Tin-Empty Palm Bunch Ash Impregnated Zeolite as Suitable Catalyst for Simultaneous Transesterification-Esterification Reaction of Palm Oil

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Abstract. A single-step method was developed for methyl ester production from palm oil using tin-empty palm bunch ash impregnated zeolite (Sn-PBA-Zeolite) as heterogeneous catalyst. The weight ratios between Sn solution and zeolite 1:4, while the weight of the PBA was varied from 5, 10, 15, 20, 25, and 30 g in 60 mL of distilled water. Effects of reaction time, molar ratio of reactants, and catalyst concentration on the yield of methyl ester were studied. Characteristics of methyl ester produced were also investigated. The optimal conditions for transesterification reaction carried out by using a Sn-PBA-Zeolite of 1:4:25 weight ratio were a palm oil/methanol molar ratio 1:6, catalyst concentration (3% wt/wt), and 3 hours reaction time, whereas the maximum yield of methyl ester reached 76.21% wt/wt. The optimal conditions for esterification reaction carried out by using a Sn-PBA-Zeolite of 1:4:5 weight ratio were a palm oil/methanol molar ratio 1:12, catalyst concentration (3% wt/wt), and 3 hours reaction time, and the maximum yield of methyl ester reached 94.76% wt/wt. The methyl ester resulted has a density of 0.89 g/mL, viscosity of 7.82 cSt, and dominated by a methyl oleate, methyl palmitate, and methyl stearate.

1. Introduction

Methyl esters are type of fatty acid ester that are derived by transesterification of fats with methanol. They are used to produce detergents and biodiesel. The process feedstock can be derived from edible oils such as palm, soybean, groundnut, sunflower, sesame, safflower, waste cooking oil or non-edible oils such as *Jatropha curcas* and *Pongomia pinnata* [1-6]. One of the largest oil sources in Indonesia is palm (*Elais guineensis* Jack.) oil. The oil extracted from the palm fruit mesocarp and it is the largest source of vegetable oil. However, the oil palm contains high lipase activity that increases free fatty acids (FFA).

A conventional transesterification reaction usually uses strong alkali (i.e. NaOH or KOH) or acid (i.e. H_2SO_4 or H_3PO_4) solutions. These homogeneous catalysts are quite sensitive to FFA in the oil feed stocks. FFA can react with the basic catalyst and form soaps. This soap formation complicates the glycerol separation, and drastically reduces the methyl ester yield [7, 8]. For conventional processes using homogenous catalysts, the FFA content in the feedstock must be lower than 0.50 %wt. Instead, the two-step conversion process: an acid-catalyzed esterification pretreatment to lower the FFA content

followed by the alkali-catalyzed transesterification, are widely used in both industry and laboratory [9]. The strong acid or alkali catalysts used are corrosive. It must be removed from the methyl ester product by multiple washing. Thus, a significant amount of waste water is generated, together with lost of catalyst.

Based compounds of Sn are one of the compounds which are potentially to be developed as heterogeneous catalysts in methyl ester production. This metal presents higher Lewis acidity in comparison to other transition metal such as zinc (Zn), lead (Pb), and mercury (Hg) [10]. Cardoso et al. [11] reported that $SnCl_2$ used as a catalyst in the esterification reaction of oleic acid and showed catalytic activity which was very similar to H_2SO_4. Therefore, it is advantageous to develop a new class of heterogeneous catalysts, which has a higher tolerance to FFA in oils, and can simultaneously catalyze both of esterification and transesterification reactions.

Xie et al. [12] has mentioned that the SnO_2/SiO_2 materials with various Sn loadings ranging from 1 to 16 wt.% had been prepared and used as heterogeneous acid catalyst for soybean oil transesterification to produce biodiesel. The dispersed amorphous SnO_2 species on the silica surface are considered to be active sites for the transesterification reaction. Several catalyst based on tin compound (tin(II) acetate, tin(II) chloride, tin(II)2-ethylhexanoate and tin(II) stearate) has been tested by Casas et al. [13] for esterification and transesterification of acid vegetable oils. However, Sn was soluble in methanol and glycerol. To overcome this, Sn metal needs to be entrusted to the supporting matrix, one of them by impregnating Sn metal in the zeolite [10].

Zeolite is microporous crystalline alumino silicates, chemically similar to clay minerals, but they are different in their well-defined three dimensional microporous structure. Silicon, aluminum, and oxygen are arranged in a regular structure of $[SiO_4]$ and $[AlO_4]$ tetrahedral units that form a framework with regular pores form of channels, tunnels, or cavities of about 0.12 nm diameter running through the material [14]. Zeolite has been used as ion exchange and molecular sieves in the separation and removal of gasses and solvents. They also have the ability to act as a catalyst for chemical reactions which take place within the internal cavities [15]. Zeolite has been widely used as industrial heterogeneous catalysts because they are inexpensive and environmentally benign. They offer generous surface area and high porosity [16].

Since Sn-Zeolite is acidic, it is favorable for low-qualified oil feedstock with high FFA. In present study, to develop a simultaneous esterification-transesterification reaction, PBA from palm buch ash was used for increasing alkali sites of Sn-Zeolite. Usman et al. [17] has investigated that PBA contains more than 40% of alkali based potassium. From practical point of view, the use of PBA is advantageous since it is highly available as palm oil waste and renewable.

2. Materials and Methods

2.1 Materials

Palm oil and PBA were acquired in PTPN 13, West Kalimantan, Indonesia. Zeolite was purchased from one of the markets in West Kalimantan, Indonesia. The following chemicals, all analytical grades: oxalic acid ($C_2H_2O_4$), sulfuric acid (H_2SO_4), dichloromethane (CH_2Cl_2), ethanol (C_2H_5OH, 95%), phenolphthalein indicator, potassium hydroxide (KOH), anhydrous magnesium sulfate ($MgSO_4$), methanol (CH_3OH), n-hexane (C_6H_{14}), sodium chloride (NaCl), tin (II) chloride ($SnCl_2$), and G F254 silica gel were supplied by Sigma-Aldrich, Germany.

2.2. Methods

2.2.1 Materials Preparation

Zeolite particles were washed 3 times with distilled water, and dried in an oven at 110^{o}C. Dry zeolite was then crushed using a mortar until smooth shape with a size of 100 mesh. PBA was also crushed using a mortar until smooth shape with a size of 100 mesh, and activated in a furnace at a temperature

of 600°C for 2 hours. Preparation of palm oil was conducted by determining its water content, acid values, and FFA content.

2.2.2 Synthesis of Cayalysts

Six series of PBA solutions, while the weight of the PBA was varied from 5, 10, 15, 20, 25, and 30 g in 60 mL of distilled water, were soaked and stirred for 6 hours. The resulting filtrate was mixed with 5 grams of pre-prepared of Sn impregnated zeolite (Sn-Zeolite) as has been done by Alimuddin et al. [10]. The preparation process of Sn-PBA-Zeolite was carried out in a three necked flask (250 mL) equipped with a condenser, a thermometer and a magnetic stirrer bar. Impregnation of PBA with Sn-Zeolite was performed at 60^{o}C for 2 hours. After impregnation process had completed, the Sn-PBA-Zeolite was separated from solutions using vacuum filtration. Products were dried in an oven at 105^{o}C for 24 hours to remove the water content followed by calcination in a furnace at 450^{o}C for 4 hours. The final products obtained are referred as to Sn-PBA5-Zeolite, Sn-PBA10-Zeolite, Sn-PBA15-Zeolite, Sn-PBA20-Zeolite, Sn-PBA25-Zeolite, and Sn-PBA30-Zeolite for using 5, 10, 15, 20, 25, and 30 g of weight of PBA respectively. Catalysts obtained were characterized by XRD and XRF.

2.2.3 Transesterification and Esterification Reactions of Palm Oil by using Sn-PBA Zeolite Catalyst

Production of methyl ester was carried out in a three necked flask (250 mL) equipped with a condenser, a thermometer and a magnetic stirrer bar by mixing palm oil, methanol, and catalyst at 65^{o}C. The molar ratio of the reactants was varied from 1:2 to 1:16, Sn-PBA-Zeolite catalysts concentration was varied from 1 to 9 weight percent, time reaction was varied from 1 to 5 hours. After reaction was completed, mixture was centrifuged, and product was washed with warm distilled water. Anhydrous $MgSO_4$ was added to remove water content and filtered. Methyl ester yield and methyl ester product conversion percentage were calculated by following equation 1 and 2.

$$\text{Methyl ester yield} = \text{product mass/sample mass x } 100\% \quad (1)$$

$$\text{Conversion percentage } (\%) = (FFA_{intial} - FFA_{end})/FFA_{initial} \text{ x } 100\% \quad (2)$$

Physical properties (i.e. density, solubility, and viscosity) of solvent-free methyl ester product and residual catalyst were determined. Their chemical properties were also identifying by using GC-MS.

3. Results and Discussion

3.1. Characterization of Catalyst

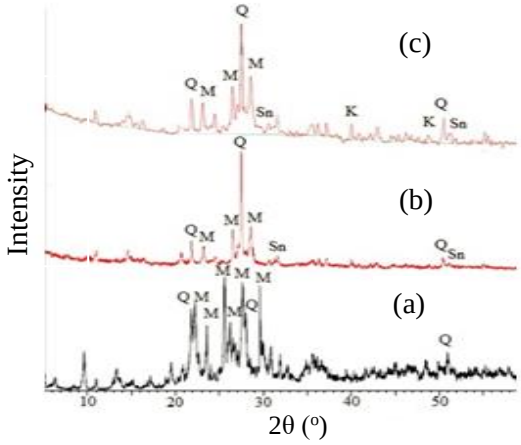

Figure 1. *XRD patterns of natural zeolite (a), Sn-Zeolite (b), and Sn-PBA-Zeolite (c)*

Since catalytic properties of zeolites is dependent on crystallite size and structure, materials used in this study were characterized by using XRD. Figure 1 illustrates XRD patterns of natural zeolite, Sn-Zeolite, and Sn-PBA-Zeolite. As can be seen in Figure 1a, the major mineral found in the natural zeolite is mordenite with a small content of quartz. Mordenite is one of the highest silica zeolites. It has two pore channels, i.e. 6.5 × 7.0 Å, which are parallel to c axis are connected by tortuous pores of 2.6×5.7 Å, and also to b axis that form side pockets. Since the latter are too small for most molecules to enter, mordenite is generally regarded as a mono-dimensional zeolite, which is widely used in catalysis because of its uniform, small pore size, high internal surface area, flexible framework, and controlled chemistry [18,19]. The presence of quartz in the sample, since the zeolite used originated from nature and in this study was not purified further.

Figure 1b and 1c show the loading of Sn and PBA into natural zeolite decrease the crystallinity as indicated by a decrease in the intensity of some characteristic peaks of modernite. Potassium was detected on the XRD pattern after loading of PBA. This proves that potassium is a major element in PBA and can play a role in providing base sites to zeolite. Impregnation is also selective. The presence of potassium (K) as the largest element in PBA is confirmed by the results of XRF analysis (Table 1).

Table 1. XRF Analysis Date

Sample	Number of Compositions (% w/w)						
	Si	Al	Sn	K	Mg	Ca	Fe
Natural zeolite**	33.09	7.68	-	3.85	0.68	1.87	1.89
Sn/zeolite**	31.71	6.83	5.52	3.46	0.44	1.49	1.65
PEFB ash	10.14	1.67	-	26.0	8.43	7.41	2.45
Sn-PBA5-Zeolite	64.61	11.91	7.72	7.97	1.32	3.28	1.64
Sn-PBA10-Zeolite	54.87	8.34	11.2	11.08	2.28	5.67	2.89
Sn-PBA15-Zeolite	62.91	12.24	7.98	8.69	0.86	3.35	1.58
Sn-PBA20-Zeolite	61.38	11.34	8.55	9.28	1.07	3.69	1.74
Sn-PBA25-Zeolite	54.84	8.84	10.4	13.3	1.45	4.64	2.38
Sn-PBA30-Zeolite	57.99	8.91	9.79	12.9	1.50	4.34	2.35

** Source: Alimuddin et al. [12]

XRF data analysis confirms that the Si/Al ratio of natural zeolite is 4.32. Si/Al ratios of zeolites slightly increase in Sn-Zeolite (4.64), but increase significantly when PBA had been impregnated (5.42, 6.57, 5.13, 5.41 for Sn-PBA5-Zeolite, Sn-PBA10-Zeolite, Sn-PBA15-Zeolite, and Sn-PBA20-Zeolite respectively). Changes in cation composition, in particular alkali and alkaline earth cations indicate that there has been a cation exchange to neutralize the zeolite charge and increase the base site of zeolite.

3.2. Transesterification and Esterification Reaction of Palm Oil by Using Sn-PBA-Zeolite as a Catalyst

3.2.1 Effects of Reaction Time, Molar Ratio of Reactants, and Catalyst Concentration on the Yield of Methyl Ester

Effects of reaction time, molar ratio of reactants, and catalyst concentration on the yield of methyl ester were studied by using Sn-PBA5-Zeolite as a catalyst. The transesterification reaction was carried out by using palm oil that have a water content of 0.09%, acid number of 9.27 g/mol, and FFA level of 4.23%. Meanwhile, the esterification reaction was carried out by using palm oil that had a water content of 1.98%, acid number of 145.36 g/mol, and FFA level of 66.32%.

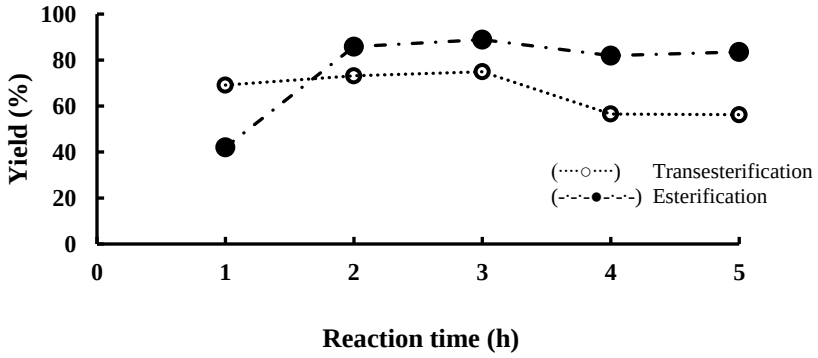

Figure 2. Methyl Ester Resulted at Varied Reaction Time of Transesterification and Esterification.

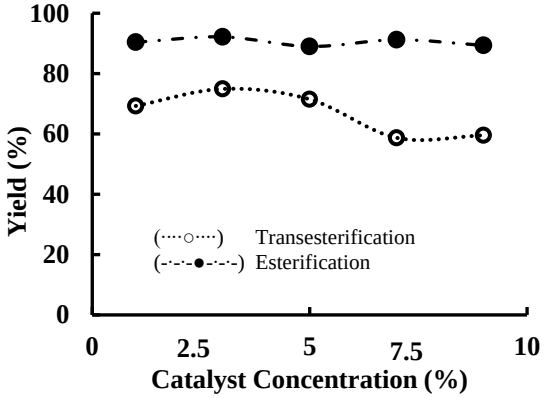

Figure 3. Methyl Ester Resulted at Varied Catalyst Concentration for Transesterification and Esterification.

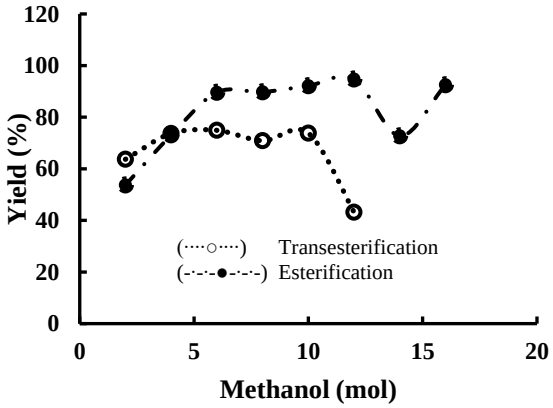

Figure 4. Methyl Ester Resulted Varied Molar Ratio of Reactants for Transesterification and Esterification.

Figure 2 shows the optimum reaction time reached at 3 hours, for both transesterification and esterification reactions. The maximum yield of methyl ester obtained in this time was 74.91% and 88.89% for transesterification and esterification reactions respectively. The longer reaction time provides a great opportunity for the reactant molecules to collide and react to one another to form methyl esters. However, since transesterification and esterification reactions are a reversible reaction, a longer reaction time lead to decreasing of methyl ester yield.

The optimum catalyst concentration in transesterification reaction was at 3% weight percent which was able to produce 74.91% of methyl ester and 92.17% when esterification reaction was applied (Figure 3). Generally, increasing of catalyst concentration increase the reaction rate where the number of molecules and chance to collide will increase [20]. The use of a larger catalyst concentration causes a decrease in the resulting methyl ester yield. This is due to the excess reaction of the catalyst with triglycerides in palm oil to produce a more glycerol by-product. In addition, this may also be due to the increasing amount of methanol that acts as a catalyst solvent rather than as a reactant thereby decreasing the conversion of the product because methanol may act as a reactant as well as a protic solvent.

Figure 4 shows that the optimum molar ratio of reactats in transesterification reaction is 1:6 which was able to produce 74.91% of methyl ester. The optimum molar ratio of reactats in esterification reaction was 1:12 which was able to produce 94.76% of methyl ester. Increase in methanol molar ratio: palm oil actually decreases percent yield. This occurs because of excessive use of methanol will cause the difficulty of separating the glycerol from the reaction product.

3.2.2 Effects of concentration of PBA in Sn-PBA-Zeolite Catalyst

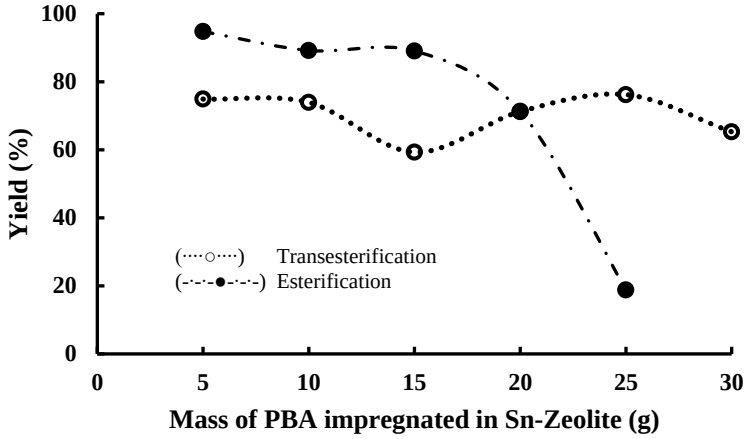

Figure 5. Methyl Ester Resulted Varied of Catalysts for Transesterification and Esterification.

As described above, the optimal conditions for transesterification reaction carried out by using a Sn-PBA5-Zeolite were a palm oil/methanol molar ratio 1:6, catalyst concentration (3% wt/wt), and 3 hours reaction time. Meanwhile, the optimal conditions for esterification reaction carried out by using a Sn-PBA5-Zeolite were a palm oil/methanol molar ratio 1:12, catalyst concentration (3% wt/wt), and 3 hours reaction time. To determine the optimum concentration of PBA to be impregnated as base sites in Sn-Zeolite, weight of PBA used were varied.

Figure 5 shows that use of Sn-PBA25-Zeolite in esterification reaction produced maximum percentage of methyl ester yield, and use of Sn-PBA5-Zeolite for that the esterification reaction. These results were influenced by the concentration of potassium impregnated in Sn-Zeolite. This proves that the presence of base sites on Sn-Zeolite-based catalyst greatly affects the type of reaction would be applied. Transesterification reaction requires a catalyst that has a higher alkalinity than esterification reaction.

3.3. Characteristics of Methyl Ester

Characteristics of methyl ester obtained in this study was determined its physical and chemical properties including density, viscosity, and composition. The density and viscosity of methyl ester at 40°C is 0.89 g/mL and 7.82 Cst respectively. The result of GC-MS analysis (Table 2) shows that the percentage of methyl ester obtained up to 91.86%. The major component of methyl ester on the transesterification-esterification reaction of palm oil with Sn-PBA-Zeolite are methyl oleate (38.92%), methyl palmitate (20.59%), and methyl stearate (14.67%).

Table 2. Chemical Composition of Methyl Esters in Products of Transesterification and Esterification Reactions of Palm Oil by Using Sn-PBA-Zeolite as a Catalyst

Methyl esters	Area (%)
Methyl caprylate	0.10
Methyl pelargonate	0.06
Methyl stearate	14.69
Methyl azelaaldehidat	0.06
Methyl laurate	0.15
Methyl myristate	0.92
Methyl palmitate	20.59
Methyl margarine	0.44

Methyl linoleate		6.94
Methyl oleate		38.92
Methyl linoleate		0.35
Methyl ricinoleate		1.49
Methyl trans-9,10-epoxystearate		0.49
Methyl Cis-9,10-epoxystearate		0.22
Methyl 10-ketostearate		1.60
Methyl arachidate		2.84
Methyl 10-hydroxy-hexadecanoate		0.58
Methyl behenat		0.55
Methyl tricosanoate		0.11
Methyl Lignocerate		0.50
	Amount	91.60

4. Conclusions

The presence of base sites on Sn-Zeolite-based catalyst greatly affects the type of reaction would be applied. Transesterification reaction requires a catalyst that has a higher alkalinity than esterification reaction. Empty palm bunch ash has the potential to be increased in useful value, one of them in Sn-Zeolite-based catalyst. The optimal conditions for transesterification reaction carried out by using a Sn-PBA-Zeolite of 1:4:25 weight ratio were a palm oil/methanol molar ratio 1:6, catalyst concentration (3% wt/wt), and 3 hours reaction time. The optimal conditions for esterification reaction carried out by using a Sn-PBA-Zeolite of 1:4:5 weight ratio were a palm oil/methanol molar ratio 1:12, catalyst concentration (3% wt/wt), and 3 hours reaction time. The methyl ester resulted has a density of 0.89 g/mL, viscosity of 7.82 cSt, and dominated by methyl oleate, methyl palmitate, and methyl stearate.

5. References

[1] Hameed B.H., Chin C.S.G.L.H. 2009 Process optimization for methyl ester production from waste cooking oil using activated carbon supported potassium fluoride *Fuel processing Technology* **90** 1532-1537

[2] Satyanarayana M, Muraleedharan C 2011 A comparative study of vegetable oil methyl esters (biodiesels) *Energy 36* 2129-2137

[3] Babu R, Godiganur S 2015 Use of vegetable edible oil methyl esters as fuel in internal combustion (CI) engines-a review, *International Journal of Latest Research in Science and technology* **4** 85-89

[4] Mofijur M, Masjuki H.H, Kalam M.A, Rasul M.G, Atabani A.E, Hazrat Mahmudul, M.A, H.M. 2015 Effect of biodiesel-diesel blending on physico-chemical properties of biodiesel produced from Moringa oleifera *Procedia Engineering* **105** 665-669

[5] Thunyaratchatanon C, Luengnaruemitchai A, Chollacoop N, Yoshimura Y 2016 Catalytic upgrading of soybean oil methyl esters by partial hydrogenation using Pd catalysts, *Fuel* **163** 8-16

[6] Abdullah, R.N.R. Sianipar, D. Ariyani, I.F. Nata 2017 Conversion of palm oil sludge to biodiesel using alum and KOH as catalyst, *Sustainable Environment Research* **27** 291-295

[7] Yan S, Salley S.O, Simon K.Y 2009 Simultaneous transesterification and esterification of unrefined or waste oils over ZnO-La_2O_3 catalysts, *Applies Catalysis A: General* **353** 203-212

[8] Olutoye M.A, Lee S.C, Hameed B.H. 2011 Synthesis of fatty acid methyl ester from palm oil (Elais guineensis) with Ky(MgCa)2xO3 as heterogeneus catalyst, *Bioresource Technology* **102** 10777-10783

[9] Thoai D.N, Tongurai C, Prasertsit K, Kumar A 2017 A novel two-step transesterification process catalyzed by homogeneous base catalyst in the first step and heterogeneous acid catalyst in the second step *Fuel Processing Technology 168* 99-104

[10] Alimuddin A.H, Usman T, N. Wahyuni, Rudiyansyah, Y.E. Prawatya, I. Astar, Y. Yustira 2017 Synthesis and characterization of Sn/zeolite and catalytic activity test in the esterification reaction of sludge oil, *AIP Conference Proceedings* **1823** 020052-1-5
[11] Cardoso A.L, Neves S.C.G, Silva M.J 2008 Esterification of oleic acid for biodiesel production catalyzed by $SnCl_2$: a kinetic investigation, *Energies* **1**
[12] Xie W., Wang H., Li H. 2012 Silica-supported tin oxides as heterogeneous acid catalysts for transesterification of soybean oil with methanol *Industrial and Engineering Chemistry Research* **51** 225–231
[13] Casas A, Ramos M.J, Rodríguez, Pérez Á, 2013 Tin compounds as Lewis acid catalysts for esterification and transesterification of acid vegetable oils, *Fuel Processing Technology* **106** 321-325
[14] Zaarour M. Dong B, Naydenova I, Retoux R., Mintova S 2014 Progress in zeolite synthesis promotes advanced applications *Microporous and Mesoporous Materials* **189** 11-21
[15] Manadee S, Sophiphun O, Osakoo N, Supamathanon N, Kidkhunthod P, Chalenk N, Wittayakun J, Prayoonpokarach S 2017 Identification of potassium phase in catalysts supported on zeolite NaX and performance in transesterification of Jatropha seed oil *Fuel Processing Technology* **156** 62-67
[16] Hassani M, Najafpour G.D, Mohammadi M, Rabiee M 2014 Preparation, characterization and application of zeolite-based catalyst for production of biodiesel from waste cooking oil, Journal of Scientific & Industrial Research **73** 129-133
[17] Usman T, Ariani L, Rahmalia W, Advant R 2009 Esterifikasi asam lemak dari limbah kelapa sawit (*sludge oil*) menggunakan katalis tawas, *Indonesian Journal Chemistry* **9** 474-478
[18] Bhadauria J, Singh B.K, Tomar A, Tomar R 2011 Synthesis and characterization of analogue of mordenite and its role as a catalyst for Friedel-Crafts acylation of anisole **3**(2):245-257
[19] Smail H, Shareef K, Ramli Z 2017 Synthesis of mesoporous mordenite zeolite by different natural raw materials *Australian Journal of Basic and Applied Sciences* **11** (2017) 27-34
[20] A.B.M.S. Hossain, M.A. Mazen 2010 Effects of catalyst types and concentrations on biodiesel production from waste soybean oil biomass as renewable energy and environmental recycling process, *Australian Journal of Crop Science* **4** 550-555

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