Biodiesel production from black acid oil using KOH/zeolite LTA catalyst

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บทคัดย่อ

ประสิทธิภาพของโพแทสเซียมไฮดรอกไซด์รองรับบนซีโอไลต์แอลทีเอเป็นตัวเร่งปฏิกิริยาสำหรับการผลิตไบโอดีเซลเป็นสิ่งที่ศึกษา ตัวเร่งปฏิกิริยาโพแทสเซียมไฮดรอกไซด์รองรับบนซีโอไลต์แอลทีเอถูกเตรียมโดยวิธีการฝังในอัตราส่วนของโพแทสเซียมต่อซีโอไลต์แอลทีเอเป็น 1:100, 2:100, 3:100 และ 4:100 ตัวเร่งปฏิกิริยา KOH/zeolite LTA ถูกวิเคราะห์คุณสมบัติด้วยเทคนิค XRD และ SEM อิทธิพลของตัวแปรที่มีผลต่อผลได้ไบโอดีเซลเป็นสิ่งที่ศึกษา พบว่า ผลิตภัณฑ์ไบโอดีเซลที่ได้สูงสุดร้อยละ 58±1.47 ที่อัตราส่วนของ KOH/zeolite LTA 1:100 เวลาในการทำปฏิกิริยา 4 ชั่วโมง ปริมาณตัวเร่งปฏิกิริยาร้อยละ 3 อัตราส่วนของเมทานอลต่อน้ำมันที่ 6:1 และอุณหภูมิในการทำปฏิกิริยาที่ 60 องศาเซลเซียส

คำสำคัญ: ไบโอดีเซล, น้ำมันกรดดำ, ซีโอไลต์แอลทีเอ, ทรานเอสเทอริฟิเคชัน

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Abstract

A potential application of KOH/zeolite LTA as a catalyst for biodiesel production was studied. A series of KOH/zeolite LTA catalysts was prepared by impregnation of zeolite LTA with potassium hydroxide. The ratios between KOH and zeolite LTA were 1:100, 2:100, 3:100, and 4:100. The characterization of KOH/zeolite LTA was conducted by XRD and SEM analysis. The effects of various reaction variables on the yield of biodiesel were investigated. The highest yield of biodiesel over KOH/zeolite LTA catalyst was 58±1.47%. It was obtained at KOH/zeolite LTA 1:100, reaction time of 4 h, 3% catalyst, methanol to oil ratio of 6:1, and the reaction temperature at 60°C.

Keywords: Biodiesel, Black acid oil, Zeolite LTA, Transesterification

1. Introduction

Biodiesel is meant to be used in standard diesel engines and is thus distinct from the vegetable and waste oils used to fuel converted diesel engines. Biodiesel can be used alone, or blended with petrodiesel in any proportions (Omidvarborna, Kumar & Kim, 2014). Biodiesel blends can also be used as heating oil. Biodiesel refers to a vegetable oil or animal fat-based diesel fuel consisting of long-chain alkyl esters. Biodiesel is typically made by chemically reacting lipids with an alcohol producing fatty acid esters (Bioenergy of Association, Australian Government, 2007). Biodiesel can be used in pure form (B100) or may be blended with petroleum diesel at any concentration in most injection pump diesel engines. New extreme high-pressure (29,000 psi) common rail engines have strict factory limits of B5 or B20, depending on manufacturer (Biodiesel Organization, 2014). Biodiesel has different solvent properties from petrodiesel, and will degrade natural rubber gaskets and hoses in vehicles, especially mostly vehicles manufactured before 1992, although these tend to wear out naturally and most likely will have already been replaced with fluorocarbon rubber, which is nonreactive to biodiesel. Biodiesel has been known to break down deposits of residue in the fuel lines where petrodiesel has been used (Mc Cormick, 2006). As it has become more popular, biodiesel has garnered high-level support from big names like Willie Nelson and Dave Matthews, and is becoming increasingly easy to find. Keep reading to learn more about biodiesel production, celeb support (Dunn, 2007), and where this researcher team would be found for designing methodology of this research study.

Biodiesel is a mixture of alkyl esters with long-chain fatty acids and is produced from renewable biological sources as an alternative energy source to replace the currently used diesel fuel (Singh & Varun Chauhan, 2016; Imdadul, Masjuki, Kalam, Zulkifli, Rashed, Rashedul, Monirul & Mosarof, 2015; Tan, Abdullah & Nolasco-Hipolito, 2015). Biodiesel is basically produced by the esterification of free fatty acids as Eq. (I) (Lourinho & Brito, 2015; Lee, Bennett, Manayil & Wilson, 2014), or the transesterification process of animal fats, vegetable oils and waste cooking oils (Mazubert, Poux & Aubin, 2013; Chen, Zhang, Dong, Wu, Zheng, Huang, Guan & Zheng, 2016), as shown in Eq. (II), with short-chain alcohols in presence of suitable catalysts. For biodiesel production, methanol is chemically more preferred to ethanol or other short-chain alcohols because of the relevant physicochemical properties and milder reaction conditions (Alaba, Sani, Mohammed, Abakr & Daud, 2016; Wong, Tan, Taufiq-Yap, Ramli & Tee, 2015; Amani, Asif & Hameed, 2016). Also, triglycerides are more frequently used as feed stocks for biodiesel than free fatty acids.

$$\text{Fatty acid} + \text{Alcohol} \leftrightarrow \text{Water} + \text{Fatty acid alkyl ester} \quad \text{(I)}$$

$$\text{Triglyceride} + \text{Alcohol} \leftrightarrow \text{Glycerol} + \text{Fatty acid alkyl ester} \quad \text{(II)}$$

Biodiesel is commonly produced by the transesterification of the vegetable oil or animal fat feedstock, and other non-edible raw materials such as frying oil, etc. There are several methods for carrying out this transesterification reaction including the common batch process, heterogeneous catalysts (Hernández, Reyes-Labarta & Valdes, 2010), supercritical processes, ultrasonic methods, and even microwave methods. Chemically, transesterified biodiesel comprises a mix of mono-alkyl esters of long chain fatty acids. The most common form uses methanol to produce methyl esters as it is the cheapest alcohol available, though ethanol can be used to produce an ethyl ester biodiesel and higher alcohols such as isopropanol and butanol have also been used. Using alcohols of higher molecular weights improves the cold flow properties of the resulting ester, at the cost of a less efficient transesterification reaction. There are three basic routes to biodiesel production from oils and fats: Base catalyzed transesterification of the oil, Direct acid catalyzed transesterification of the oil, and Conversion of the oil to its fatty acids and then to biodiesel. A lipid transesterification production process is used to convert the base oil to the desired esters. Any free fatty acids (FFAs) in the base oil are both converted to soap and removed from the process, or they are esterified (yielding more biodiesel) using an acidic catalyst (Carbon Recycling International, 2013). Originally, there was a valuable market for the glycerol, which assisted the economics of the process as a whole (Biodiesel-derived Glycerol News and Events, 2008). Usually this crude glycerol has to be purified, typically by performing vacuum distillation. The refined glycerol (98% + purity) can then be utilized directly, or converted into other products (Chemweek's Business Daily, 2007). Almost all biodiesel is produced using base catalyzed transesterification as it is the most economical process requiring only low temperatures and pressures and producing a 98% conversion yield.

Zeolites are used as catalysts for esterification of large carboxylic acids, but their catalytic reaction was quite slow. So, only large-pore zeolites showed positive results in fatty acid esterification. Catalytic activity of zeolites for esterification in free fatty acids was normally productive when Si/Al ratio was increased that meant reactivity was affected by acid site strength and surface hydrophobicity. Pore size, channel system dimensionality (related to diffusion of reagents and products), and zeolite aluminum content illustrated positive effect on catalytic activity. Zeolite LTA, synthetic zeolite with tiny pores, has a pore diameter of 4 Å and can be modified either to 5 or 3 Å by ion exchange with aqueous solutions of calcium or potassium salts (Yang, Chen, Du, Hawkins, Craig, Ring, Omotoso, Munoz & Mikula, 2009). Zeolite LTA has three dimensional pore structure and is commonly synthesized in Na^+ form, $Na_{12}Al_{12}Si_{12}O_{48}\bullet 27H_2O$. It is structure comprises sodalite cages similar to that of faujasite but connected through double four-membered rings (D4R) of $[SiO_4]^{4-}$ and

$[AlO_4]^{5-}$. As a result, three cages are formed: D4R, sodalite cage, and α-cage. The pore diameter is determined by eight-member oxygen ring with diameters between 0.23 and 0.42 nm (Salama, Ali, Hanafy & Al-Meligy, 2009). For its low budget and high thermal stability, zeolite LTA is attractive as potential choice in separation process and shape-selective catalysis (Yang, Chen, Du, Hawkins, Craig, Ring, Omotoso, Munoz & Mikula, 2009). Various types of solid materials were chosen for heterogeneous catalysts or catalyst supports in biodiesel production as reviewed in the aforementioned paragraphs. However, studies on utilization of zeolite such as LTA as the catalyst or catalyst support for biodiesel preparation was still limited.

Therefore, in this regard, this study aims to perform utilising zeolite LTA as catalyst in biodiesel production. The preliminary investigation of this study was conducted on preparation of zeolite LTA base catalyst for biodiesel production by implementing KOH loading optimization. And, black acid oil was used as feedstock for biodiesel production because of the budget-wise purpose.

2. Materials and methods

2.1 Materials

Zeolite LTA used in this study was obtained from Thai Silicate Chemical Co., Ltd. The elemental analysis of the Zeolite LTA was conducted using an X-Ray Fluorescence (XRF) using Bruker AXS SRS 3400 equipment, and the results were as follow: Al 14.5%, Si 15.2%, Na 29.2%, O 40.7%, S 0.11%, and Cu 0.13%. The black acid oil or coconut oil mill waste used in this study was supplied by Saengsook Industry Co.,Ltd. Methanol and potassium hydroxide were the Laboratory Reagent (LR) grade.

2.2 Catalyst preparation

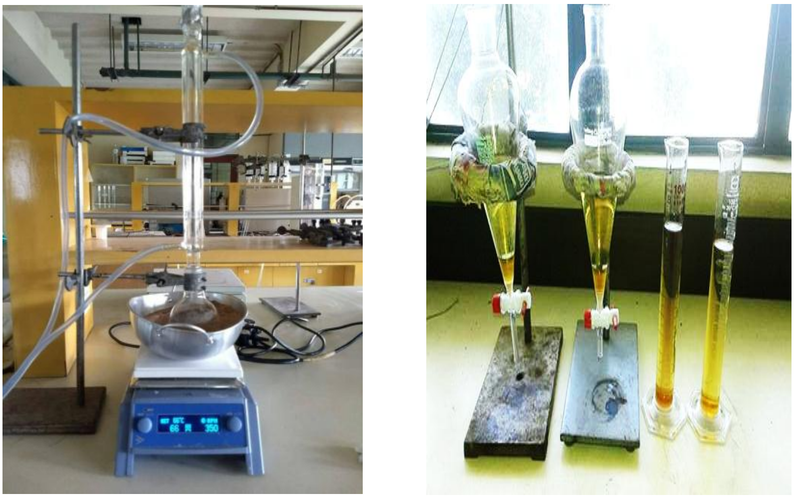
A series of KOH/Zeolite LTA catalysts for biodiesel production was prepared using the following procedure. The ratios between KOH and Zeolite LTA were 1:100, 2:100, 3:100, and 4:100. The preparation of catalysts was conducted in a round bottom flask (500 mL) equipped with a reflux condenser, temperature indicator, and mechanical stirrer. The impregnation of Zeolite LTA with KOH was conducted at a temperature of 60°C for 24 h under continuous stirring. After completing the impregnation process, the slurry was dried in an oven at 110°C for 24 h to remove water. The catalyst was then calcined in a tubular muffle furnace at a temperature of 450°C for 4 h (Ricky, Johan, Aning, Felycia & Suryadi, 2013).

2.3 Catalyst characterization

X-ray powder diffraction (XRD) analysis was conducted using a Bruker D8 diffractometer with a Cu-Kα radiation was used to record all of the diffraction spectra. Morphology of catalyst was observed using a Scanning Electron Microscope (SEM; Carl Zeiss, AURIGA), using an accelerating voltage of 15 kV. Fourier-transform infrared spectroscopy (FTIR) method of catalyst was recorded with FTIR Microscope (Tensor 27).

2.4 Transesterification of oil

As Figure 1a, transesterification of black acid oil was carried out in a round bottom flask (500 mL) equipped with a reflux condenser, temperature indicator, and mechanical stirrer. The reactor was placed in a controlled water bath heater. A known amount of catalyst (0.5–3 g) was added to a known volume of methanol. The mixture was then heated to the desired temperature (60°C) in a controlled temperature water bath. Subsequently, black acid oil was added into the mixture under vigorous stirring (300 rpm). The volume ratio of methanol to oil used in this study was 3–8 and the transesterification reaction was carried out for 2–6 h. At the end of the reaction time, the glycerin and biodiesel layers were separated as Figure 1b.



(1a) (1b)

Figure 1 (1a) Reflux set for biodiesel production (1b) Biodiesel yield

3. Results and discussion

3.1 Catalyst characterization

As shown in Figure 2, the XRD patterns of commercial zeolite LTA obviously exhibited peaks at 2θ of 7.2°, 10.2°, 12.6°, 21.7°, 24.0°, 27.2°, 30.0°, 32.5° and 34.2° (Arifuzzaman Khan, Arafat, Reza, Abdur Razzaque & Shamsul Alam, 2010). During calcinations, potassium hydroxide was converted to K_2O as indicated in the XRD pattern. Reflections observed around 2θ at 12.8x°, 18.8°, 24.8°, 27.4°, 28.9°, 31.6°, 32.5°, 34.2° and 36.8° belong to the K_2O phase (Noiroj, Intarapong, Luengnaruemitchai & Jai-In, 2009; Soetaredjo, Ayucitra, Ismadji, Maukar, 2011).

The next analysis for catalyst characterization was morphology as shown in Figure 3. Scanning electron micrographs (SEM) of the zeolite revealed the presence of crystals with the same cubic morphology.

In the FTIR spectrum of the zeolite LTA as illustrated in Figure 4, the characteristic bands for zeolite framework at 546 cm^{-1} due to the external vibration of double four-rings, 971 cm^{-1} for the internal vibration of (Si, Al)-O asymmetric stretching, 673 cm^{-1} for the internal vibration of (Si, Al)-O symmetric stretching, and 462 cm^{-1} for the internal vibration of (Si, Al)-O bending were observed. The band related to OH also appeared at about

1644 cm^{-1} (Stevens, Siriwardane & Logan, 2008; Yamada, Yokoyama, Watanabe, Uno & Tamura, 2005; Huang & Jiang, 1997; Iyer & Singer, 1994; Ismail, Mohamed, Ibrahim, Kini & Koopman, 2010).

3.2 Effect of KOH/Zeolite LTA loading

The catalytic effect of KOH/Zeolite LTA loading on transesterification was investigated from the percentage of yield. The experimental conditions for studying the effect of KOH/ Zeolite LTA loading on the transesterification reaction were: the amount of catalyst at 0.5, 1.5 and 3% (based on the weight of oil), methanol to oil volume ratio of 8:1, reaction time of 6 h, and the reaction temperature at 60°C. The results clearly indicate that the amount of KOH loaded in Zeolite LTA affected the conversion of oil into biodiesel (Table 1). Increasing the loading amount of KOH from 1% (KOH/ Zeolite LTA 1: 100) to 4% (KOH/Zeolite LTA 4:100) also decreased the yield of biodiesel. The highest yield (56%) was obtained at 1% KOH loading. However, further increases in KOH loading (higher than 0.5%) resulted in a decreased yield of biodiesel. With high levels of KOH, the interactions between KOH and the internal layer of Zeolite LTA were excessive and during the calcinations, when a high concentration of the KOH, the catalytic activity of the catalyst became lower, leading to a decrease in the biodiesel yield. To determine the effect of catalyst on the yield of biodiesel, the amount of catalyst was varied among 0.5, 1.5 and 3% by weight based on the amount of oil. The yield of biodiesel increased from 36% at 1% KOH/Zeolite LTA catalyst to 56% at 3% catalyst. The increase in the conversion of oil into fatty acid methyl esters ranged from 0.5 to 3% catalyst addition was due to an increase in the number of active basic sites (K_2O) in the reaction system.

3.3 Effect of reaction time

The operating conditions used to study the effect of reaction time on biodiesel yield were similar to those used in Section 3.2. Since the highest yield of biodiesel was obtained with KOH/ Zeolite LTA 1: 100 catalyst, this ratio was used in subsequent experimental studies. The optimum reaction time for the biodiesel production was 4 h. During the first three hours the yield of biodiesel increased with the increase in reaction time (Table 2). After four hours, the yield of biodiesel was almost constant as the equilibrium conversion had been reached.

3.4 Effect of methanol to oil volume ratio

The methanol to oil volume ratio is one of the important parameters that affect the yield of FAME. Theoretically, the transesterification of oil requires 3 mol of methanol per mole of triglyceride (Rajabathar & Ming, 2009). Since transesterification of triglyceride is a reversible reaction, the excess methanol shifts the equilibrium toward the direction of ester formation (Rajabathar & Ming, 2009). In the present work, with optimized reaction parameters, the methanol to oil volume ratio was varied in the range of 3 – 8 and its influence on yield was investigated. Table 3 shows the effect of the methanol to oil volume ratio on yield at the end of 4 h of reaction time at 333 K. It can be clearly seen from the activity profile that, when the volume ratio increased from 3 to 6, yield was found to increase from 45% to 58%. The highest conversion of 58% was registered at the volume ratio of 6:1. Further increase in the methanol amount has not shown any significant improvement in yield.

4. Conclusion

A heterogeneous catalyst KOH/zeolite LTA can be used as a solid based catalyst for biodiesel production via transesterification of black acid oil. The catalyst synthesized with 1% KOH loading gave the best performance for biodiesel production. The operating condition to produce the highest yield of biodiesel was: reaction time 4 h, amount of catalyst 3%, methanol to oil ratio 6, and the reaction temperature at 60°C.

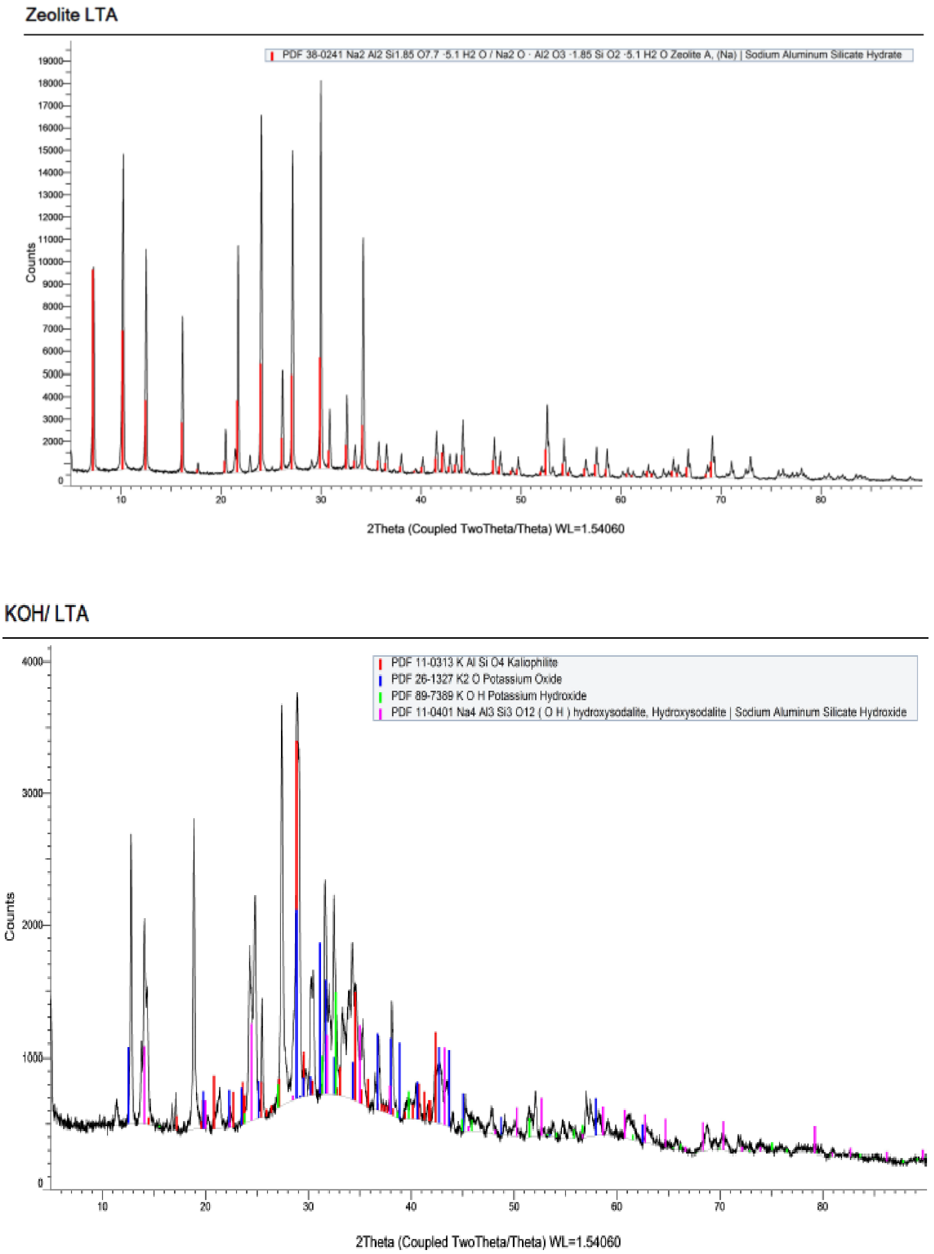


Figure 2 XRD patterns of zeolite LTA and 4%KOH/LTA

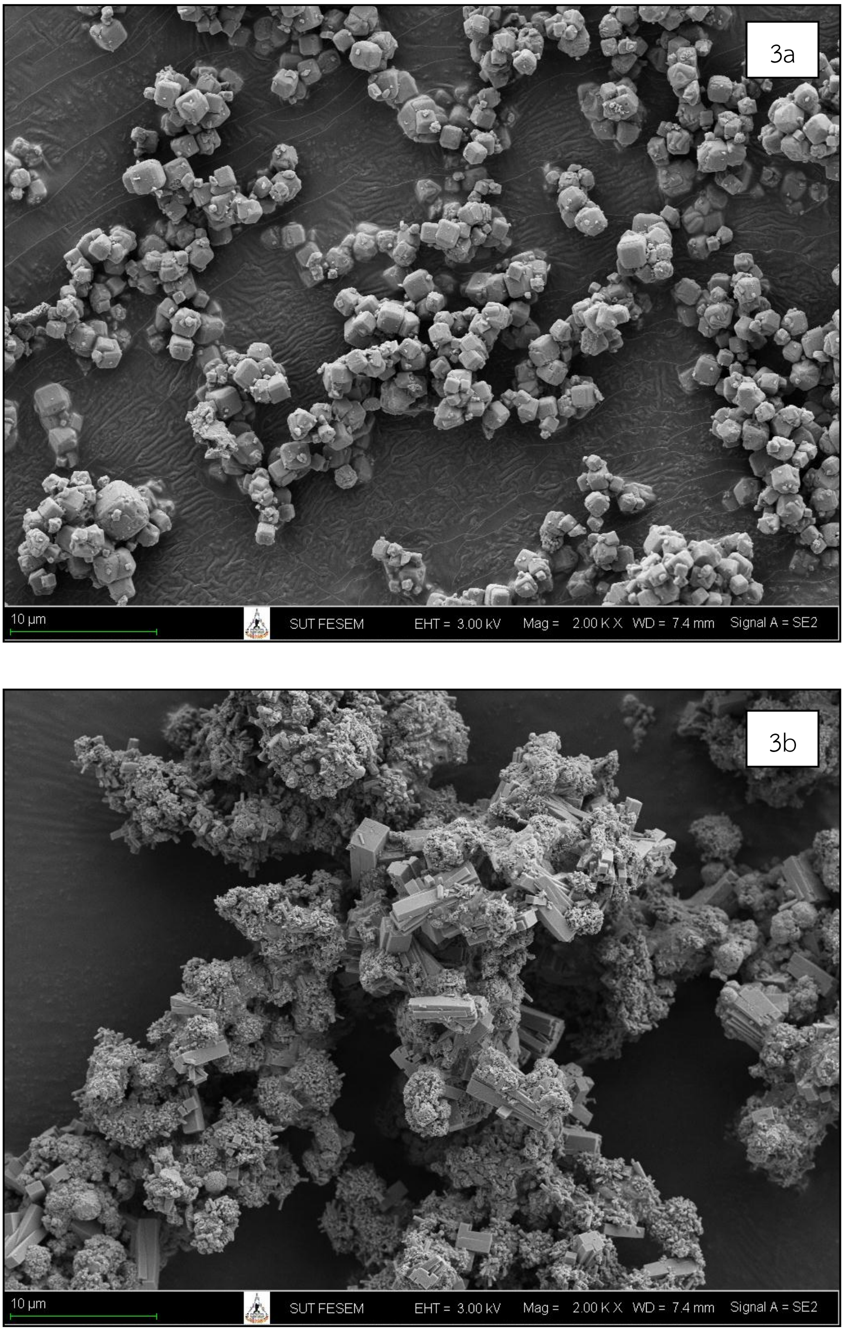


Figure 3 SEM images of (3a) zeolite LTA and (3b) 4%KOH/LTA

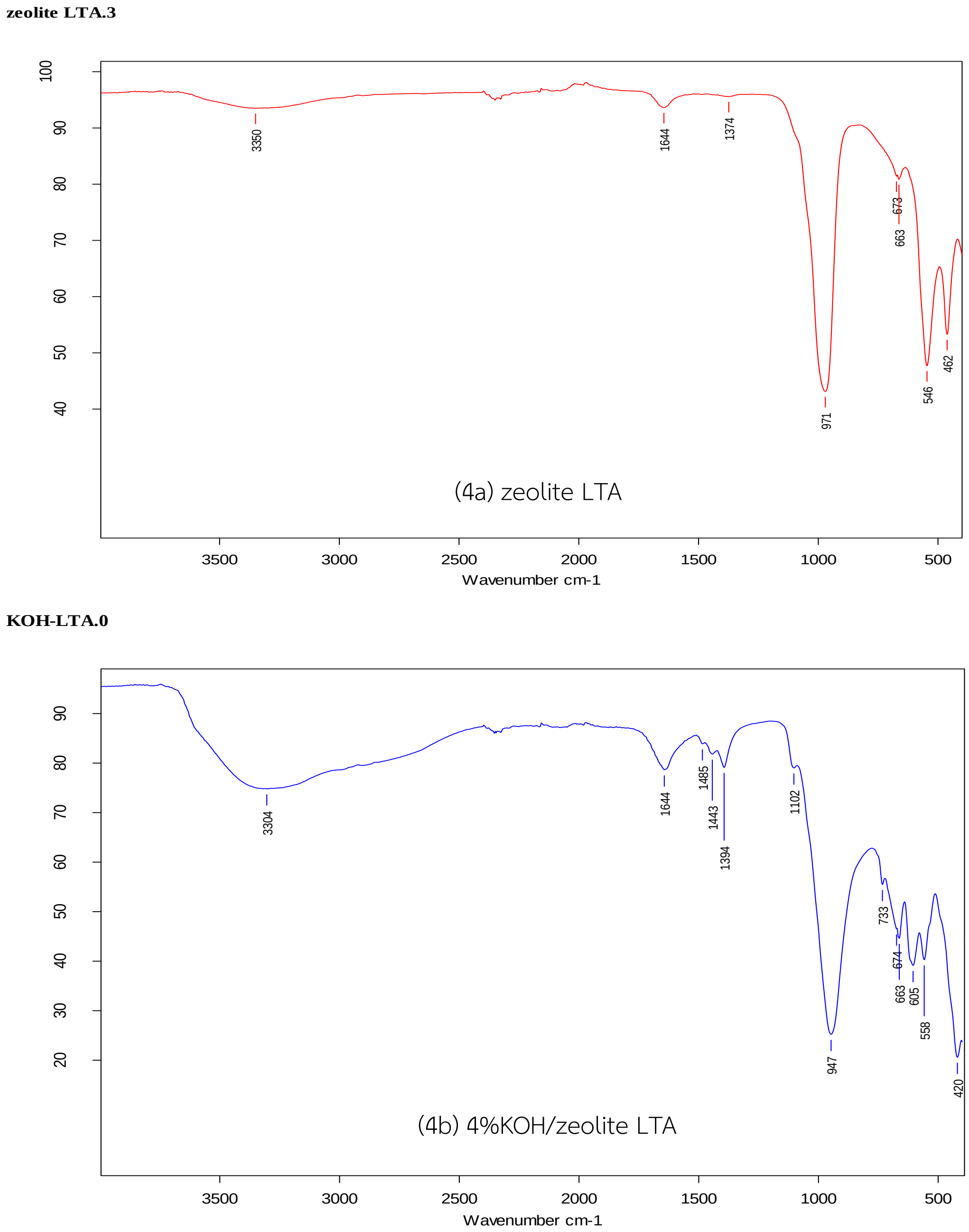


Figure 4 FTIR spectrums of (4a) zeolite LTA and (4b) 4%KOH/zeolite LTA

Table 1

The effect of amount of catalyst on the yield of biodiesel

KOH:zeolite LTA ratio	0.5% wt	1.5% wt	3.0% wt
1:100	36±1.91	45±1.46	56±1.58
2:100	35±1.53	41±1.58	54±1.57
3:100	35±1.96	40±1.17	54±1.93
4:100	31±1.47	40±1.47	51±1.63

Table 2

The effect of reaction time on the yield of biodiesel

KOH:zeolite LTA ratio	2 h	4 h	6 h
1:100	51±1.73	56±1.73	56±1.37
2:100	50±1.26	55±1.49	54±1.73
3:100	51±1.72	55±1.82	55±1.27
4:100	48±1.37	51±1.65	50±1.58

Table 3

The effect of methanol to oil volume ratio on the yield of biodiesel

KOH:zeolite LTA ratio	3:1	6:1	8:1
1:100	45±1.23	58±1.47	57±1.37
2:100	48±1.56	54±1.75	54±1.28
3:100	52±1.41	52±1.61	52±1.68
4:100	44±1.39	50±1.59	50±1.72

References

Alaba P.A., Sani Y.M., Mohammed I.Y., Abakr Y.A., & Daud W.M.A.W. (2016). Synthesis and application of hierarchical mesoporous HZSM-5 for biodiesel production from Shea butter. *Journal of the Taiwan Institute Chemical Engineers*, 59, 405–412.

Amani H., Asif M., & Hameed B.H. (2016). Transesterification of waste cooking palm oil and palm oil to fatty acid methyl ester using cesium-modified silica catalyst. *Journal of the Taiwan Institute Chemical Engineers*, 58, 226–234.

Arifuzzaman Khan G.M., Arafat S.M.Y., Reza M.N., Abdur Razzaque S.M., & Shamsul Alam M. (2010). Linde Type-A zeolite synthesis and effect of crystallization on its surface acidity. *Indian Journal of Chemical Technology*, 17, 303–308.

Bioenergy of Association, Australian Government. (2007). Biofuels in Australia — issues and prospects. *Rural Industries Research and Development Corporation.* Publication No. 07/071. Project No. CSW – 44A.

Biodiesel-derived Glycerol News and Events. (2008). Biodiesels and glycerol. Theglycerolchallenge.org. Archived from the original on 2008-05-23. Retrieved 9 July 2008 from http://www.theglycerolchallenge.org

Biodiesel Organization. (2014). Biodiesel. *National Biodiesel Board*, 1 Dec. 2014. Retrieved on 19 November 2015 from http://biodiesel.org/using-biodiesel/oem-information/oem-statement-summary-chart.

Carbon Recycling International. (2013). Product. Archived from the original on 29 July 2013. Retrieved 13 July 2012 from http://carbonrecycling.is/index.php?option=com_content&view=article&id=4&Itemid=3&lang=en

Chemweek's Business Daily. (2007). Biodiesel production. Tuesday, May 8, 2007.

Chen Y., Zhang X., Dong M., Wu Y., Zheng G., Huang J, Guan X., &

Zheng X. (2016). MCM-41 immobilized 12-silicotungstic acid mesoporous materials: structural and catalytic properties for esterification of levulinic acid and oleic acid. *Journal of the Taiwan Institute Chemical Engineers*, 61, 147–155.

Dunn C. (2007). Biodiesel: How it's made, environmental impact, where to find a fueling station, and more. Retrieved on 14 July 2007 from https://www.treehugger.com/cars/biodiesel-how-its-made-environmental-impact-where-to-find-a-fueling-station-and-more.html

Hernández M.R., Reyes-Labarta J.A., & Valdes F.J. (2010). New heterogeneous catalytic transesterification of vegetable and used frying oil. *Industrial & Engineering Chemistry Research*, 49, 9068–9076.

Huang Y., & Jiang Z. (1997). Vibrational spectra of completely siliceous zeolite A. *Microporous Materials*, 12, 341–345.

Imdadul H.K., Masjuki H.H., Kalam M.A., Zulkifli N.W.M., Rashed N.M., Rashedul H.K., Monirul I.M., & Mosarof M.H. (2015). A comprehensive review on the assessment of fuel additive effects on combustion behavior in CI engine fuelled with diesel biodiesel blends. *RSC Advances*, 5, 67541–67567.

Ismail A.A., Mohamed R.M., Ibrahim I.A., Kini G., & Koopman B. (2010). Synthesis, optimization and characterization of zeolite A and its ion-exchange properties. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 366, 80–87.

Iyer K.A., & Singer S.J. (1994). Local-mode analysis of complex zeolite vibrations: Zeolite-A. *The Journal of Physical Chemistry*, 98, 12679–12686.

Lee A.F., Bennett J.A., Manayil J.C., & Wilson K. (2014). Heterogeneous catalysis for sustainable biodiesel production via esterification and transesterification. *Chemical Society Revies*, 43, 7887–7916.

Lourinho G., & Brito P. (2015). Advanced biodiesel production technologies: novel developments. *Reviews in Environmental Science and Bio/Technology*, 14, 287–316.

Mazubert A., Poux M., & Aubin J. (2013). Intensified processes for FAME production from waste cooking oil: a technological review. *Chemical Engineering Journal*, 233, 201–223.

Mc Cormick R.L. (2006). Biodiesel handing and use guide third edition. *National Renewable Energy Laboratory*. Retrieved 18 December 2006 from https://www.nrel.gov/vehiclesandfuels/npbf/pdfs/40555.pdf

Noiroj K., Intarapong P., Luengnaruemitchai A., & 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.

Omidvarborna H., Kumar A., & Kim D.S. (2014). Characterization of particulate matter emitted from transit buses fueled with B20 in idle modes. *Journal of Environmental Chemical Engineering*, 2, 2335–2342.

Rajabathar J., & Ming K.W. (2009). Review of recent developments in solid acid, base, and enzyme catalysts (heterogeneous) for biodiesel production via transesterification. *Industrial & Engineering Chemistry Research*, 48, 6162–6172.

Ricky I.K., Johan P.H., Aning A., Felycia E.S., & Suryadi I. (2013). Natural zeolite from Pacitan Indonesia, as catalyst support for transesterification of palm oil. *Applied Clay Science*, 74, 121–126.

Salama T.M., Ali I.O., Hanafy AI., & Al-Meligy W.M. (2009). A novel synthesis of NaA zeolite encapsulated iron(III) Schiff base complex: Photocatalytic oxidation of direct blue-1 dye with hydrogen peroxide. *Materials Chemistry and Physics*, 113, 159–165.

Singh P., & Varun Chauhan S.R. (2016). Carbonyl and aromatic hydrocarbon emissions from diesel engine exhaust using different feedstock: a review. *Renewable Sustainable Energy Reviews*, 63, 269–291.

Soetaredjo F.E., Ayucitra A., Ismadji S., & Maukar A.L. (2011). KOH/bentonite catalysts for transesterification of palm oil to biodiesel. *Applied Clay Science*, 53, 341–346.

Stevens J.R.W., Siriwardane R.V., & Logan J. (2008). In situ fourier transform infrared (FTIR) investigation of CO_2 adsorption onto zeolite materials. *Energy & Fuels*, 22, 3070–3079.

Tan Y.H., Abdullah M.O., & Nolasco-Hipolito C. (2015). The potential of waste cooking oil-based biodiesel using heterogeneous catalyst derived from various calcined eggshells coupled with an emulsification technique: a review on the emission reduction and engine performance. *Renewable Sustainable Energy Reviews*, 47, 589–603.

Wong Y.C., Tan Y.P., Taufiq-Yap Y.H., Ramli I., & Tee H.S. (2015). Biodiesel production via transesterification of palm oil by using CaO-CeO_2 mixed oxide catalysts. *Fuel*, 159, 484–490.

Yamada H., Yokoyama S., Watanabe Y., Uno H., & Tamura K. (2005). Micro-cubic glass from pseudomorphism after thermal treatment of ammonium-exchanged zeolite A. *Science and Technology of Advanced Materials*, 6, 394–398.

Yang H., Chen H., Du. H., Hawkins R., Craig F., Ring Z., Omotoso O., Munoz V., & Mikula R. (2009). Incorporating platinum precursors into a NaA-zeolite synthesis mixture promoting the formation of nanosized zeolite. *Microporous and Mesoporous Materials*, 117, 33–40.