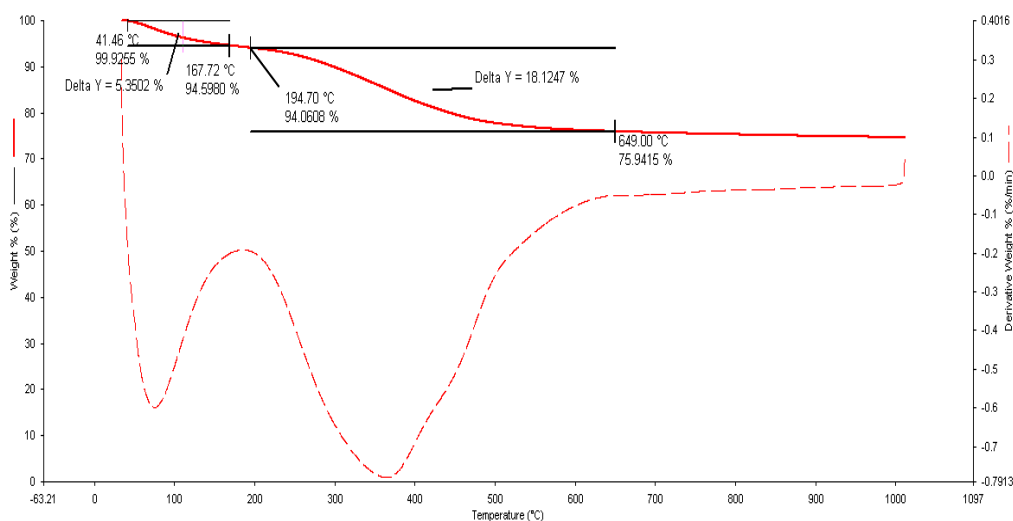


Figure 1 TGA analysis of KI-Al₂O₃ with nickel dopant

Effect of Catalyst Loading on The Biodiesel Yield

Transesterification of palm oil with methanol was carried out by using KI/Al₂O₃ doped with nickel to identify the effect of biodiesel produced on variety of catalyst loading. As shown in the **Figure 2**, the highest FAME content calculated was 37.22% where the amount of catalyst loading used was 4 wt.%. The increase of catalyst loading up to 4 wt.% has caused higher FAME yield to final product. This is due to the fact that greater amounts of the catalyst provide greater number of catalytically active sites. The results also agreed with the previous research that obtained by Islam et al., (2015). The more efficient contacts between both reactants and catalytically active sites in the applied reaction conditions will lead to the highest FAME yield of product (Marinkovic et al., 2016).

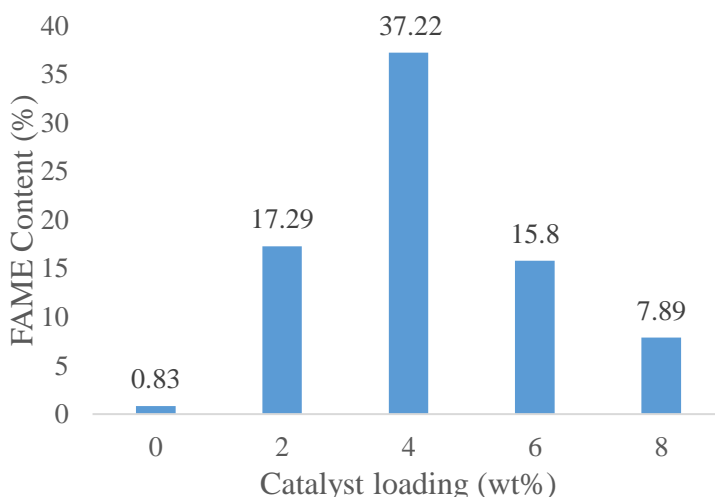


Figure 2 The effect of catalyst loading on the FAME yield (Reaction at 65°C for 5 hours)

However, as the catalyst loading increased above 4 wt.%, the pure FAME content yield started to decrease at similar reaction conditions. This is due to the mixing problems of the reaction mixture involving reactants, products and solid catalyst. According to Evangelista et al. (2016), agglomeration of the excess potassium compounds in the active phase will lower the surface

area of the catalyst. Some studies by Razak et al., (2018) and Anita & Muhammad (2015), also reported a similar finding indicating the further increasing of catalyst loading. Therefore, the optimum catalyst amount of 4 wt.% was chosen in this study. In this study, the biodiesel produced was also being quantitatively examined using GC-MS analysis. The purpose of adding heptadecanoic acid (C17) as the internal standard was to improve the accuracy of the quantitative analysis (Wang et al., 2016). The internal standard is utilized to correct any possible errors during sample preparation and sample injection in the GC (Sobrado et al., 2016).

Effect of Methanol to Oil Molar Ratio to The Biodiesel Yield

The transesterification of palm oil in the presence of heterogeneous base catalyst support alumina bead (KI- Al_2O_3) doped with nickel(II) nitrate hexahydrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were studied thoroughly by varying the methanol to oil molar ratio at 1:15, 1:25, 1:35, 1:45 and 1:55. Other reaction conditions were optimized such as the amount of catalyst loading of 4 wt.%, under constant reflux temperature at 65°C and the reaction time for 5 h.

As shown in **Figure 3**, the FAME yield was obtained when the molar ratio used was 1:35 where the percentage of FAME content was 53.34%. With an increase in the ratio, the FAME yield was increased considerably until it reached the maximum but decreased beyond that. According to Islam et al. (2015), higher molar ratios are required since stoichiometrically, three moles of methanol are required for each mole of triglycerides. Higher molar ratio is required to increase the miscibility and the contact between the alcohol molecule and the triglyceride. Numerous researchers also had been practicing a higher molar ratio in order to boost up the reactions towards completion thus producing more methyl esters (Xie & Li., 2006; Islam et al., 2015).

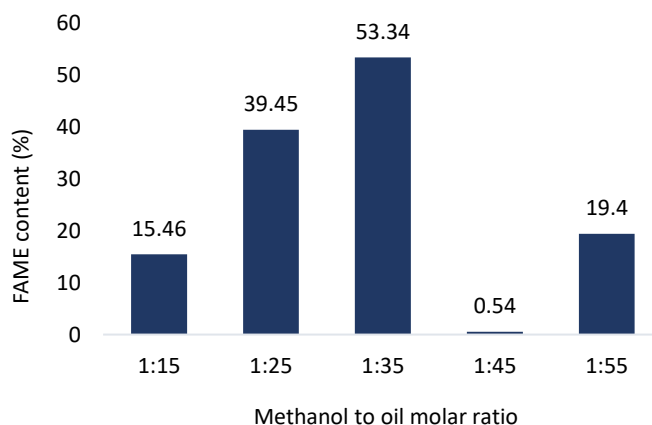


Figure 3 The effect of methanol to oil ratio on the FAME yield (4 wt%, 65°C , 5 hours)

In addition, beyond the molar ratio of 1:35, the excessively added methanol had no significant effect on the FAME yield. This is because, higher molar ratio aids to the recombination of glycerol and ester, thus decreasing the biodiesel yield (Verma & Sharma., 2016). While at the molar ratio of 1:15, the separation of glycerol was complicated, and the apparent yield of biodiesel was reduced because a fraction of the glycerol remained in the biodiesel phase. The separation of glycerol is difficult because of the solubility of the glycerol in the alcohol has increased. Thus, it reflects the percentage yield obtained at 1:15 ratio which was considerably low of only 15.46%.

Identification of FAME Using GC-MS

Figure 4 shows the GC-MS chromatogram of the biodiesel produced. Six methyl ester peaks were identified in the biodiesel. The identified FAMEs were methyl laurate, methyl myristate,

methyl palmitate, methyl stearate, methyl oleate and methyl linoleate. All peaks were identified by comparing their retention times with those of the authentic standards. They were further confirmed using the MS-NIST database. **Table 1** shows the details of the FAME composition. As compared to a previous research done by Shohaimi & Marodzi (2017), there is a little difference between the FAME composition of the biodiesel produced. This is probably due to the different type of oil used.

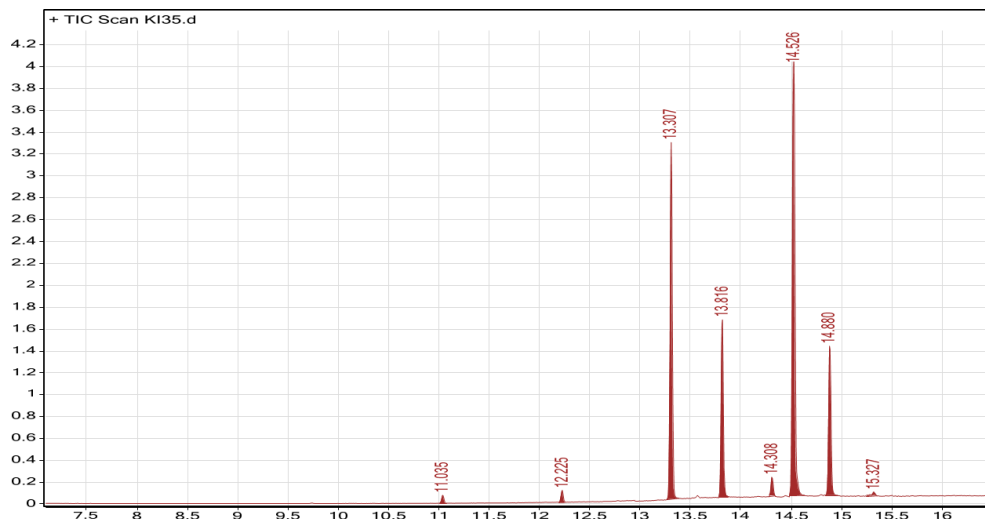


Figure 4 GC-MS chromatogram of biodiesel layer from transesterification reaction

Table 1 FAME composition in biodiesel

Retention Time (min)	Compound	Chemical Formula
11.035	Methyl laurate	$C_{13}H_{26}O_2$
12.225	Methyl myristate	$C_{15}H_{30}O_2$
13.307	Methyl palmitate	$C_{17}H_{34}O_2$
13.816	Methyl heptadecanoate	$C_{18}H_{36}O_2$
14.308	Methyl stearate	$C_{19}H_{38}O_2$
14.526	Methyl oleate	$C_{19}H_{36}O_2$
14.880	Methyl linoleate	$C_{19}H_{34}O_2$

Conclusion

In conclusion, the highest FAME yield for transesterification reaction using alumina supported potassium iodide catalyst with nickel dopant was 53.34% with optimum conditions of 5 hours reaction time, 4 wt.% catalyst loading refluxed at 65°C and 1:35 methanol to oil ratio. The GCMS result show the confirmation of six methyl ester present.

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Conflict of interests

Author declares no conflict of interest.

References

- Anita, R & Muhammad, F. (2015). Optimization of process parameters for the production of biodiesel from waste cooking oil in the presence of bifunctional γ -Al₂O₃-CeO₂ supported catalysts. *Malaysian Journal of Analytical Sciences*, 19(1), 8-19.
- Dey, S., Dhal, G. C., Prasad, R. & Mohan, D. (2017). Effects of doping on the performance of CuMnOx Catalyst for CO oxidation. *Bulletin of Chemical Reaction Engineering & Catalysis*, 12(3), 370-383.
- Evangelista, J. P. D. C., Gondim, A. D., Souza, L. D., & Araujo, A. S., (2016). Alumina-supported potassium compounds as heterogeneous catalysts for biodiesel production: A review. *Renewable and Sustainable Energy Reviews*, 59, 887–894.
- Gashaw, A., Getachew, T., & Teshita, A., (2015). A review on Biodiesel Production as Alternative Fuel. *Journal of Forest Products & Industries*, 4(2), 80-85.
- Guo, N., Xi, Y., Liu, S. & Zhang, C. (2015). Greatly enhancing catalytic activity of graphene by doping the underlying metal substrate. *Scientific reports*, 5, 12058.
- Islam, A., Taufiq-Yap, Y. H., Ravindra, P., Teo, S. H., Sivasangar, S., & Chan, E. S., (2015). Biodiesel synthesis over millimetric γ -Al₂O₃/KI catalyst. *Energy*, 89, 965–973.
- Islam, A., Taufiq-Yap, Y. H., Chu, C. M., Chan, E. S. & Ravindra, P. (2013). Studies on design of heterogeneous catalysts for biodiesel production. *Process Safety and Environmental Protection*, 91(1–2), 131–144.
- Leung, D. Y. C., Wu, X. & Leung, M. K. H. (2010). A review on biodiesel production using catalyzed transesterification. *Applied Energy*, 87(4), 1083–1095.
- Loganathan, S., Valapa, R.B., Mishra, R., Pugazhenti, G., & Thomas, S., (2017). Thermogravimetric Analysis for Characterization of Nanomaterials.
- Marinkovic, M. M., Stojkovic, N. I., Vasic, M. B., Ljupkovic, R. B., Rancic, S. M., Spalovic, B. R. & Zarubica, A. R. (2016). Synthesis of biodiesel from sunflower oil over potassium loaded alumina as heterogeneous catalyst : The effect of process parameters. *Chemical Industry*, 639–648.
- Razak, A. Z. K., Kamarullah, S. H., Khazaai, S. N. M. & Maniam, G. P. (2018). Synthesis of alumina-cao-ki catalyst for the production of biodiesel from rubber seed OIL. *Malaysian Journal of Analytical Sciences*, 22(2), 279-285.
- Shajaratun Nur, Z. A., Taufiq-Yap, Y. H., Rabiah Nizah, M. F., Teo, S. H., Syazwani, O. N. & Islam, A. (2014). Production of biodiesel from palm oil using modified Malaysian natural dolomites. *Energy Conversion and Management*, 78, 738–744.
- Sharma, S., Saxena, V., Barnwal, A., Chandra, P., & Pandey L. M., (2018). Engineered nanoporous materials mediated heterogeneous catalyst and their implication in biodiesel production. *Materials Science for Energy Technologies*, 1, 11-21.

Shohaimi, M. N. A. & Marodzi, F. N. S., (2017). Malaysian Journal of Analytical Sciences Transesterification of Waste Cooking Oil in Biodiesel Production Utilizing CaO/Al₂O₃ heterogeneous catalyst. *Malaysian Journal of Analytical Sciences*, 22(1), 157-165.

Sobrado, L. A., Freije-Carrelo, L., Moldovan, M., Encinar, J. R. & Alonso, J. I. G. (2016). Comparison of gas chromatography-combustion-mass spectrometry and gas chromatography-flame ionization detector for the determination of fatty acid methyl esters in biodiesel without specific standards. *Journal of Chromatography A*, 1457, 134-143.

Verma, P., & Sharma, M. P. (2016). Review of process parameters for biodiesel production from different feedstocks. *Renewable and Sustainable Energy Reviews*, 62, 1063–1071.

Wang, M., Wang, C., & Han, X., (2016). Selection of internal standards for accurate quantification of complex lipid species in biological extracts by electrospray ionization mass spectrometry-What, how and why?, *Mass Spectrometry Reviews*, (36), 693-714.

Xie, W., & Li, H., (2006). Alumina-supported potassium iodide as a heterogeneous catalyst for biodiesel production from soybean oil. *Journal of Molecular Catalysis A: Chemical*, 255(1–2), 1–9.

Yahya, N. Y., Ngadi, N., Jusoh, M., & Halim, N. A. A. (2016). Characterization and parametric study of mesoporous calcium titanate catalyst for transesterification of waste cooking oil into biodiesel. *Energy Conversion and Management*, 129, 275-283.

Zhen, M., & Zaera, F., (2006). Surface and Nanomolecular Catalysis. In *Characterization of Heterogeneous Catalysts*. Taylor & Francis (CRC Press). 9-1