

Solid Catalyst Nanoparticles derived from Oil-Palm Empty Fruit Bunches (OP-EFB) as a Renewable Catalyst for Biodiesel Production

H Husin^{1,2*}, T M Asnawi¹, A Firdaus¹, H Husaini³, I Ibrahim⁴, and F Hasfita⁴

¹Department of Chemical Engineering, Syiah Kuala University, Darussalam, 23111, Banda Aceh, Indonesia

²Graduate Program in Chemical Engineering, Syiah Kuala University, Darussalam, 23111, Banda Aceh, Indonesia

³Department of Mechanical Engineering, Syiah Kuala University, Darussalam, 23111, Banda Aceh, Indonesia

⁴Department of Chemical Engineering, Malikussaleh University, Lhoekseumawe, 24300, Aceh Utara, Indonesia

husni_husin@che.unsyiah.ac.id*

Abstract. Solid nanocatalyst derived from oil-palm empty fruit bunches (OP-EFB) fiber was successfully synthesized and its application for biodiesel production was investigated. The OP-EFB was treated by burning, milling and heating methods to generate ashes in a nanoparticle size. The nanoparticle palm-bunch ash was characterized by scanning electron microscopy (SEM) and x-ray diffraction (XRD). The effects of the calcination temperature and catalyst amounts for transesterification reactions were investigated. XRD analysis of palm bunch ash exhibited that the highest composition of peaks characteristic were potassium oxide (K₂O). SEM analysis showed that the nano palm bunch ash have a particle size ranging of 150-400 nm. The highest conversion of palm-oil to biodiesel reach to 97.90% was observed by using of palm bunch ash nanocatalyst which heated at 600°C, 3 h reaction time and 1% catalyst amount. Reusability of palm bunch ash catalysts was also examined. It was found that of its high active sites, reusable solid catalyst was obtained by just heating of palm bunch ash. It has a capability to reduce not only the amount of catalyst consumption but also reduce the reaction time of transesterification process.

1. Introduction

Recently, alternative energies, for example, hydrogen energy [1-3], solar energy [4, 5], and biodiesel [6, 7], have been focused worldwide because of recent energy. Biodiesel is one of popular alternative energy in the world due to biodegradable and renewable fuel [8]. Biodiesel is mono-alkyl esters of long chain fatty acids. Biodiesel has physical and chemical properties that resemble diesel fuel. In addition, biodiesel is an environmentally friendly fuel due to its nontoxic and lower emissions of CO emission [9]. Currently, most commercial processes used for biodiesel synthesis employ a homogeneous base catalyst, such as NaOH or KOH. However, it suffers several drawbacks, such as equipment corrosion and deal with H₂SO₄ waste produced from neutralization process [10, 11]. This situation has deficiency not only due to high catalyst consumption but also biodiesel purification process would be difficult. This will certainly lead to increase production costs[12]. On the other hand, heterogeneous catalysts could replace homogeneous ones to eliminate the problems associated with homogeneous catalysts. Solid based catalysts are easily regenerated and less corrosive, safer, cheaper



and more environmentally friendly process, and therefore, attracted considerable attention recently [13, 14].

Oil-palm empty fruit bunch (OP-EFB) is a solid lignocellulosic waste, abundantly generated in Southeast Asia (SEA), particularly Indonesia, Malaysia, and Thailand, with total production almost 88.5% of world's palm oil (48.99 million metric tons per year) [15, 16]. Pyrolysis of OP-EFB will produce volatile matters, carbonaceous substances and ash residue. Ash residue contains organic and inorganic materials. Inorganic constituent of OP-EFB ash is mainly potassium in crystalline forms. This metal rich constituent is easily converted into potassium oxide (K_2O) by burning and calcination in air atmosphere at moderate temperature [17]. So far, studies on the preparation and application of biomass catalyst are very limited in open literatures. These results have motivated the present study involving the conversion of EFB biomass to catalyst for transesterification reaction of palm oil into biodiesel. Therefore, it is possible to utilize potassium oxide from palm bunch ash as a low-cost solid catalyst for biodiesel production. The aim of the present work is to obtain an active and cheap solid catalyst from empty fruit bunch ash for transesterification of vegetable oils into biodiesel. For this purpose, the EFB was treated by burning, milling and heating methods to generate ashes in a nanoparticle size. The catalysts were characterized by analytical techniques. In this work, the performance of non-nanocatalyst and nanocatalyst on transesterification of palm oil into biodiesel were investigated.

2. Materials and methods

2.1. Preparation of Nanocatalyst Palm Bunch Ash

Oil-palm empty fruit bunch was cleaned up from impurities, washed and dried for 1 to 2 days, respectively. The dried materials then burned in open air to get ashes and put into siever screening 100 mesh. OP-EFB ash pass through a 100 mesh Siever can be directly used for nanocatalyst preparation stage. While the ash retained on Siever recycled into milling and sieved again. K_2O -riched ash put into a porcelain mortar and calcined at temperature of 600 °C under air atmosphere for 4 hours to vaporize remaining volatile substances and impurities to its enhance active sites.

2.2. Catalyst Characterization

The catalysts were characterized by powder X-Ray Diffraction (XRD) and scanning electron microscopy (SEM). In the XRD method, the samples were recorded on Bruker diffractometer using $Cu-K\alpha$ radiation ($\lambda = 0.154$ nm) operating at 40 kV and 100 mA. The diffractograms were recorded in the 2θ ranges of 10 – 60° at a scanning speed of 5° min^{-1} . Diffraction peaks of crystalline phases were compared with those of standard compounds reported in the JCPDS (Joint Committee of the Powder Diffraction Standards) database (JCPDS-International Center for Diffraction Data (ICCD), 2000). The morphology and structure of OP-EFB ash nanocatalyst powder was recorded by Scanning Electron Microscopy (SEM). Fatty acid composition of biodiesel was determined by gas chromatography with Mass Spectrometry (GC-MS).

2.3. Evaluation of transesterification reaction

Testing of the catalysts was conducted by transesterification reaction in a set of three-neck flask 500 ml as a reactor and equipped with impeller, temperature controller, and reflux cooling system. The catalytic reaction was carried out at 65°C for 3 h. Catalyst loading of 0.1- 5.0 wt.% and methanol to palm-oil mole ratio of 6:1 were used in the catalyst testing. After the reaction finished, the biodiesel product (FAME) was separated after aged for 24 h forming 3 layers (residual methanol, FAME, and glycerol as well as used solid catalyst). The resulted FAME biodiesel was characterized and identified using GC-MS (SHIMADZU) equipped with Agilent DB-1 column and helium as a gas carrier.

3. Results and discussion

3.1. Characterization Palm Bunch Ash Catalyst by XRD

Figure 1.a shows the XRD pattern OP-EFB ash non-calcined catalyst. K_2O formation was confirmed by XRD patterns obtained from the study. According to XRD pattern, OP-EFB ash composes of K_2O as a major component. XRD spectra show that K_2O have identical crystal structures to cubic type

(JCPDS card no. 26-1327, space group Fm3m). The characteristic peaks of K_2O appear at $2\theta = 25.121^\circ$, 28.607° , 31.843° , 40.625° , and 50.101° , respectively. It also demonstrated that the highest intensity of characteristic peaks of K_2O of non-calcined catalyst at $2\theta = 28.607^\circ$ reaches up to 674 cps, as can be seen in Figure 1.a.

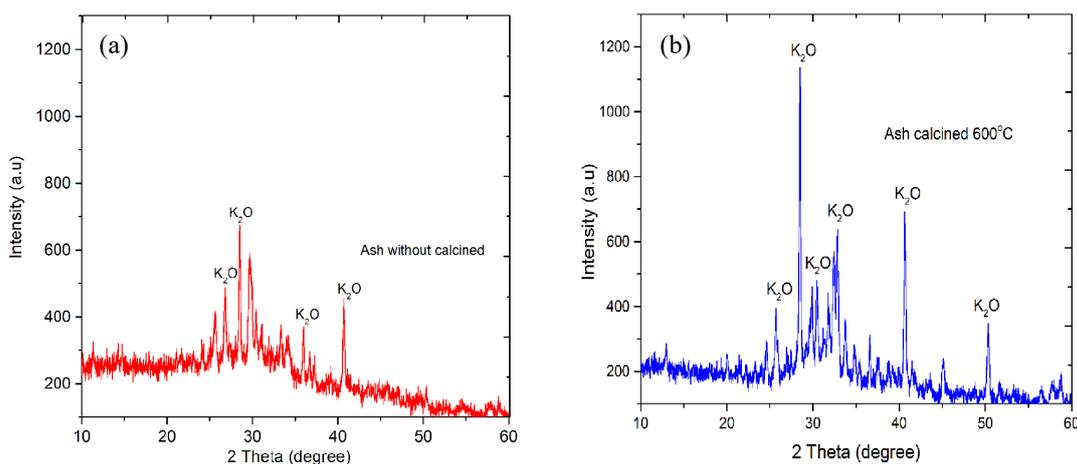


Figure 1. XRD patterns of (a) OP-EFB ash without calcined, (b) palm bunch ash calcined at 600°C .

Figure 1.b depicts the XRD pattern of the sample after annealed at 600°C . The OP-EFB ash nanocatalyst powder showed a significant increase of the intensity of K_2O main peak up to 1135 cps, as depicted in Figure 1.b. The K_2O as major compound in OP-EFB ash possess basic surface sites, which make them highly efficient in catalytic process applications, although it can be seen some small peaks due to phases of silica compound. Comparing the XRD pattern of non-calcined and calcined catalyst demonstrated that the intensity of K_2O increased from 674 to 1135 cps (at $2\theta = 28.607^\circ$). This findings indicated that calcination temperature at 600°C led to increase the degree of crystallinity of K_2O . Calcination can enhance crystals growth of a compound, wherein the crystals growth will increase with increasing temperature of heating to form a complete crystalline structure at optimum temperature. It can vaporize impurities or volatile matters that cover the pores of the catalyst.

3.2. Characterization of Palm Bunch Ash by SEM

In order to elucidate the effect of milling on particle sizes of palm bunch ash, the SEM measurement of ash catalysts was also performed. The SEM morphologies of non-nano and nanocatalyst are shown in Figure 2. The palm bunch ash catalyst was previously calcined in a muffle furnace for 4 h at 600°C . The non-nanocatalyst sample is composed by large particles, exposing irregular particles, which sizes ranged between 2000-5000 nm, as illustrated in Figure 2.a. The SEM image of non-nanocatalyst showed a compact agglomeration. After milling process the particle sizes of catalyst become smaller, as can be seen in Figure 2.b. The nanoparticles with average size around 150 to 400 nm are observed. The catalyst in nanosizes is able to increase the catalyst surface area significantly.

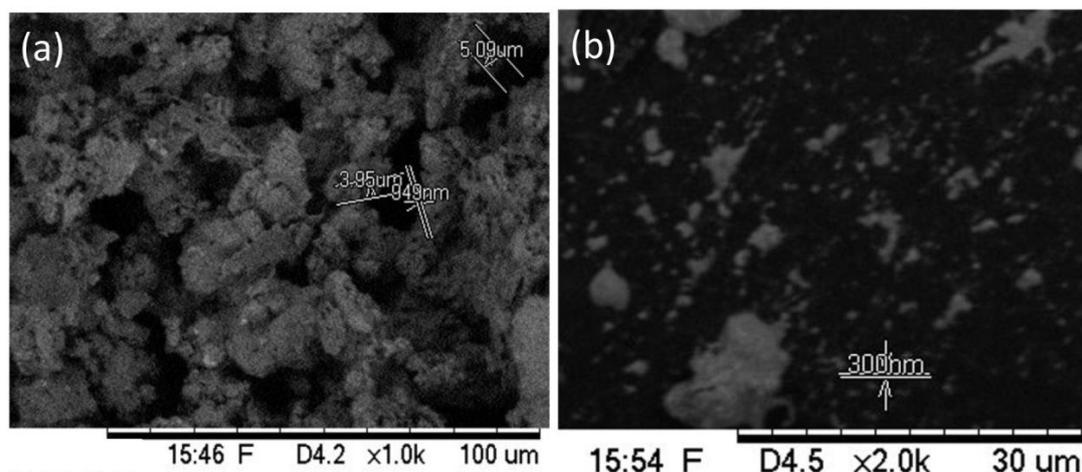


Figure 2. SEM Images of palm bunch ash: a) non-nano and b) nanosizes

3.3. Effect of Catalyst Loading on Biodiesel Production

Catalyst weight is one of parameters determining the performance of a catalyst. Reactivity of the catalyst can be known from its ability to accelerate the reactions in which reactants are converted into products obtaining optimum yield with less consumption of the catalyst. In this study, the weight of catalyst is used as one of the parameters to determine catalyst performance. The effect of the catalyst loading on the biodiesel yield was investigated by varying the catalyst mass ratio from 0.1-5.0 wt.%. Then biodiesel yield from transesterification reaction compared between nanocatalyst and non-nanocatalyst loadings were also determined. Nanocatalyst palm bunch ash denoted as N-catalyst, while the non nanocatalyst denoted as S-catalyst.

The activity of N-catalyst and S-catalyst was evaluated in terms of ester conversion during transesterification of palm-oil. The biodiesel yield exhibited a gradually increasing trend as the catalyst loading increased. However, further increase in the amount of catalyst, the biodiesel yield decreased. In detail, the highest biodiesel yield gains (optimum), i.e 97.13% results from N-catalyst loading with ratio catalyst 1% by weight of oil and earned the highest yield (optimum), i.e 93.32% resulting from the use of S-catalyst by weight of the catalyst 3% by weight oil. This evidence demonstrated that the use of N-catalyst requires less amount of catalyst compared to S-catalyst to produce optimum yield of biodiesel. This is resumed due to the catalyst in nanometer size has a specific surface area greater than the mass or volume of the same of non-nanocatalyst. The active compound potassium oxide (K_2O) contained in the ash palm bunches catalyst distributed not only on the surface of the catalyst but also inside of the catalyst particles. During high speed grinding treatment bulk catalyst was initially broken up and reduced in nanometer size to form new higher surface area, as well evidenced by SEM images.

Potassium oxide compounds play an active role in the formation of methoxide anion in the catalyst activation process. Methoxide anion formation becomes very important because the anion active role in the termination of the carbonyl carbon bond of triglycerides to form methyl esters (biodiesel). If the distribution of potassium oxide on the surface of the catalyst increases, the possibility of methoxide anions will be increased. Increasing the amount of methoxide anion in the catalyst activation process will accelerate the reaction time required by anion methoxide break the chains of carbon carbonyl compounds of triglycerides. By utilizing nanocatalyst which has a high reactivity then the transesterification process would be more effective due to the process only requires less amount of catalyst loading. Conversely, biodiesel yield decreased after optimum yield is reached with a higher amount of catalyst loading. This is because by increasing the amount of the catalyst in the transesterification process, the density of the particles of the catalyst will increase. If the densities of catalyst particles are high, it will trigger agglomeration of catalyst particles. Catalyst agglomeration will affect the active surface area of the catalyst decreases which subsequently decreasing the

reactivity. That situation will complicate the process of activation of the catalyst. Where the active compound will be difficult ionized of potassium oxide resulting in a decrease in the amount of methoxide anions in the process.

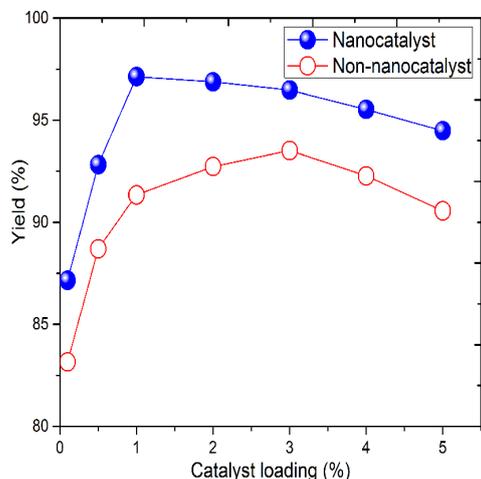


Figure 3. Effect of catalyst loading on biodiesel production

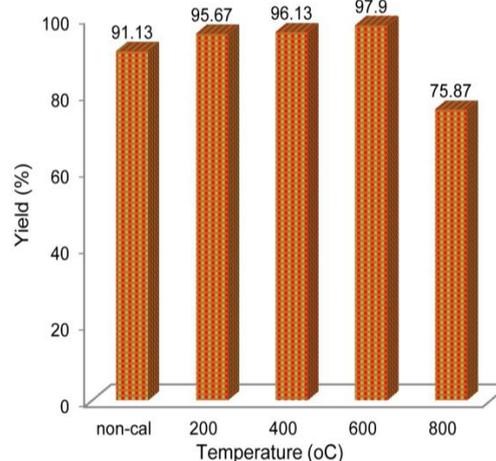


Figure 4. Effect of calcination temperature of catalyst on biodiesel production

In addition agglomeration of catalysts may also affect the process of mass transfer of the reactants that inhibit diffusion onto the surface of the catalyst after being covered by the other agglomerated particles. This is because most of the active compound which is located on the surface of the catalyst particles is covered by other particles. Where the active compound will be difficult ionized of potassium oxide resulting in a decrease in the amount of methoxide anions in the process. Decreased amount of methoxide anions in the catalyst activation and mass transfer process would lead to suppressed biodiesel yield. It is caused due to insufficient of methoxide anion availability to break carbonyl carbon bonds so that the conversion of triglycerides into methyl ester decreased, consequently lowering the yield of biodiesel. There is slight reduction of conversion of reactants due to reaction system being as viscous slurry and emulsified [18].

3.4. Effect of calcination temperature of ash catalyst

In this study, the calcination temperature of ash catalyst is used as one of the parameters to determine catalyst performance. In order to study the influence of the calcination temperature on the catalyst performance, N-catalysts have been calcined from 200 to 800°C. As presented in Figure 4, it can be seen that the increase of biodiesel yield is in accordance with increasing of calcination temperature which lead to enhance crystal growth. The improved crystal growth affected by increasing heating at appropriate temperature would lead to form a complete crystal structure of the compound. In addition, from Figure 4 can also be seen that the yield of biodiesel at temperature 600°C and 800°C drastically decreased from 97.89 to 75.87%. The decrease was due to reduced active compound in crystal phase of potassium oxide (K_2O) contained in nanocatalyst. The active phase on the catalyst was sintered at higher temperature and total basicity [19, 20]. As evidenced by the catalyst XRD characterization, the ash catalyst comprises of K_2O . The active species of the solid catalysts were K_2O . The K_2O is incorporated on the surface of empty fruit bunch ash support, leading to the improved activity of the catalyst. The calcination process for the solid ash catalyst is favourable for the interaction between K_2O and other metal oxides, which may lead to the enhanced stability of catalyst [21]. However, the declining of the crystal phase of the compound would be caused by calcination temperature at 800°C is above K_2O melting point 740 °C. Heating at excessive high temperatures would developed crystals agglomeration which decreasing catalyst surface area and subsequently suppressed nanocatalyst reactivity and lead to decline biodiesel yield drastically [22].

3.5. Composition of palm oil

Figure 5 displays biodiesel chromatogram spectra that identify the presence of methyl esters contained in biodiesel. Methyl myristate and methyl palmitate are identified at peak 1 and 2. Methyl stearate, methyl oleate and methyl linoleate are demonstrated at peak 3, 4 and 5. While, methyl linolenate and methyl arachidate are identified at retention time of 25.167 and 25.31 seconds, as recorded at peak 6 and peak 7, respectively. All data of the biodiesel composition are tabulated in Table 1. From Table 1, it is reported that methyl oleate is the highest concentration of 38.98%. The lowest concentration of methyl ester biodiesel constituents are methyl myristate and methyl linolenate.

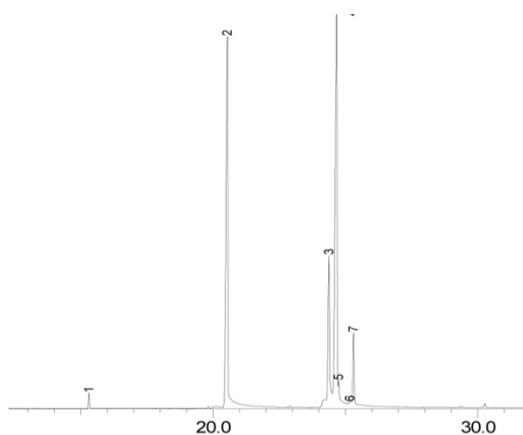


Figure 5. GC-MS chromatogram of biodiesel product

Table 1. Fatty Acid Methyl Ester (biodiesel)

Peaks No.	Component	Composition (%)
1	Methyl Myristate (C16:0)	0,76
2	Methyl Palmitate (C16:1)	35,52
3	Methyl Stearate (C18:0)	11,88
4	Methyl Oleate (C18:1)	38,98
5	Methyl Linoleate (C18:2)	3,16
6	Methyl Linolenate (C18:3)	0,76
7	Methyl Arachidate (C20:0)	8,94

3.6. Characteristic of biodiesel

To study the physicochemical properties, the transesterification reaction was carried out in the presence of the nanocatalyst under calcined at 600 °C. The characteristics of the biodiesel sample were shown in Table 2.

Table 2. Characteristic of biodiesel of this work, standard ASTM, prEN & SNI

Parameter	This work	ASTM	prEN	SNI
Kinematic viscosity (cSt)	3,59 – 3,69	1,90 – 6,00	3,50 – 5,00	2,30 – 6,00
Density (gr/cm ³)	0,8717 – 0,8741	0,80 – 0,88	0,86 – 0,90	0,85 – 0,89
Acid number (mg KOH/gr)	0,11 – 0,2805	max 0,80	max 0,3	max 0,80

As listed in Table 2, the fuel properties of the prepared biodiesel have been found to comply with the ASTM, prEN and SNI standards. Refer to Table 2, there can be seen that the kinematic viscosity of biodiesel is ranging from 3.59 - 3.69 cSt. It can be seen that the density of biodiesel is ranging from 0.8717 - 0.8741 g/cm³ and the acid number is ranging from 0.1122 - 0.2805 mg KOH/g. These values are also in compliance with ASTM standards, prEN and SNI [23-25].

4. Conclusions

A palm bunch ash solid catalyst was successfully synthesized through calcination method. The catalyst was calcined at temperature of 600 °C. The major component of nanocatalyst derived from palm bunch ash is potassium oxide (K₂O). The particle sizes of palm bunch ash ≤ 400 nm. Utilization of as-produced nanocatalyst derived palm bunch ash resulting the highest conversion of palm oil into biodiesel reached up to 97.90%, reactions for 1 h and catalyst loading 1.0 wt.%.

Acknowledgment

We acknowledge the financial support through the Research Grants of of Scopus h-index of Syiah Kuala University, Republic of Indonesia (No: 1712/UN11/SP/PNBP/2016).

References

- [1] Husin H, Mahidin Zuhra and Hafita F 2014 H₂ evolution on Lanthanum and Carbon co-doped NaTaO₃ Photocatalyst *Bulletin of Chemical Reaction Engineering & Catalysis* **9** p 81-86.
- [2] Husin H, Pontas K, Sy Y, Syawaliah and Saisa 2014 Synthesis of Nanocrystalline of Lanthanum Doped NaTaO₃ and Photocatalytic Activity for Hydrogen Production *Journal of Engineering and Technological Sciences* **46** p 318-327
- [3] Husin H, Adisalamun A, Sy Y, Asnawi TM and Hasfita F 2017 Pt nanoparticle on La_{0.02}Na_{0.98}TaO₃ catalyst for hydrogen evolution from glycerol aqueous solution in *AIP Conference Proceedings* p 030073
- [4] Susanti D, Nafi M, Purwaningsih H, Fajarin R, and Kusuma G E 2014 The Preparation of Dye Sensitized Solar Cell (DSSC) from TiO₂ and Tamarillo Extract *Procedia Chemistry*. **9** p 3-10
- [5] Husin H, Mahidin Yunardi and Hafita F 2015 Visible Light Driven Photocatalytic Hydrogen Evolution by Lanthanum and Carbon-co-Doped NaTaO₃ Photocatalyst *Key Engineering Materials*. **659** p 231-236
- [6] Taufiq YH, Lee HV, Hussein MZ and Yunus R 2011 Calcium-based mixed oxide catalysts for methanolysis of *Jatropha curcas* oil to biodiesel *Biomass and Bioenergy* **35** p 827-834
- [7] Husin H, Mahidin and Marwan 2011 Studi penggunaan katalis abu sabut kelapa, abu tandan sawit dan K₂CO₃ untuk konversi minyak jarak menjadi biodiesel *Reaktor* **13** p 254-261
- [8] Fidalgo W R R, Ceron A, Freitas L, Santos J C and de Castro H F 2016 A fluidized bed reactor as an approach to enzymatic biodiesel production in a process with simultaneous glycerol removal *Journal of Industrial and Engineering Chemistry* **38** p 217-223
- [9] Dai YM, Chen KT, Wang PH and Chen CC 2016 Solid-base catalysts for biodiesel production by using silica in agricultural wastes and lithium carbonate *Advanced Powder Technology* **27** p 2432-2438
- [10] Istadi I, Anggoro D D, Buchori L, Rahmawati D A and Intaningrum D 2015 Active Acid Catalyst of Sulphated Zinc Oxide for Transesterification of Soybean Oil with Methanol to Biodiesel *Procedia Environmental Sciences* **23** p 385-393
- [11] Abomohra AEF, Jin W, Tu R, Han SF, Eid M, and Eladel H 2015 Microalgal biomass production as a sustainable feedstock for biodiesel: Current status and perspectives, *Renewable and Sustainable Energy Reviews* **64** p 596-606
- [12] Zuhra, Husin H, Hasfita F and Rinaldi W 2015 Preparasi Katalis Abu Kulit Kerang Untuk Transesterifikasi Minyak Nyamplung Menjadi Biodiesel *Agritech* **35** p 69-77

- [13] Alonso D M, Granados M L, Mariscal R and Douhal A 2009 Surface chemical promotion of Ca oxide catalysts in biodiesel production reaction by the addition of monoglycerides, diglycerides and glycerol *J Catal.* **276** p 229-236
- [14] Feng Y, Zhang A, Li J and He B 2011 A continuous process for biodiesel production in a fixed bed reactor packed with cation-exchange resin as heterogeneous catalyst, *Bioresource Technology* **102** p 3607-3609
- [15] Abdullah N and Gerhauser H 2008 Bio-oil derived from empty fruit bunches. *Fuel* **87** p 2606-2613
- [16] Idris J, Shirai Y, Ando Y, Ali A A M, Othman M R, Ibrahim I 2014 Production of Biochar With High Mineral Content from Oil Palm Biomass *Malaysian Journal of Analytical Sciences* **18** p 700-704.
- [17] Purwandari F A, Sanjaya A P, Millati R, Cahyanto M N, Horvath I S and Niklasson C 2013 Pretreatment of oil palm empty fruit bunch (OPEFB) by N- methylmorpholine-N-oxide (NMMO) for biogas production: structural changes and digestion improvement *Bioresour Technol* **128** p 461-667
- [18] Boro J, Deka D, and Thakur A J 2012 A Review on Solid Oxide Derived from Waste Shell as Catalyst for Biodiesel Production *Renewable and Sustainable Energy Reviews* **16** p 904-910
- [19] Chen G, Shan R, Shi J, Liu C, and Yan B 2015 Biodiesel production from palm oil using active and stable K doped hydroxyapatite catalysts *Energy Conversion and Management* **98** p 463-469
- [20] Husin H, Zuhra, Hasfita F and Rinaldi W 2013 Waste shells of cockle (*Clinocardium nuttalli*) as solid catalysts for transesterification of calophyllum inophyllum L. oil to biodiesel production in *The Annual International Conference Syiah Kuala University AAC Hall Syiah Kuala University Darussalam Banda Aceh Indonesia* **3** p 14-18
- [21] Xie W and Zhao L 2013 Production of biodiesel by transesterification of soybean oil using calcium supported tin oxides as heterogeneous catalysts, *Energy Conversion and Management* **76** p 55-62
- [22] Bet-Moushoul E, Farhadi K, Mansourpanah Y, Nikbakht A, Molaei R, and Forough M 2016 Application of CaO-based/Au Nanoparticles as Heterogeneous Nanocatalysts in Biodiesel Production *Fuel* **164** p 119-127
- [23] *ASTM D6751-15ce1 2015 Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels* ASTM International West Conshohocken, PA, www.astm.org.
- [24] ACEA 2009 "Biodiesel Guidelines" European Automobile Manufacturers Association, Brussels, Belgium March 2009 http://www.acea.be/uploads/publications/20090423_B100_Guideline.pdf
- [25] *Standar Nasional Indonesia SNI 04-7182-2006 Biodiesel* ICS 75.160. Badan Standardisasi Nasional. bsn.go.id/index.php?/sni_main/sni/detail_sni/7240