Research Article

Modification of Turen's Bentonite with AlCl₃ for Esterification of Palmitic Acid

A. Abdulloh [1,2], Siti Maryam [2], Nanik Siti Aminah [2], T. Triyono [1], Wega Trisunaryanti [1], M. Mudasir [1], Didik Prasetyoko [3*]

[1] *Department of Chemistry, Faculty of Mathematics and Natural Science, Universitas Gadjah Mada, Yogyakarta, Indonesia*
[2] *Department of Chemistry, Faculty of Science and Technology, Universitas Airlangga, Surabaya, 60115, Indonesia*
[3] *Laboratory of Material Chemistry and Energy, Department of Chemistry, Faculty of Mathematics and Natural Science, Institut Teknologi Sepuluh Nopember, Surabaya, 60111, Indonesia*

Abstract

Natural Turen's bentonite has been purified, modified and applied as catalyst for palmitic acid esterification. Modification of natural Turen's bentonite was conducted by cation exchange method using AlCl3 solution. Catalyst characterization was performed on X-ray Fluorescence, X-ray Diffraction, nitrogen adsorption-desorption and infrared spectroscopy techniques. The catalytic activity test in the esterification reaction of palmitic acid with methanol was conducted by bath at 65 °C with a variation of reaction time of 1, 2, 3, 4 and 5 h. Catalytic activity has been observed qualitatively using GC-MS and quantitatively by changes in acid number. The analysis showed the formation of Al^{3+}-bentonite. Observation on the elements has shown that the presence of calcium decreased from 10.2 to 4.17 %, with an increase of aluminium content from 9.9 to 13 %. Diffraction line at 2θ 5.7379º became 5.6489º, along with changes in *d*-spacing of 15.3895 to 15.6319 Å. The surface area increased from 83.78 to 91.26 m²/g, while Brönsted acid sites increased from 10.2 to 67.5 µmol/g and Lewis acid sites increased from 94.9 to 132 µmol/g. Furthermore, Al^{3+}-bentonite has showed as active catalyst in the esterification reaction of palmitic acid with palmitic acid with conversion of 78.78 % for 7 h. © 2014 BCREC UNDIP. All rights reserved

How to Cite: Abdulloh, A., Maryam, S., Aminah, N.S., Triyono, T., Trisunaryanti, W., Mudasir, M., Prasetyoko, D. (2014). Modification of Turen's Bentonite with AlCl₃ for Esterification of Palmitic Acid. *Bulletin of Chemical Reaction Engineering & Catalysis*, 9 (1): 66-73. (doi:10.9767/bcrec.9.1.5513.66-73)

Permalink/DOI: http://dx.doi.org/10.9767/bcrec.9.1.5513.66-73

1. Introduction

Fuel scarcity is solution current issue which continues to demand the finding of new solutions. Government and the society continue to seek alternative energy sources to substitute petroleum-based energy. One of the new and renewable energy sources (renewable resources) which could be relied upon is derived from various types of vegetable oils, as raw material for the manufacture of biodiesel. Synthesis of biodiesel from vegetable oils can be made through transesterification reaction using an acid or base catalyst. The profitable use of basic catalysts for the reaction is because of fast reaction [1]. However, the use of basic catalysts can lead

* Corresponding Author.
  E-mail: didikp@chem.its.ac.id;
  didik.prasetyoko@gmail.com (D. Prasetyoko

to the formation of soap if FFA content in vegetable oils is greater than 2%, which can complicate the separation of glycerol from biodiesel.

Tiwari et al. [2] reported that in order to avoid the formation of soap, the synthesis of biodiesel from Jatropha oil containing 14% free fatty acids can be carried out in two stages, namely esterification catalyst with H_2SO_4 and transesterification with KOH catalyst to generate conversions up to 99 %. The results of the conversion are slightly reduced to 90 % if the FFA Jatropha oil contains 15 % KOH in the transesterification process and replaced with NaOH [3]. Although the method is quite effective, the use of catalysts KOH, NaOH and H_2SO_4 are relatively less effective in large-scale production [4]. Therefore, the catalyst used needs to be replaced with heterogeneous catalysts.

One of the heterogeneous catalysts that has been used for the esterification reaction is Al^{3+}-montmorillonite. The use of Al^{3+}-montmorillonite in the esterification reaction of succinic acid with 1-butanol can produce dibutyl succinate 94 %, penilacetate acid esterification with p-cresol produced 67 % p-cresol penilacetate [5], succinic acid esterification with p-cresol generated 75 % p-cresol succinate [6], succinic acid esterification with isobutanol producing isobutyl succinate 94 % [7], propanoic acid esterification with p-cresol ester with 88 % conversion [8].

Montmorillonite is the main constituent of bentonite component. In East Java, bentonite can be found mainly in the area of Pacitan, Trenggalek, Blitar, and Malang with quartz and iron oxide as significant impurities. Based on this background, this study has been done to purify and modify the natural bentonite of Turen-Malang, East Java to Al^{3+}-bentonite via mechanical separation (purification) and apply for the esterification of palmitic acid. This due to the palmitic acid found in any vegetable oil can be used as the raw material for biodiesel production. A total of 42.47 % of palmitic acid is found in red palm oil, 36.77 % in palm oil, 12.43 % in corn oil, 9.16 % coconut oil (9) and 11.30 % within jatropha oil [2].

2. Materials and Methods

2.1. Materials

Natural bentonite comes from Turen-Malang (East Java). Another materials include palmitic acid, methanol, $AlCl_3$, $H_2C_2O_4$, Na_2SO_4, anhydrous, KOH, ethanol, phenolphtalein indicator, bromothymol, $AgNO_3$ and n-hexane.

2.2. Preparation and Characterization of Catalysts

Natural Turen's bentonite was purified by pouring in water with ratio bentonite:water 1:4 (wt./wt.), stirring for 15 minutes, and letting the mixture stand a day. This process was repeated seven times. Finally, one third of solids at the top was taken and dried at 110 ºC for 24 h.

A total of 5 g of purified natural Turen's bentonite (said Turen's bentonite) was placed into a glass beaker containing 200 ml of 0.5 M $AlCl_3$ and stirred with a magnetic stirrer for 24 h. The mixture was then centrifuged to separate the precipitated Al^{3+}-bentonite with a solution of $AlCl_3$. The Al^{3+}-bentonite was then washed with distilled water until free of Cl^- ions. Test of Cl^- ions were performed by adding 2 drops of $AgNO_3$ 0.1 M into the former washing water until no more white precipitate formed [8].

Characterization to determine the surface area and pore size of the catalyst was performed by N_2 adsorption-desorption method. Concentration of elements in the samples were determined by a XRF spectrophotometer, while the structural analysis were monitored using a XRD spectrophotometer with CuKα radiation (λ = 1.5405 Å). The types and amounts of acid sites were determined using pyridine adsorption coupled with infrared spectrophotometer [8].

2.3. Catalytic Activity

For catalytic activity determination, a total of 0.25 grams of Al^{3+}-bentonite, palmitic acid and methanol with a molar ratio of 1:30 to palmitic acid was used in the reaction. Methanol and Al^{3+}-bentonite was mixed in the reaction flask and then refluxed for 30 minutes [10]. Further esterification reaction achieved at a temperature of 65 ºC, by addition of palmitic acid into the reaction flask. To observe how the reaction of palmitic acid esterification by Al^{3+}-bentonite can take place, the reaction was stopped after 1 h, the mixture of substances in the reaction flask was taken and separated from the catalyst and methanol.

Characterization by GC-MS spectrophotometer was conducted to observe the formation of methyl palmitate. Conversion to methyl palmitate from palmitic acid ($x(\%)$) was determined by changes in acid number according to the equation [11]:

$$x(\%) = \left(1 - \frac{AV_t}{AV_o}\right) \times 100\%$$

(1)

in which AV_t and AV_o as the number before and after esterification reaction.

3. Result and Discussion

3.1. Characterization of Al³⁺-Bentonite Catalyst

Testing the characteristics of the structure by XRD, and elemental content by XRF samples of Turen's bentonite were done first to prove that the sample was bentonite. Based on the XRD analysis, Turen's bentonite samples have multiple diffraction angle 2θ (Figure 1): 5.7380°, 17.3511°, 19.8309°, 20.8906°, 23.6664°, 25.0697°, 26.6773°, 29.0217°, 35,1642°, and 41.3079°. The peaks have compatibility with XRD pattern of montmorillonite (bentonite constituent minerals) with PDF number 00-029-1498 $(Na_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2.4H_2O)$ and clinoptilolite with PDF number 00-039-1383 $(K,Na_2Ca_2(Si_{29}Al_7)O_{72}.24H_2O)$ with cristobalite (SiO_2) with PDF number 00-039-1425 and quartz (SiO_2) with PDF number 00-046-1045 as an impurities.

The results of the XRF elemental analysis also showed that the bentonite samples contained elements of Si, Al, Ca, Mg and Fe (Table 1). The results of elemental analysis also showed isomorphic substitution of Al^{3+} in an octahedral field by Fe^{2+}, as the ratio of the amount of Si and Al in the coating unit was 2:1 (consisting of two sheets of silica tetrahedral and one sheet of alumina octahedral) on montmorillonite, without any element of O and H, was 67.47 % and 32.53 %. Results of XRF analysis of bentonite samples showed contents of Si and Al, at 43.3 % and 9.9 %, respectively. Isomorphic substitution of Al^{3+} by Fe^{2+} bentonite

deficiency caused a positive charge so that in general the montmorillonite interlayer cations that serves as a balancing charge, usually Ca or Na. Based on the results of elemental analysis (Table 1), cations balancing the charge in Turen Malang's bentonite samples were Ca^{2+}, so the bentonite samples including Ca-bentonite occurs isomorphic substitution of Fe^{2+} in octahedral field.

Characterisation of the structure and content of elements was also performed on samples of Turen's bentonite to observe changes in the structure by shifting the field (change 2θ and d-spacing) and the percentage change in Al and Ca to prove the exchange of Ca^{2+} cations in the interlayer region of Al^{3+} from $AlCl_3$ solution. Based on the analysis of the elements of Ca and Al, Table 1 shows that the total percentage of elemental Ca decreased from 10.2 to 4.17 % and the Al elements increased from 9.9 to 13%. This suggests that there has been an exchange of cations. The cation exchange of Ca^{2+} by Al^{3+} was also observed by a shift in the field, shown by the shift in angle 2θ from 5.7379° to 5.6489° and d-spacing changes from 15.3895 Å to 15.6319 Å from the XRD structure analysis (Figure 2). Cation exchange processed Ca^{2+} by Al^{3+} ions due to differences in the interaction of Ca^{2+} and Al^{3+} to the siloxane cavity $(-SiO_3)$ on the surface of bentonite. Ca^{2+} ions interacted with the siloxane cavity in the form of hydrates forming cation outer-sphere surface complex of which bonds are weaker than the Al^{3+} ions
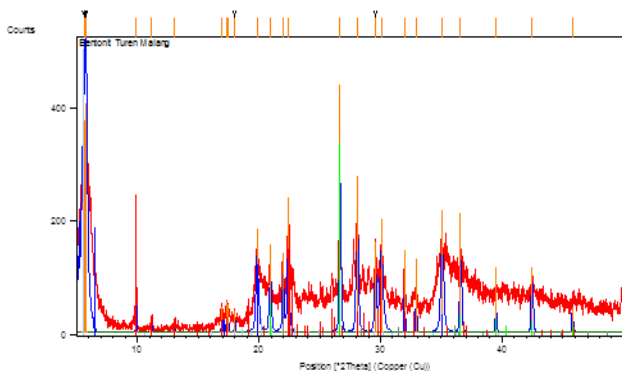
Table 1. Number and percentage of elements from natural Turen bentonite, before and after cation exchange using a solution of $AlCl_3$

| Element	Turen's bentonite (%)	Al³⁺-Turen's bentonite (%)
Al	9.90	13.00
Si	43.30	48.20
Ca	10.20	4.17
Fe	30.90	30.20
K	1.50	1.40
Cu	0.19	0.19
Ti	1.10	1.10
V	0.05	0.07
Cr	0.08	0.08
Mn	0.10	0.14
Ni	0.27	0.36
Zn	0.14	0.17
Sr	1.10	0.59
Ba	0.49	0.30
Re	0.30	0.10

Figure 1. XRD pattern of Turen's bentonite

which could interact directly with siloxane cavity, forming an inner-sphere surface complex [12]. Besides, there were no other significant changes of shifting 2θ and d-spacing. This indicates that after the cation occurs exchange process, bentonite structure did not collapse.

Characterization of the surface area and the amount of acid sites was also done because both are factors that can affect the catalytic activity in heterogeneous catalytic reactions. Pyridine was used to determine of the number of acid sites in the samples. This was done because pyridine could be coordination covalently bonded with the Lewis acid sites and covalently bonded with Brönsted acid sites. Reddy et.al. [8] reported that the interaction of pyridine with Brönsted, both Brönsted and Lewis, and Lewis acid sites were observed at wavenumbers 1545, 1490, and 1450 cm^{-1}, respectively. In this study, the acidity of Turen's bentonite was indicated by the peak at 1551.81, 1491.25 and 1443.44 cm^{-1}. For the Al^{3+}-bentonite, the peak was indicated at 1549.40, 1489.71, and 1441.32 cm^{-1} (Figure 3).

Quantitatively, the amount of acid sites was determined by area under the peak [13]. Based on FTIR spectrum curves of Turen's bentonite, peaks area at 1551.81 and 1443.44 cm^{-1} were 0.3670 and 2.5745, respectively. Therefore, Turen's bentonite had Brönsted acid sites of 10.2 µmol/g and Lewis of 94.9 µmol/g. The peak area of 1549.40 and 1441.32 cm^{-1} in the infrared spectra of Al^{3+}-bentonite were 2.4240 and 3.5825 in which Al^{3+}-bentonite having Brönsted acid sites of 67.5 µmol/g and Lewis of 132 µmol/g. Increasing the amount of acidity in Al^{3+}-bentonite (Brönsted from 10.2 µmol/g to 67.5 µmol/g and Lewis from 94.9 µmol/g to 132 µmol/g) due to the ability of ion Al^{3+}-dissociated

hydrate water molecules bound to the interlayer region into H^{+} (equation 2) and provided an empty orbital which increased the amount of Lewis acid sites [14].

$$[Al(H_2O)_6]^{3+} \rightleftharpoons [Al(H_2O)_5OH]^{2+} + H^+$$

(2)
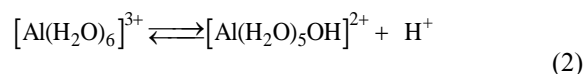
The BET surface area analysis shows that the cation exchange of Ca^{2+} by Al^{3+} caused an increased surface area of 83.781 to 91.266 m^2/g and pore size increase of 6.32 to 20.09 Å. Adsorption-desorption isotherm of Al^{3+}-bentonite Turen Malang (Figure 4) showed hysteresis loupe starting at *P/P$_0$* of 0.4, which is the type IV isotherm of adsorption-desorption that occurs in mesoporous materials [15].
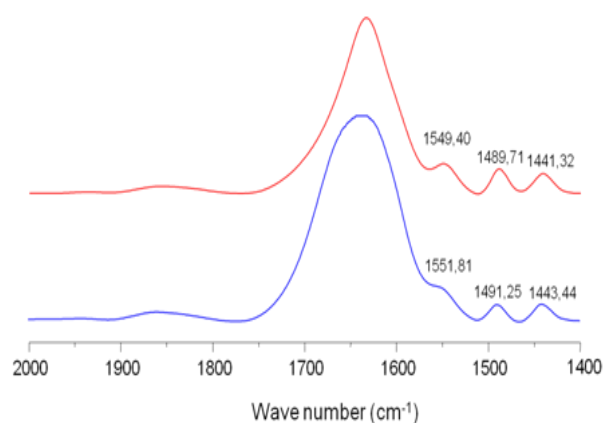

Figure 3. Infrared spectra of Turen's bentonite and Al^{3+}-Turen's bentonite after adsorption of pyridine and evacuation at 150 °C
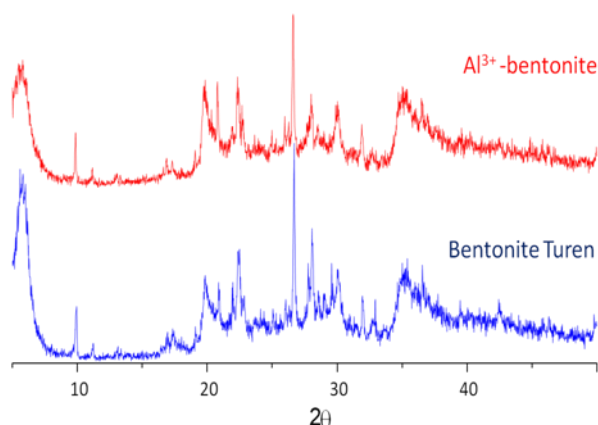

Figure 2. XRD patterns of natural Turen's bentonite and Al^{3+}-bentonite (modified from Turen's bentonite)
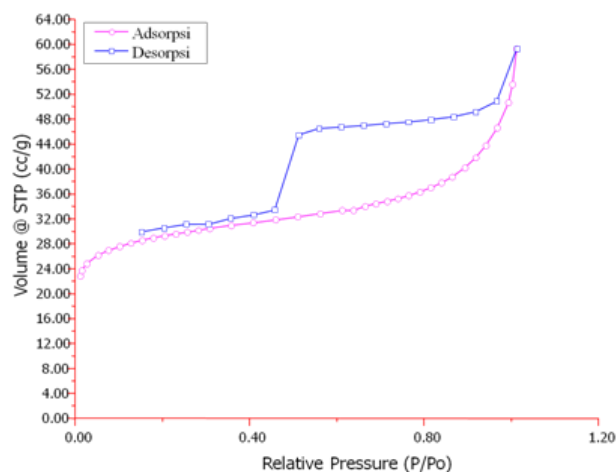

Figure 4. Nitrogen adsorption-desorption isotherm of Al^{3+}-Turen's bentonite
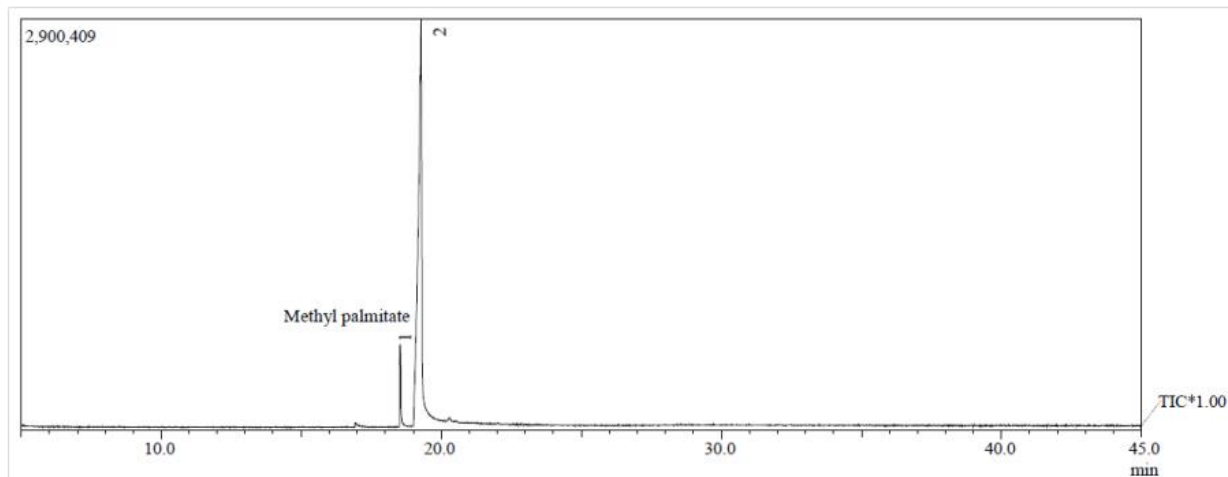
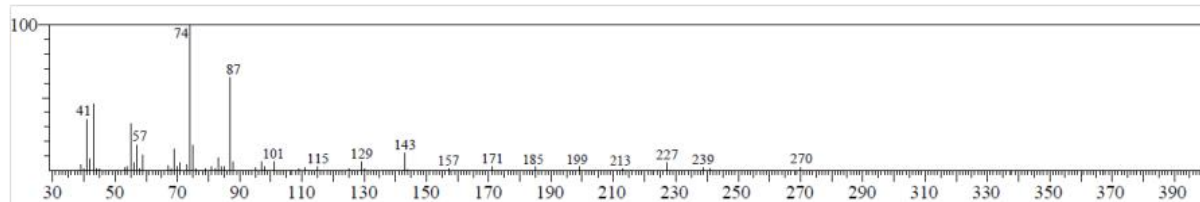**Figure 5**. Chromatogram results of palmitic acid esterification

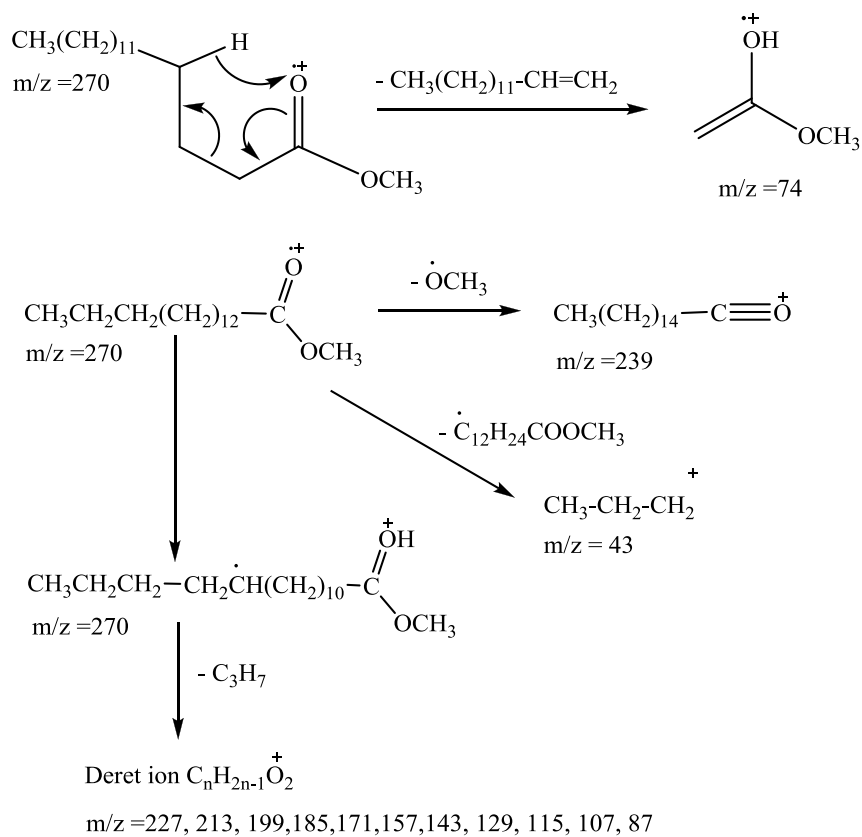Figure 6. The mass spectra of the product of palmitic acid esterification

Figure 7. Mechanism of methyl palmitate fragmentation [17]

3.2 Catalytic Activity

Qualitatively, catalytic activity of Al^{3+}-bentonite in the esterification reaction between methanol to palmitic acid is determined by the formation of methyl palmitate. Analysis of methyl palmitate was performed using GC-MS on a non-polar phase, as the methyl ester is classified as a non-polar compound and mixed with fatty acids after esterification reaction. The studies on this, after esterification formed three layers, namely layer deposition of catalyst Al^{3+}-bentonite, nonpolar layers and layers of methanol (polar compounds) which have not reacted.

Based on the analysis of the GC chromatogram of the non-polar layer, a second peak was seen with a retention time of 18.536 min and 19.284 min (Figure 5). Based on the mass spectra data library, peaks on the chromatogram 1 is methyl palmitate (or similarity index SI = 95) and the top 2 are palmitic acid (SI = 95) which is a products of the esterification reaction and the reactants which did not react.

In the spectrum of peak No. 1 from the esterification reaction using catalysts Al^{3+}-bentonite (Figure 6) appeared molecular ion m/z 270 derived from the $C_{17}H_{34}O_2^+$ (ion molecule methyl palmitate), while the base peak m/z 74 derived from $C_3H_6O_2^+$ was formed by the breakdown of -ß through McLafferty rearrangement. A fragments of m/z 239 derived from the $C_{16}H_{31}O^+$ was produced by the loss of a methoxy group from the molecular ion peak. The fragment with m/z 43 was derived from th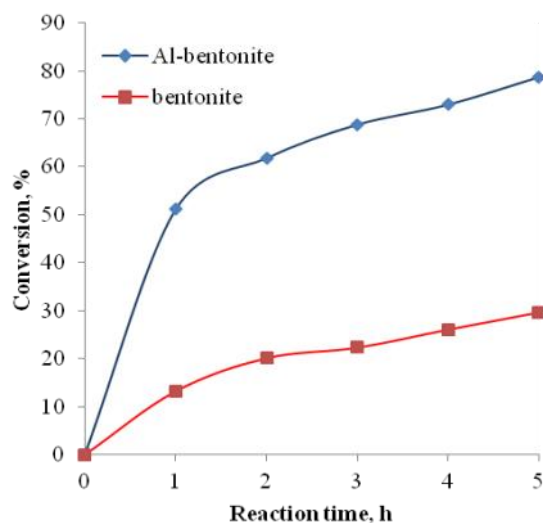e release of radical $C_{12}H_{24}COOCH_3$. Peaks at m/z 87, 101, 115, 129, 143, 157, 171, 185, 199, 213 and 227 were due to the fragmentation pattern of the solution at each CH_2CH_2 bonds, known as ion fragmentation pattern of the series $C_nH_{2n-1}O_2^+$ [16]. Mechanism of fragmentation of methyl palmitate is shown in Figure 7 [17].

Determination of acid number indicates that during the reaction time of 1 hour, the amount of palmitic acid converted to methyl palmitate was 51.12 % (Figure 8). Catalytic activity reaction of Al^{3+}-bentonite tended to decrease, although the resulting conversion always increased. At the beginning of the reaction, catalytic activity of Al^{3+}-bentonite was quite large at 51.12 % per 1 hour (51.12 %/h), but then decreased with increasing reaction time into 61.88 % per 2 hours (30.94 %/h), 68.48 % by the reaction of 3 hours (22.83 %/h), 73.04 % per reaction of 4 hours (18.26 %/h), and 78.78 % with a reaction time of 5 hours (15.76 %/h.) This was because the interaction of the catalyst-reactant,
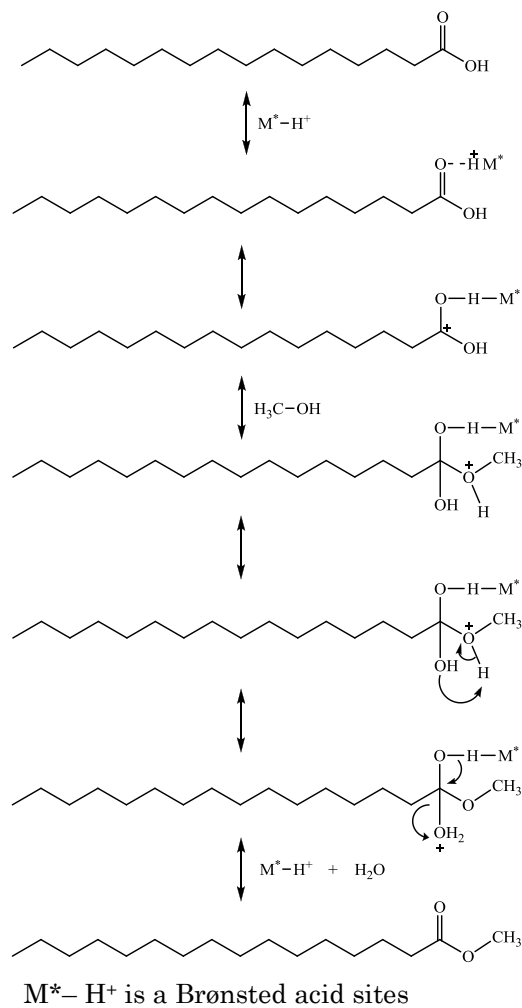

Figure 8. Conversion of palmitic acid in the esterification reaction using Al^{3+}-bentonite

M*– H+ is a Brønsted acid sites

Figure 9. Palmitic acid esterification reaction mechanism using Al^{3+}-bentonite

catalyst-oxygen intermediates, catalysts and reaction products played a significant role in the esterification reaction with the catalyst Al^{3+}-bentonite, although the reaction mechanism of catalyst esterification which occurred in Al^{3+}-bentonite (Figure 9) was similar to the mechanism of the esterification reaction in homogeneous acid catalyst (H_2SO_4).

Based on the principle of Sabatier, interactions of catalyst-reactant, catalyst-oxygen intermediates, catalysts and reaction products in reactions using heterogeneous catalysts must be just right. If the interactions are too weak, the reactants will move away from catalyst, so that reaction will not take place and if it happened too strong, reactants or the reaction will not leave the catalyst which could eventually poison the catalyst, or inhibit the reaction. Hydrophobicity of the surface of the catalyst in the esterification of fatty acids is a crucial factor. If the amount of Brönsted acid sites are too low, then the activity is lower. Otherwise if Brönsted acid sites appeared too much, it will lead to water adsorption and deactivation [18].

There are three types of relationship in which appeared the activity of catalyst surface hydrophobicity. Firstly, if the Brönsted acid sites appeared in an isolated environment
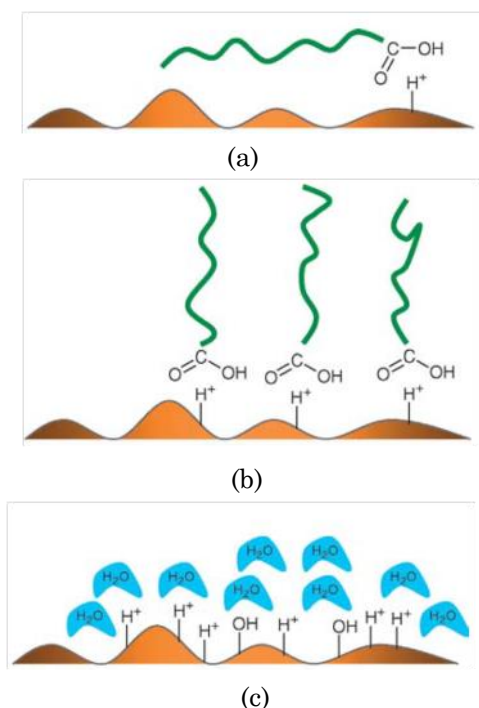

(a)

(b)

(c)

Figure 10. Catalyst surface hydrophobicity relations of the catalytic activity of fatty acid esterification: (a) isolated Brönsted acid sites (too little) (b) some Brönsted acid sites (too much) (c) too many Brönsted acid sites [18]

around hydrophobic (neutral siloxane O atoms from the surface of the Al^{3+}-bentonite), tail palmitic acid is hydrophobic which will be adsorbed parallel to the surface hydrophobic of catalyst Al^{3+}-bentonite (Figure 10a). Secondly, if there are several sites in the vicinity of Brönsted acid, fatty acid molecules can be adsorbed perpendicular to the surface (Figure 10 b). Thirdly, if the catalyst is highly acidic or hydrophilic (lots of acid sites adjacent or group hydroxyl), esterification reaction will produce water, which can be adsorbed on the surface of catalyst and will prevent access of fatty acids towards the catalyst, and thus the catalyst can lose its activity (Figure 10c). These three phenomena caused the catalytic activity of Al^{3+}-bentonite in the esterification reaction of palmitic acid changes.

4. Conclusions

Turen's bentonite Malang as Ca-bentonite can be modified to be Al^{3+}-bentonite with a characteristic number of Brönsted acid sites of 67.5 mmol/g, Lewis acid sites of 132 µmol/g, a surface area of 91.266 m^2/g and also as a mesoporous material (having pores of 20, 0956 Å). Al^{3+}-bentonite can be used as a catalyst in the esterification reaction of palmitic acid into methyl palmitate by the number of conversions 78.78 % at a reaction time of 5 hours.

Acknowledgments

References

[1] Schuchardt, U., Sercheli, R., Vargas, R.M. (1998). Transesterification of vegetable oils: A review, *J. Braz. Chem. Soc.*, 9: 199 – 210.

[2] Tiwari, A.K., Kumar, A., Raheman, H. (2007). Biodiesel production from jatropha oil (Jatropha Curcas) with high free fatty acid: An optimized process, *Biomass Bioenerg.*, 31: 569 – 575.

[3] Berchmans, H.J., Hirata, S. (2008). Biodiesel production from crude Jatropha curcas L. seed oil with a high content of free fatty acids, *Bioresour. Technol.* 99: 1716 – 1721.

[4] Jothiramalingam, R., Wang, M.K. (2009). Review of Recent Developments in Solid Acid, Base, and Enzyme Catalysts (Heterogeneous) for Biodiesel Production via Transesterification, *Ind. Eng. Chem. Res.* 48: 6162–6172.

[5] Reddy, C.R., Iyengar, P, Nagendrappa, G., Prakash, B.S.J. (2005). Esterification of succinic anhydride to di-(p-cresyl) succinate over Mn+-Montmorillonite Clay Catalysts, *J. Mol. Catal. A: Chemical*, 229: 31 − 37.

[6] Reddy, C.R., Iyengar, P, Nagendrappa, G., Prakash, B.S.J. (2005). Esterification of dicarboxylic acid to diester over M^{n+}-montmorillonite clay catalysts, *Catal. Lett.*, 101: 87 − 91.

[7] Reddy, C.R., Nagendrappa, G., Prakash, B.S.J. (2005). Surface acidity of M^{n+}-montmorillonite clay catalysts by FTIR spectroscopy: Correlation with esterification activity, *Catal. Commun.*, 8: 241 − 246.

[8] Reddy, C.R., Bhat, Y.S., Prakash, B.S.J. (2009). Brönsted and Lewis acidity of modified montmorillonite clay catalysts determined by FT-IR spectroscopy, *Catal. Today*, 141: 157 − 160.

[9] Dauqan, E.M.A, Sani, A.H., Abdullah, A., Kasim, M.Z. (2011). Fatty Acids Composition of Four Different Vegetable Oils (Red Palm Olein, Palm Olein, Corn Oil and Coconut Oil) by Gas Chromatography, *2nd Int. Conf. on Chem. and Chem. Eng.*, IPCBEE Vol.14, p. 31 − 34

[10] Meunier, J.N.F.C. (2007). Esterification of free fatty acids in sunflower oil over solid acid catalysts, *Appl. Catal. A*, 333: 122 − 130.

[11] Mengyu, G., Deng, P., Li, M., En, Y., Jianbing, H. (2009). The kinetics of the esterification of free fatty acids in waste cooking oil using $Fe_2(SO_4)_3$/C catalyst, *Chinese. J. Chem. Eng.*, 17: 83 − 87.

[12] Kehew, E.A. (2001). *Applied Chemical Hydrogeology*, Prentice Hall, New

[13] Emeis, C.A. (1993). Determination of integrated molar extinction coefficients for infrared absorption of pyridine adsorbed on solid acid catalysts, *J. Catal.*, 141: 347 − 354.

[14] Stylish, F., Theng, B.K.G., Lagaly, G. (2006). *Handbook of Clay Science*, 1st ed., Elsevier, Amsterdam.

[15] Lowel, S., Shields, E.J., Thomas, A.M., Thommes, M. (2006). *Characterization of Porous Solids and Powder: Surface Area, Pore Size and Density*, Kluwer academic Publ., Dordrecht., p. 12 − 14

[16] Silverstein, R.M., Bassler, G.C., Morrill, T.C., (1991). *Spectrometric identification of organic compounds*, Wiley, New York.

[17] Soerya, D.M., Desi, S.H. (2003). Analisis Spektrofotometer Infra Merah dan Kromatografi Gas-Spektrometri Massa Kandungan Senyawa Non polar Ekstrak Biji Kakao (Theobroma cacao Linn.) Fermentasi. *J. Alchemy*, 2: 57 − 66.

[18] Rothenberg, G. (2008). *Catalysis: Concept and Green Application*, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, p. 64 − 65, 186 − 187