Research article

Green Nano-Composite of CaO/K-Sulfated TiO_2 and Its Potential as a Single-Step Reaction Solid Catalyst for Biofuel Production

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Published 07 June 2022

Publishing services provided by Knowledge E

Selection and Peer-review under the responsibility of the PGPR 2021 Conference Committee.

Abstract.
In the esterification-transesterification method, a catalyst increases the reaction rate to produce biofuel (biodiesel). This study investigated the use of a solid catalyst consisting of green nano-CaO as a support modified by KOH solution and sulfated TiO_2 for converting waste frying oil (WFO) into biodiesel in a single-step esterification-transesterification reaction. With nano-CaO prepared from eggshell, a green nanocomposite of CaO/K-sulfated TiO_2 was synthesized by physical mixing and the hydrothermal method. Crystallite size, surface basicity-acidity, functional groups, and surface morphology were used to characterize the solid catalyst, which was then tested for its ability to convert WFO into biodiesel. The results showed that green-CaO had nanoparticles (93.13 nm) and that its size decreased after being modified with KOH (46.43 nm) and sulfated TiO_2 (62.10 nm), with CaO/K-sulfated TiO_2 being the optimum surface acidity-basicity. The optimum conditions for conversion were found to be 5% catalyst concentration to oil, a molar ratio of methanol/oil of 9:1, and a reaction time of 60 minutes, which resulted in a biodiesel mass yield of 94.17% higher than CaO/K (67.88%). WFO was successfully converted into fatty acid methyl esters, according to the GC-MS analysis of the biodiesel. The synthesized solid catalyst has the potential to be used in single-step esterification-transesterification reactions to produce biodiesel.

Keywords: Biofuel, CaO/K-sulfated TiO_2Green Nano-composite, Eggshell, Single-step Reaction, Waste Frying Oil

1. Introduction

Biodiesel is considered for substituting fossil-diesel due to biodegradable, renewable nature, and environmentally non-toxicity. The biodiesel is a liquid fuel which produced from long chain fatty acids of biological sources (animal fats, virgin vegetable oils, and waste oil). It is popular synthesized in transesterification and esterification methods with ethanol or methanol and catalyst [1-3]. When free fatty acids (FFAs) more than 1% in oil, biodiesel production is carried out in double-steps reaction, namely the

How to cite this article: I Nengah Simpen*, I Nyoman Suprapta Winaya*, I Dewa Gede Ary Subagia, and I Wayan Budiarsa Suyasa , (2022), “Green Nano-Composite of CaO/K-Sulfated TiO_2 and Its Potential as a Single-Step Reaction Solid Catalyst for Biofuel Production” in *First Asian PGPR Indonesian Chapter International e-Conference 2021*, KnE Life Sciences, pages 382–392. DOI 10.18502/kls.v7i3.11146

esterification with liquid acid catalyst to reduce FFAs content and the transesterification with liquid base catalyst to convert triglycerides [4]. The double-steps process have lack, such as double methanol consumption and longer reaction time. Moreover, in the transesterification reaction, basic catalyst is used to neutralize the remaining acid catalyst in previous process, so the residue can cause engine problems. Residual basic catalyst causes high levels of unburned ash, while residual acid catalyst causes engine corrosion [5].

The waste frying oil (WFO) is a promising solution for biodiesel feedstock, because its availability becomes cheap and it is also overcoming waste oil problem. However, WFO has high contents of FFAs (over 15% for brown grease and less 15% for yellow grease) [2, 6]. The high FFAs cause a saponification process which makes it difficult to separate in mixture, so low biodiesel yield. Solid catalyst in the biodiesel production was chosen to overcome the lack of liquid catalyst properties. Advantages of solid catalysts are simple separation process, could be reused, environmentally friendly, and more effective in separation from product reaction and non-corrosive problems [7-10]. The solid acid-base catalyst allows to catalyze esterification and transesterification reactions in a single-step reaction [11], so biodiesel production process from WFO can be simplified.

Researches on the synthesis of solid catalysts from mixture of metal oxides have basic and acidic active sites for biodiesel production were studied, namely catalyst of K/TiO_2 for esterification reaction of canola oil [12]. Istadi et al. (2015), studied the catalytic activity of K_2O/CaO-ZnO in transesterification of soybean oil [13]. According to Carlucci et al. (2019), solid catalysts suitable developed for the esterification reaction is sulfated TiO_2 [14]. According to He et al. (2016) and Carlucci et al. (2019), the sulfated TiO_2 compound is to be super-acid which has excellent catalytic activity for esterification reactions and good stability [14, 15]. However, all the use of solid catalysts for production of biodiesel is only in the transesterification or esterification and not yet for the single-step esterification-transesterification reactions. In addition, the solid sulfated TiO_2 catalyst used is pure raw material with nano-sized particles, so its difficulty in separation process and high operational cost in industrial scale.

The CaO (calcium oxide) is a solid catalyst suitable in transesterification reaction into biodiesel because it has high activity, insoluble in methanol, relatively longer use time, and economic [16, 17]. However, pure CaO has weaknesses, namely at room temperature it is easily carbonated, quickly hydrated, and a paste forming easily when mixed methanol, so its less stable and biodiesel production decreases [18, 19]. This weakness can be overcome by using CaO support from eggshell which is structurally more stable, high basicity, and low production cost. The high content of calcium carbonate in eggshell can be converted into CaO which has the potential to be used for a solid catalyst in synthesis of biodiesel. The activity of the CaO catalyst can be increased by modifications to enhance surface basicity-acidity, catalyst surface area, and stability.

In this study, it is focused on the characterization of CaO prepared from thermal decomposition of eggshells (green-CaO) modified with KOH solution to form CaO/K for increasing surface basicity sites and loaded solid sulfated TiO_2 as source of surface acid sites. The mixture of CaO/K and sulfated $TiO_2$to form a composite of CaO/K-sulfated TiO_2.Green nano-composite of CaO/K-sulfated TiO_2 is used for solid catalyst in a single-step esterification-transesterification reactions of WFO into biodiesel.

1.1. Methodology

1.2. Materials

WFO and chicken eggshell from household waste in Batubulan, Gianyar Bali, TiO_2 (purity of 98%), methanol (purity of 99.9%), sulfuric acid (purity of 95-97%), and KOH (purity of 99.8%) were used in this the experiments.

1.3. Synthesis of CaO/K-sulfated TiO_2 catalyst

First, green nano-CaO was prepared by thermal decomposition of eggshell powder at 800^{o}C for 5 hours. Then, 100 g CaO is put into 200 mL distilled water and 25 mL 1.25 M KOH solution and stirred for 3 hours. Its mixture is washed repeatedly until free of residual base and filtered, then dried at 110°C for 3-5 hours and calcined at 600^{o}C for 5 hours [20]. The CaO which is modified by KOH solution as CaO/K. Second, the sulfated TiO_2 was prepared with 10 g TiO_2 powder impregnated with 200 mL 0.5 M sulfuric acid solution and stirred with a magnetic stirrer of medium speed for 24 hours. After that, it was filtered using filter paper of Whatman 1, then washed until free of sulfate ions (negative test for 0.1 M $BaCl_2$ solution). Next, it was calcined at 500^{o}C for 4 hours [21]. Third, nano-composite of CaO/K-sulfated TiO_2 was synthesized by physical mixing and hydrothermal method. The CaO/K was mixed evenly with sulfated TiO_2 powder in a porcelain dish with a mass ratio of 3:1 and added destilled water in ratio of 1:2, then calcined at 550^{o}C for 3 hours. The obtained composite was characterized by their physico-chemical properties, such as crystallinity by X-ray diffraction (XRD) of X'pert pro panalytical, surface basicity-acidity by acid-base titration method, surface functional groups by using Fourier transform infrared (FTIR) of Shimadzu/IR Prestige-21, and surface morphology by scanning electron microscope (SEM) of JEOL JSM-6510 LA/Japan.

1.4. Performance test of catalyst into biodiesel production

The WFO was filtered first to remove impurities, followed by evaporating water at 110^{o}C for 30 minutes. The oil is allowed to cool down in temperatures ranging 50-55^{o}C [22]. Furthermore, biodiesel synthesis in a single-step esterification and transesterification reactions was carried out using CaO/K-sulfated TiO_2 catalyst at optimization conditions of catalyst concentration to oil of 3 to 7%; molar ratio of methanol/oil of 6:1 to 15:1; and reaction times of 30 to 180 minutes. All process are conducted at 65^{o}C and mixing intensity of low scale. Produced biodiesel mass yield is calculated as percent yield $= \frac{amount\ of\ produced\ biodiesel}{amount\ of\ oil} x\ 100$ [23]. The biodiesel composition is analyzed by gas chromatography-mass spectrometry (GC-MS) of GC-7890A, MSD-5975C.

2. Results and Discussion

2.1. Characterizations of catalyst

The crystalline structure and crystallite size. The XRD patterns of catalysts were presented in Fig. 1.

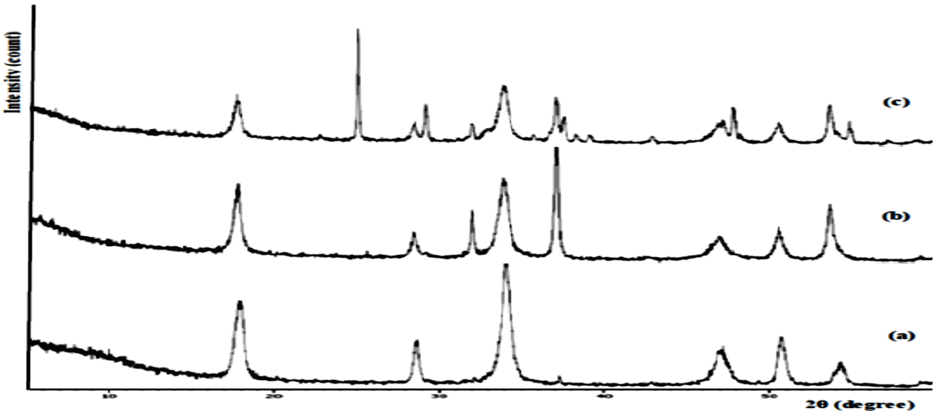

Figure 1: The XRD patterns of catalysts for (a) CaO, (b) CaO/K, and (c) CaO/K-sulfated TiO_2.

All diffraction peaks showed that CaO, KOH activated (K_2O) and TiO_2 were classified as crystalline and semi-crystalline. Diffraction peaks of K_2O appeared at 2θ=32.04^o with relative intensity of 39.84 percent and 2θ=33.91^o of 62.94 percent intensity. Meanwhile, TiO_2 appeared at 2θ=25.22^o and 34.12^o with a relative intensity of 100 percent and 44.39

percent, respectively. The relative intensity was less than 6.5 percent at 2θ=35.92^o; 38.47^o; and 39.31^o, respectively. The peak of sulfated TiO_2 appeared at 2θ=57.34^o with a relative intensity of 2.15 percent which tends to form semi-crystalline [12, 24]. The crystallite size of catalysts were calculated by Scherrer's formula of $D = \frac{k\lambda}{\beta cos\theta}$ [25, 26]. Where D is the mean crystallite size (nm), k is Scherrer constant (an emperical to 0.9), λ is wavelength of the X-ray diffraction source (CuKα-radiation of 1.5406 Å), β is FWHM (full width at half maximum) intensity in radian, and θ is angle of diffraction (^{o}).

Table 1: The crystallite size of synthesized catalyst.

Catalyst	Crystallite size (nm)
CaO	93.13
CaO/K	46.43
CaO/K-sulfated TiO_2	62.10

The crystallite size of CaO decreased due to KOH activated and loaded sulfated TiO_2(Table 1). Activating process increased crystallinity and crystallite size. In the nanomaterial terminology, all of catalyst were classified as nano-crystallines (particles) because particles have crystallite size below 100 nm (nanometers) [27].

Surface basicity-acidity and surface active sites. The surface basicity-acidity and active sites catalysts obtained were presented in Table 2.

Table 2: Surface basicity-acidity and surface active sites of catalysts.

Catalyst	Basicity (mmol/g)	Base active sites (x 10^{21}atom/g)	Acidity (mmol/g)	Acid active sites (x 10^{21}atom/g)
CaO	32.2252	19.4153	0	0
CaO/K	33.8839	20.4083	0	0
CaO/K-sulfated TiO_2	22.7946	13.7292	0.0289	0.0174

The increasing of basicity and acidity catalyst are in line with its amount of surface base active sites and surface acid active sites. The basicity on surfaces and amount of surface base active sites of catalyst (Table 2), increased significantly after KOH activated into the CaO structure but decreased with loading of sulfated TiO_2 in the CaO/K structure and the lowest in the CaO/K-sulfated TiO_2. Meanwhile, the surface acidity enhanced after the loading of sulfated TiO_2. This is caused by the loading of sulfated TiO_2 which contributed to the surface acidity and amount of surface acid active sites.

Functional groups. The surface functional groups of catalysts were presented in Fig. 2.

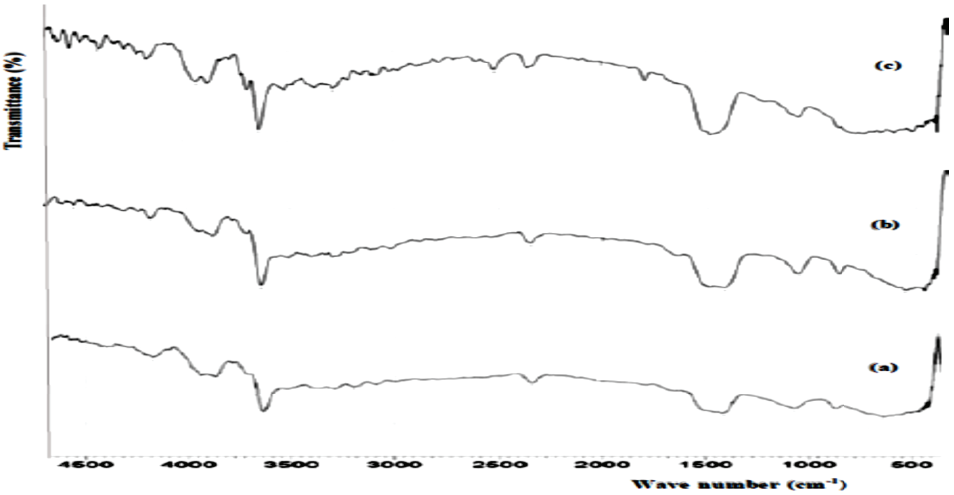

Figure 2: The FTIR spectra for (a) CaO, (b) CaO/K, and (c) CaO/K-sulfated TiO_2.

Fig. 2 showed that the FTIR spectra of CaO/K catalyst without the loading of sulfated TiO_2, showed the presence of O-H bands in the area around of 4000 $cm^{-1}$and 3600 cm^{-1}, which appeared at 4168.36 cm^{-1}, 3637.90 $cm^{-1}$from physi-sorption of water molecules on the surface. The C-O stretching band of carbonate appeared at a wave number of 1416.78 cm^{-1} due to the presence of CO_2 atmospheric and Ca-O band appeared at 549.74 cm^{-1} [24]. A wave number of 866.08 cm^{-1} indicated that the vibration of metal oxides can be identified as K-O, because of the activation of KOH in CaO/K and haven't appeared in CaO. The FTIR CaO/K-sulfated TiO_2 spectra showed almost the same absorption without sulfated TiO_2. The sulfated TiO_2 (S-O-Ti vibration) appeared at a wave number of 1056.07 $cm^{-1}$and S=O band appeared at 2513.36 cm^{-1}. The stretching vibration of Ti-O appeared tiny peak at 892.12 as of Ti-O as a characteristic absorption of TiO_2 [28].

Surface morphology. The SEM images of catalysts were illustrated in Fig. 3.

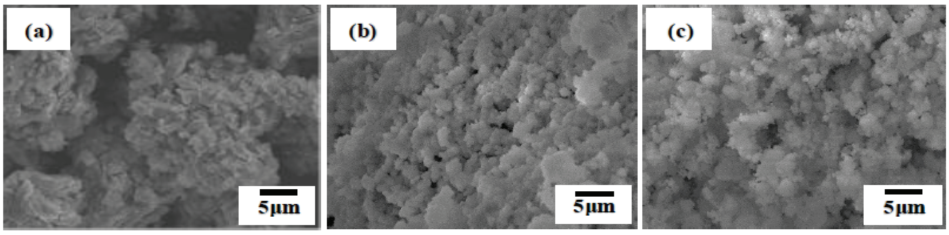

Figure 3: SEM images for (a) CaO/K and (b) CaO/K-sulfated TiO_2.

The SEM images of CaO/K-sulfated TiO_2, CaO/K, and CaO catalysts (Fig. 3) showed irregular shaped particles with a tendency approximately spherical and porous in structure [20, 25]. The particles size in CaO/K and CaO/K-sulfated TiO_2 is relatively smaller than CaO. This phenomenon is also supported by the crystallite size (Table 1), that the particle size of CaO/K catalyst is smaller (46.43 nm) than CaO/K-sulfated TiO_2 (62.10 nm) and CaO (93.13 nm).

2.2. Performance test of catalyst

The optimization of catalyst for converting WFO into production of biodiesel in a single-step esterification-esterification reactions namely catalyst concentrations, molar ratio of methanol/oil, and reaction time were illustrated below.

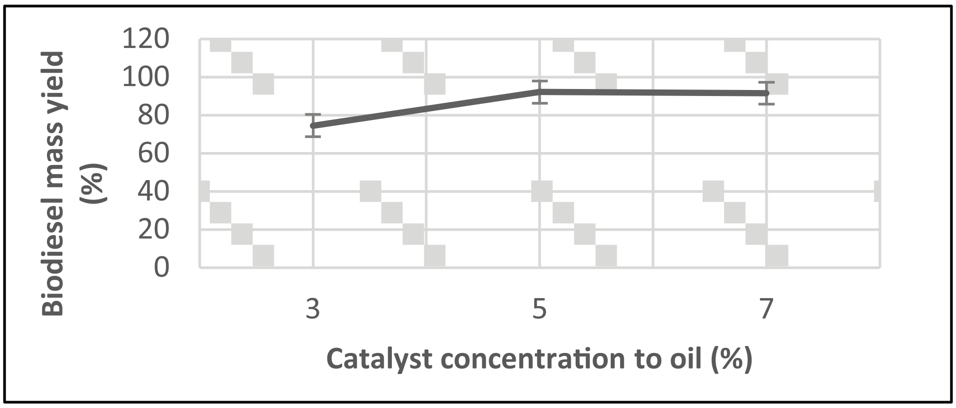

Figure 4: Optimization of catalyst concentration to oil on biodiesel mass yield.

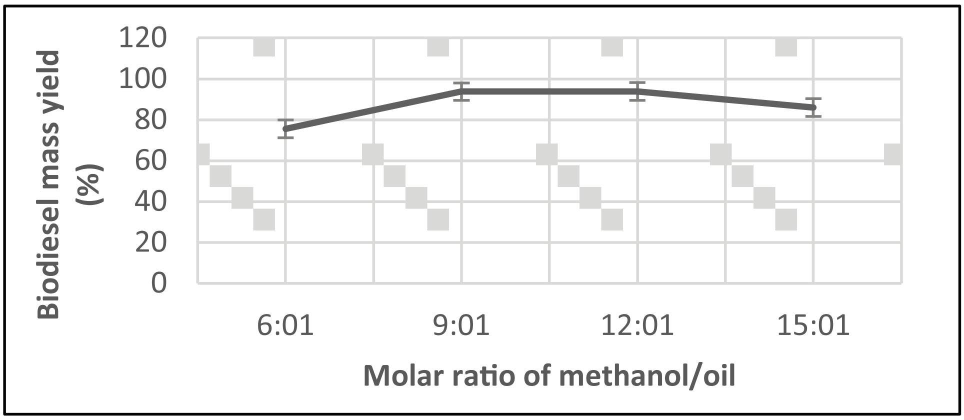

Figure 5: Optimization of molar ratio of methanol/oil on biodiesel mass yield.

Base on the optimization of catalyst concentration to oil, methanol/oil molar ratio, and reaction time on biodiesel mass yield (Fig. 4, Fig. 5, and Fig. 6) were obtained at 5% catalyst concentration, molar ratio of methanol/oil of 9:1, and 60 minutes reaction time. The obtained optimum conditions were then used for conversion of WFO into biodiesel for CaO, CaO/K, and CaO/K-sulfated TiO_2 catalysts.

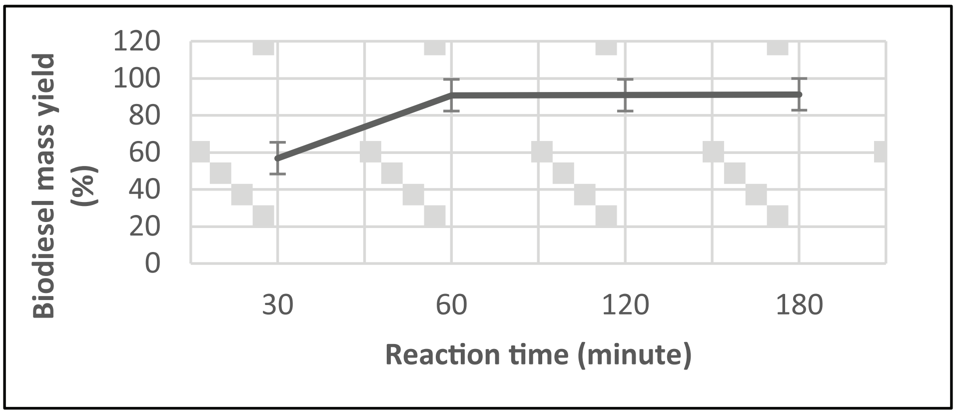

Figure 6: Optimization of reaction time on biodiesel mass yield.

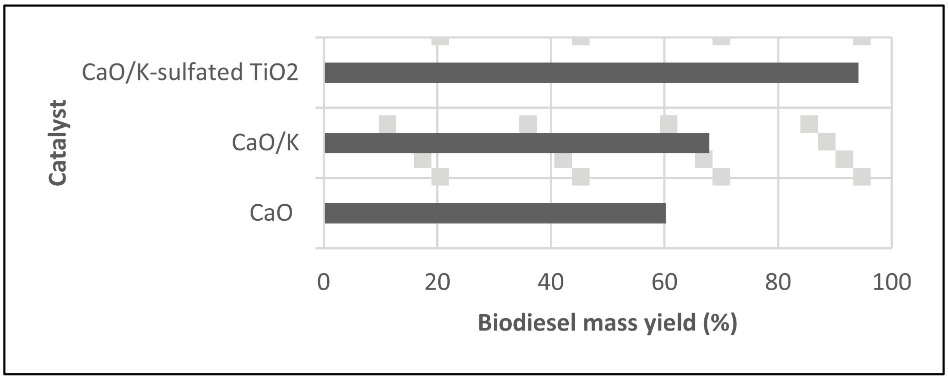

Figure 7: Biodiesel mass yield of CaO/K-sulfated TiO_2, CaO/K, and CaO catalysts at optimum conditions.

Base on Fig. 7, the highest result was obtained on the performance of CaO/K-sulfated TiO_2 catalyst with biodiesel mass yield of 94.17% higher than CaO/K (67.88%) and CaO (60.21%). It means that the loading of sulfated TiO_2 increases conversion ability of WFO into biodiesel.

The GC-MS analysis of biodiesel was obtained that the composition of fatty acid methyl esters (FAME) of 89.46% such as methyl laurate ($C_{13}H_{26}O_2$), methyl palmitate ($C_{17}H_{34}O_2$), methyl linoleate ($C_{19}H_{34}O_2$), methyl oleate ($C_{19}H_{36}O_2$), and methyl stearate ($C_{19}H_{38}O_2$). This means that the conversion of WFO into biodiesel has been relatively successful to form fatty acid methyl esters. It was compared with the biodiesel mass yield, lower value obtained. This means that its product is still other components formed. As the results, the conversion efficiency of WFO into biodiesel was 84.24%.

3. Conclusion

This study showed that the characteristics of CaO/K-sulfated $TiO_2$and CaO/K were nano particles lower than CaO as well as the CaO/K-sulfated TiO_2wasthe optimum surface acidity-basicity. The surface morphology of catalysts showed a tendency approximately spherical. The catalyst performance test for conversion of WFO into biodiesel were obtained that optimum conditions at 5% catalyst concentration to oil, molar ratio of methanol/oil of 9:1, and 60 minutes reaction time reached 94.17% biodiesel mass yield higher than using CaO/K of 67.88% and CaO of 60.21%. The composition of biodiesel was obtained FAME yield at 89.46% which has methyl laurate, methyl palmitate, methyl linoleate, methyl oleate, and methyl stearate.

References

[1] Sivasamy A, Cheah KY, Fornasiero P, Kemausuor F, Zinoviev S, Miertus S. Catalytic applications in the production of biodiesel from vegetable oils. Chemistry-Sustainability-Energy-Materials. 2009;2:278-300.

[2] Panudare DC, Rathod VK. Application of waste cooking oil other than biodiesel: Review. Iranian Journal of Chemical Engineering. 2015;12(3):55-76.

[3] Math MC, Kumar SP, Chetty SV. Technologies for biodiesel production from used cooking oil - A review. Energy for Sustainable Development. 2010;14:339-345.

[4] Zhang J, Chen S, Yang R, Yan Y. Biodiesel production from vegetable oil using heterogeneus acid and alkali catalyst. Fuel Processing Technology. 2010;89:2939-2944.

[5] Enweremadu CC, Mbarawa MM. Technical aspects of production and analysis of biodiesel from used cooking oil-a review. Renewable and Sustainable Energy Reviews. 2009;13(9):2205-2224.

[6] Kulkarni MG, Dalai AK. Waste cooking oil-an economical source for biodiesel: A review. Industrial and Engineering Chemistry Research. 2006;45:2901-2913.

[7] Guo F, Fang Z. Biodiesel production with solid catalysts. Biodiesel Feedstocks and Processing Technologies. 2011;16(1):339-358.

[8] Atadashi IM, Aroua MK, Aziz AR, Sulaiman NMN. The effects of catalysts in biodiesel production: A review. Journal of Industrial and Engineering Chemistry. 2013;19(1):14–26.

[9] Silva LCA, Silva EA, Monteiro MR, Silva C, Teleken JG, Alves HJ. Effect of the chemical composition of smectites used in KF/clay catalysts on soybean oil transesterification into methyl esters. Applied Clay Science. 2014;102:121–127.

[10] Simpen IN, Negara IMS, Puspawati NM. The characterization of heterogeneous nanocatalyst of biohydroxyapatite-lithium and its application for converting

malapari seed oil (*Milletia pinnata* L.) to biodiesel. Oriental Journal of Chemistry. 2018;34(4):1817-1823.

[11] Borges ME, Diaz L. Recent developments on heterogeneous catalysts for biodiesel production by oil esterification and transesterification reactions: A review. Renewable and Sustainable Energy Reviews. 2012;16:2839-2849.

[12] Salinas D, Guerrero S, Araya P. Transesterification of canola oil on potassium-supported TiO2 catalysts. Catalysis Communications. 2010;11:773-777.

[13] Istadi I, Prasetyo SA, Nugroho TS. Characterization of K2O/CaO-ZnO catalyst for transesterification of soybean oil to biodiesel. Procedia Environmental Sciences. 2015;23:394-399.

[14] Carlucci C, Degennaro L, Luisi R. Titanium dioxide as a catalyst in biodiesel production. Catalysts. 2019;9(75):1-25.

[15] He J-Y, Wang H, Liao D-Z, Jin Y-K. Preparation, surface acidity and catalytic esterification activity of solid acid S2O82-/TiO2–La2O3. Paper presented at: 4th Annual International Conference on Material Science and Engineering (ICMSE); June 17-19, 2016. Guangzhou, Guangdong, China.

[16] Pratigto S, Istadi. Kinetika reaksi transesterifikasi minyak kedelai menjadi biodiesel dengan katalis CaO. Jurnal Kimia Sains dan Aplikasi. 2019;22(5):213-219.

[17] Colombo K, Ender L, Barros AAC. The study of biodiesel production using CaO as a heterogeneous catalytic reaction. Egyptian Journal of Petroleum. 2016;30:1-9.

[18] Marinković DM, Stanković MV, Veličković AV et al. Calcium oxide as a promising heterogeneous catalyst for biodiesel production: current state and perspectives. Renewable and Sustainable Energy Reviews. 2016;56:1387–1408.

[19] Mazaheri H, Ong HC, Amini Z et al. An overview of biodiesel production via calcium oxide based catalysts: Current state and perspective. Energies. 2021;14(3950):1-23.

[20] Degfie TA, Mamo TT, Mekonnen YS. Optimized biodiesel production from waste cooking oil (WCO) using calcium oxide (CaO) nanocatalyst. Scientific Reports-Natureresearch. 2019;9(18982):1-8.

[21] Sani YM, Daud WMAW, Aziz ARA. Activity of solid acid catalysts for biodiesel production: A critical review. Applied Catalysis A: General. 2014;470:140-160.

[22] Bobade SN, Khyade VB. Detail study on the properties of *Pongamia pinnata* (Karanja) for the production of biofuel. Research Journal of Chemical Sciences. 2012;12(7):16-20.

[23] Abbah EC, Nwandikom GI, Egwuonwu CC, Nwakuba NR. Effect of reaction temperature on the yield of biodiesel from neem seed oil. American Journal of Energy Science. 2016;3(3):16-20.

[24] Peng Y-P, Amesho KTT, Chen C-E, Jhang S-R, Chou F-C, Lin Y-C. Optimization of biodiesel production from waste cooking oil using waste eggshell as a base catalyst under a microwave heating system. Catalysts 2018;8(81):1-16.

[25] Mirghiasi Z, Bakhtiari F, Darezereshki E, Esmaeilzadeh E. Preparation and characterization of CaO nanoparticles from Ca(OH)2 by direct thermal decomposition method. Journal of Industrial and Engineering Chemistry. 2014;20:113-117.

[26] Habte L, Shiferaw N, Mulatu D, Thenepalli T, Chilakala R, Ahn JW. Synthesis of nano-calcium oxide from waste eggshell by sol-gel method. Sustainability. 2019;11(3196):1-10.

[27] Pandya S. Nanocomposites and its application - Review. Parul University. Gujarat, India; 2015.

[28] Benito HE, Sanchez TDA, Alamilla RG, Enriquez JMH, Robles GS, Delgalo FP. Synthesis and physicochemical characterization of titanium oxide and sulphated titanium oxide obtained by thermal hydrolysis of titanium tetrachloride. Brazilian Journal of Chemical Engineering. 2014;31(3):737-745.