

# M-MMT K10 (M: Cu, Al and Fe) as Catalysts for the Esterification of Acetic Acid and Stearic Acid with Methanol

Farah W. Harun, Enas A. Almadni, and Ernie S. Ali

**Abstract**— Montmorillonite K10 (MMT K10), the major clay mineral commercially available can be treated to improve its properties and thus can be utilized for a broad range of organic reaction including esterification of fatty acids for biodiesel production. However, the use of unmodified MMT K10 in esterification of fatty acids showed that the acid conversion was less than 60 %. The aim of this study is to utilize available material i.e. MMT K10 modified with  $\text{Cu}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  at various concentrations as catalyst for the esterification of acetic acid and stearic acid. The x-ray diffraction and elemental analysis of the materials were successfully characterized. After characterization, the materials were evaluated for the esterification of acetic acid and stearic acid with methanol. Prepared catalysts were able to give the highest acid conversion of up to 75% relative to the unmodified MMT K10 revealing the potential of M-MMT K10 as catalyst for esterification in biodiesel production.

**Index Terms**—acid catalyst, esterification, montmorillonite K10, stearic acid, acetic acid, methanol

## I. INTRODUCTION

THE extensive demand for a cleaner environment is forcing the chemical industry to use less hazardous, low cost and environmentally friendly materials. Clay mineral constitutes one of these materials. Clay mineral is a group of aluminosilicates that have been widely used as heterogeneous catalysts for many types of organic synthesis, due to their favourable properties such as low cost, thermal stability, selectivity, large surface area, easily separated as well as environmentally friendly [1].

Clay catalyst was proven to have both the Lewis and Brønsted acid sites. The Lewis acidity is due to the cations at the crystal edges and this acid site can be enhanced by the exchange of the interlayer cations i.e.  $\text{Na}^+$  and  $\text{Ca}^{2+}$  with  $\text{Al}^{3+}$  ion by the reaction of clay with  $\text{AlCl}_3$  solution. While the Brønsted acid character of clays arises mainly due to the dissociation of the intercalated water molecules coordinated to cations [2]. The presence of hydroxyl group (-OH) on the

surface of clay minerals makes it as a hydrophilic material, which can link very easily to the water molecules. The chemical properties of clay minerals such as the acidity which is due to the presence of Lewis and Brønsted acidity, hydroxyl groups, and the type of exchangeable cations, make the clay catalysts as suitable heterogeneous catalysts for many chemicals and industry applications [3].

Among the clay catalyst, MMT is the most studied due to its high abundance and intrinsic acidity. MMT is commercially available in two forms; MMT K10 and MMT KSF. It is the most important smectites with a layered aluminosilicates clay mineral that can be classified as 2:1 type dioctahedral. The MMT clay has been widely used as a heterogeneous catalyst for many of organic reactions and provides several advantages such as high acidity, inexpensive, non-corrosive properties, high yields and selectivity, easy setting, separate from the reaction mixture and easily recovered and reused [4].

The surface modifications of MMT K10 have received attention because this allows the production of new materials which can be used for many applications [5]. There are considerable methods which can be used to modify MMT K10 such as pillaring, acid activation and cation exchange. The acid activated MMT K10 has been used as a heterogeneous catalyst for the esterification of 4-hydroxy benzoic acid (HBA) with three different type of alcohols i.e. methanol, ethanol and propanol to the synthesis of parabens [6]. A study was conducted on the copper(II) ion exchanged MMT K10 and its catalytic activity in the direct addition of N-H bond to the CC triple bond was successfully evaluated revealing an increase in the reactant conversion from 1 to 36 % using the MMT K10 and Cu-MMT K10 respectively [7].

Reference [8] conducted a study on using the cation exchanged i.e.  $\text{H}^+$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ce}^{4+}$ ,  $\text{Yb}^{3+}$ ,  $\text{Sc}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{La}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Na}^+$  on MMT K10 as catalysts for the acetylation of alcohol. The catalysts showed an increasing in the Lewis acid sites monitored by IR using pyridine, acetonitrile and acetone. Among the modified catalysts,  $\text{Fe}^{3+}$ -MMT K10 was the most effective (yield above 92%) towards the acetylation of cyclohexanol with acetic anhydride at room temperature.

Esterification of succinic anhydride to di-(p-cresyl) succinate was conducted over  $\text{M}^{n+}$ -MMT clay catalysts ( $\text{M}^{n+} = \text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{H}^+$ ) [9]. In this study, MMT K10 and p-toluenesulphonic acid were used as catalysts and the catalysts were characterized using XRD and BET surface area. The total acidity was measured

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using n-butylamine titration method. Among the  $M^{n+}$ -MMT catalysts tested,  $Al^{3+}$ -MMT and  $H^+$ -MMT were found to be the most active catalysts for the esterification of succinic anhydride and p-cresol with 75 % yield of esters.

## II. MATERIALS AND METHOD

### A. Preparation and Characterization of M-MMT K10

A series of M-MMT K10 catalysts were prepared by adding 10 g of MMT K10 to 0.25, 0.5, 0.7 and 1 M aqueous solutions of  $Cu(CO_2CH_3)_2 \cdot H_2O$ ,  $AlCl_3$  and  $Fe(NO_3)_3 \cdot 9H_2O$  at 80 °C for 8 hours. Then the slurry was cooled, filtered and washed thoroughly with distilled water. The samples were dried at room temperature, then at 100 °C for 12 hours, followed by calcination at 300 °C for 4 hours [10]. The crystalline phases of M-MMT K10 catalysts were characterized by XRD. XRD analysis was performed through Cu K $\alpha$  radiation. The data in intensity was plotted in a chart based on  $2\theta$  in a range of 5° – 60°. Energy-dispersive X-ray spectroscopy analysis (EDX) (Horiba EMAX model EX 250) was carried out to determine the amount of metals in the MMT K10.

### B. Catalytic Activity

The catalytic activity of M-MMT K10 was measured via esterification of acetic acid and stearic acid with methanol. The reactions were carried out at different temperatures for 3 hours with 2 g of acids in 100 ml of alcohols and 600 mg of solid catalyst. The percentage of conversion of stearic acid to ester was determined by titration with 0.02 M NaOH. The conversion of stearic acid was calculated using this formula:

$$X_{acid} = \frac{a_i - a_t}{a_i} \times 100$$

where ( $a_i$ ) is the initial acidity of at  $t_0$  and ( $a_t$ ) is the acidity at (t). Blank reaction (without addition of catalyst) and reaction catalyzed with unmodified MMT K10 were also tested in this work.

## III. RESULTS AND DISCUSSION

### A. X-ray Diffraction

X-ray pattern of pure and modified MMT K10 with concentration of 0.75 M for each samples are shown in Fig 1. The  $d_{001}$  value of peak at  $2\theta = 8.8^\circ$  indicates the presence of 2:1 (T:O:T) structure [15]. Other peaks at  $2\theta = 20.9^\circ$ ,  $26.6^\circ$  and  $27.8^\circ$  with d spacing 4.23, 3.34, and 3.19 Å, respectively were due to quartz which present as an impurity [11], [12].

The  $d_{001}$  for all modified samples were found to be in the same range to the unmodified MMT K10 and suggested that the interlayer separation of clay was not affected by the introduction of cations into the clay structure [13]-[15]. This is consistent with what has been studied previously where the metal cations were fixed solely on the outer surfaces of the clay and if any inclusion of metal cations occurred, it would increase the d values [16]-[18].

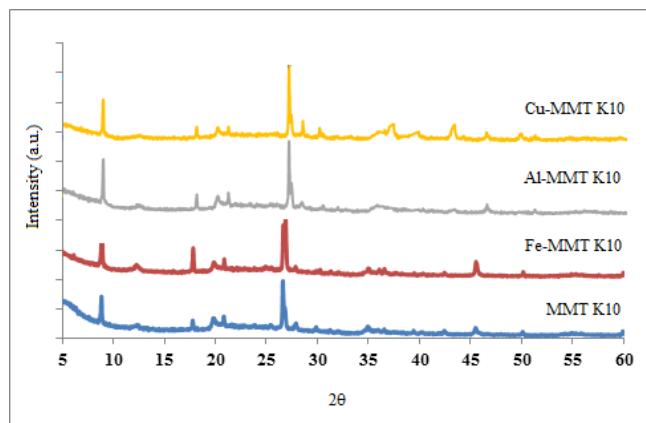


Fig. 1. XRD patterns of MMT K10 and modified samples.

### B. Energy Dispersive X-ray (EDX)

The surface composition (%) of cations from EDX analysis is given in Table 1. From the EDX data, all samples showed Fe and Al as part of elements represented the components of MMT K10. While Cu element was only detected for Cu-MMT K10 sample. The addition of aqueous solutions of  $Al^{3+}$  and  $Fe^{3+}$  had improve the amount of these element in the MMT K10 structure. This suggest that the metal cations were distributed on the surface of MMT K10 clay.

TABLE I  
ELEMENTAL COMPOSITIONS (%) FROM EDX ANALYSIS OF MMT K10 AND MODIFIED SAMPLES

Sample	Fe	Al	Cu
MMT K10	0.63±0.05	4.56±0.10	N.D.
0.25 M Fe-MMT K10	1.39±0.03	4.07±0.42	N.D.
0.5 M Fe-MMT K10	2.06±0.03	4.23±0.13	N.D.
0.75 M Fe-MMT K10	3.09±0.06	4.12±0.27	N.D.
1.0 M Fe-MMT K10	4.92±0.27	3.82±0.27	N.D.
Al-MMT K10			
0.25 M Al-MMT K10	0.56±0.02	4.79±0.19	N.D.
0.5 M Al-MMT K10	0.96±0.10	5.51±0.16	N.D.
0.75 M Al-MMT K10	0.54±0.05	6.75±0.44	N.D.
1.0 M Al-MMT K10	0.70±0.19	7.91±0.22	N.D.
Cu-MMT K10			
0.25 M Cu-MMT K10	0.56±0.12	4.87±0.94	3.44±0.11
0.5 M Cu-MMT K10	0.57±0.09	4.33±0.34	4.52±1.30
0.75 M Cu-MMT K10	0.63±0.05	4.46±0.34	7.91±0.68
1.0 M Cu-MMT K10	0.60±0.48	3.49±0.33	18.86±2.63

N.D.: Not detected

### C. Catalytic Activity

Esterification of stearic acid with methanol and acetic acid with methanol at 80 °C are shown in Figure 2 and 3 respectively. It can be observed that the reaction occurred in the absence of catalyst and unmodified MMT K10 only gave less than 45% of acid conversion for both types of acid used. This explained that the esterification reaction can also occur even in the absence of catalyst, with a small acid conversion value [19]. For the unmodified MMT K10 sample, the presence of Brønsted and Lewis acid sites [20] caused the acid conversion to occur slightly higher than the reaction without catalyst. The modified 0.75 M Cu-MMT K10 catalysts resulted in a high acid conversion for up to 75% and 70% of stearic acid and acetic acid conversion respectively. The high amount of Lewis acid site in 0.75 M Cu-MMT K10 reported by reference [21] was expected to give this good conversion of acids.

There was a noticeable difference between conversion of acetic acid and stearic acid in the esterification with methanol in the presence of catalysts. The stearic acid being a saturated fatty acid gave higher conversion values compared to acetic acid. Stearic acid had a linear structure containing hydrophilic and hydrophobic parts, and the modified catalysts had the hydrophobic property [22]. It was suggested that the hydrophobic part from stearic acid was absorbed onto the catalyst surface to be made available for the reaction. Short chain acid esters are more soluble in water, as water is the byproduct in an esterification reaction, compared to longer chain acid esters, where they lose selectively on refluxing the esterification medium [23].

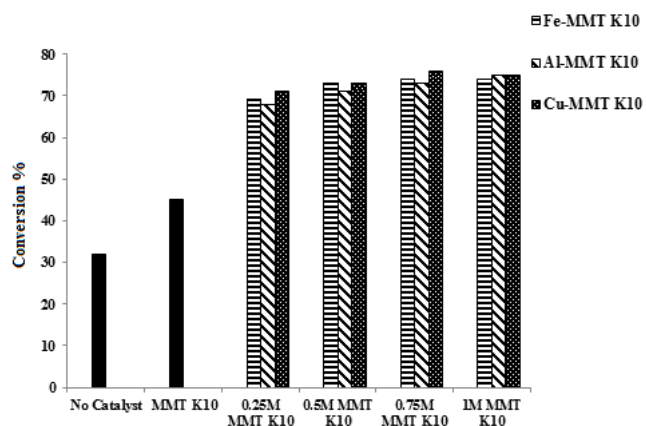


Fig. 2. Effects of catalyst on esterification of stearic acid with methanol at 80 °C after 3 hours of reaction time.

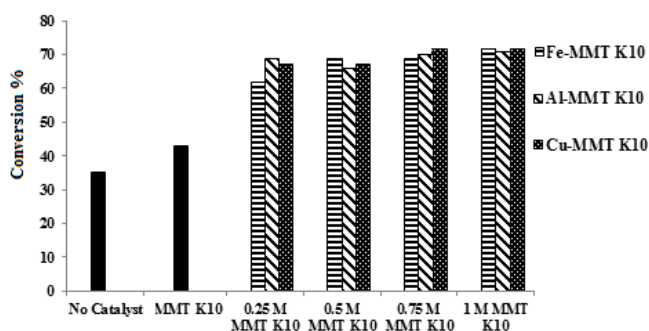


Fig. 3. Effects of catalyst on esterification of acetic acid with methanol at 80 °C after 3 hours of reaction time.

Figure 4 shows the influences of temperature on the esterification of stearic acid with methanol at three different reaction temperatures; 80, 100 and 120 °C. Figure 5 illustrates the influence of temperature on the esterification of acetic acid with methanol at 60, 70 and 80 °C.

For the percentage of stearic acid conversion, there was a significant difference in the conversion of acid with the increase of the reaction temperature from 80 to 120 °C. As shown in Figure 4, at 80 °C the conversion of stearic acid was significantly higher (ca. 78%) than the esterification at 100 °C (ca. 60%) and 120 °C (ca. 70%). This might be due to the alcohol used, as the boiling point of methanol is 64.7 °C and the reaction temperature was achieved under reflux to avoid the vapor loss during the reaction. The stearic acid solubility and miscibility with methanol can be observed at high temperature and thus facilitated the protonation of the carbonyl group of stearic acid and nucleophilic attack of methanol on the acid [24].

From Figure 5, it can be seen that the increase in the reaction temperature had a positive effect on the percentage of acetic acid conversion. The conversion increased with increasing the reaction temperature from 60 °C (57%) to 80 °C (75%). The same trend was also observed for the esterification of acetic acid with ethanol over dodecatungstophosphoric acid supported on MMT K10 and esterification of acetic acid with ethanol over acid activated MMT respectively [19], [25]. As can be seen, the optimum reaction temperature was 80 °C for both acids used (stearic acid and acetic acid).

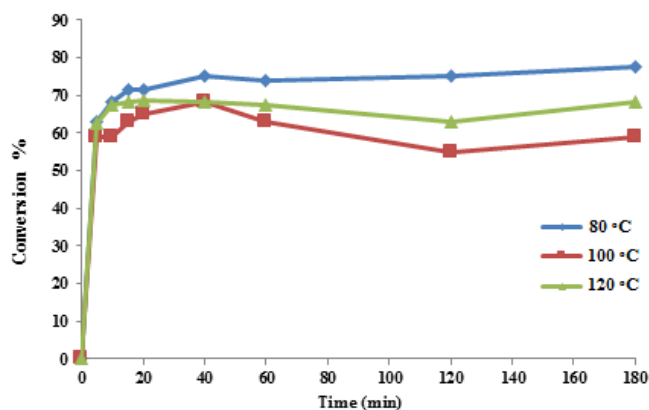


Fig. 4. Effect of temperature on esterification of stearic acid with methanol. Reaction condition: Catalyst; 0.75 M Cu-MMT K10, Reaction time; 3 hours.

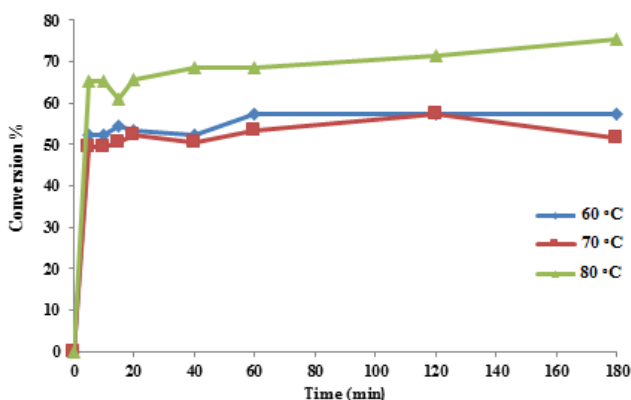


Fig. 5. Effect of reaction temperature on esterification of acetic acid with methanol. Reaction condition: Catalyst; 0.75 M Cu-MMT K10, Reaction time; 3 hours.

#### D. Kinetic Study

The rate of reaction of the change in the concentration of reactant divided by the time interval during which this change was observed. Overall, the rate of the reaction can be written using the following equation:

$$\text{Rate of reaction (R)} = - \Delta [\text{acid concentration}] / \Delta [\text{time}]$$

The rate of the esterification reactions (stearic acid with methanol and acetic acid with methanol) at 80 °C were calculated using this equation and Table 2 shows the results obtained. As can be seen from the table, the rate of reaction using modified MMT K10 was increased compared with the rate of reaction without the catalysts and unmodified MMT K10. This is due to the presence of catalyst and the catalyst can speed up for both forward and reverse reactions involving a final equilibrium state.

TABLE 2

THE RATE OF THE REACTION (IN MOL/L.MIN) USING DIFFERENT CATALYSTS FOR BOTH TYPES OF ACID WITH METHANOL

Catalyst	Acetic acid	Stearic acid
Without catalyst	0.028	0.00020
Unmodified MMT K10	0.023	0.00022
0.75 M Cu-MMT K10	0.03	0.00030

#### IV. CONCLUSION

The results showed that the 0.75 M Cu-MMT K10 was the efficient cation concentration that gave the highest acid conversion for both types of acids. In this work, it was suggested that the stearic acid ester can be synthesized at a high acid percentage using the catalysts prepared from simple and natural clay modified with the earth mineral i.e. Fe, Al and Cu. Furthermore, it required a relatively low temperature i.e. 80 °C and only a short time to achieve maximum conversion. This was in addition to the advantages of clay such as present in abundance, low cost, eco-friendly, and the modification of clay only required simple steps, with the use of clay as a catalyst for many of organic synthesis.

#### REFERENCES

[1] L. Zatta, L. P. Ramos, and F. Wypych, "Acid-activated montmorillonites as heterogeneous catalysts for the esterification of lauric acid acid with methanol," *Applied Clay Science*, vol. 80, 2013, pp. 236-244.

[2] G. Nagendrappa, "Organic synthesis using clay catalysts," *Resonance*, vol. 7, no. 1, 2002, pp. 64-76.

[3] P. Djongoue, and D. Njopwouo, "FT-IR spectroscopy applied for surface clays characterization," *Journal of Surface Engineered Materials and Advanced Technology*, vol. 3, no.4, 2013, pp. 275.

[4] L. J. Krstic, S. Sukdolak, and S. Solujic, "An efficient synthesis of warfarin acetals on montmorillonite clay K-10 with microwaves," *Journal of Serbian Chemical Society*, vol. 67, no. 5, 2002, pp. 325-329.

[5] A. H. Kianfar, W. A. K. Mahmood, M. Dinari, H. Tarrokhpour, M. Enteshari, and M. H. Azarian, "Immobilization of cobalt (III) Schiff base complexes onto montmorillonite K10: Synthesis, experimental and theoretical structural determination," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 136, 2015, pp. 1582-1592.

[6] M. K. Hazarika, R. Parajuli, and P. Phukan, "Synthesis of parabens using montmorillonite K10 clay as catalyst: A green protocol," *Indian Journal of Chemical Technology*, vol. 14, 2007, pp.104-106.

[7] T. Joseph, G. V. Shanbhag, and S.B. Haliligudi, "Copper (II) ion-exchanged montmorillonite as catalyst for the direct addition of N-H bond to CC triple bond," *Journal of Molecular Catalysis A: Chemical*, vol. 636, 2005, pp. 139-144.

[8] K. Shimizu, T. Higuchi, E. Takasugi, T. Hatamachi, T. Kodama, and A. Satauma, "Characterization of Lewis acidity of cation-exchanged montmorillonite K-10 clay as effective heterogeneous catalyst for acetylation of alcohol," *Journal of Molecular Catalysis A: Chemical*, vol. 284, 2008, pp.89-96.

[9] C. R. Reddy, P. Iyengar, G. Nagendrappa, and B. S. J. Prakash, "Esterification of succinic anhydride to di-(p-cresyl) succinate over Mn+-montmorillonite clay catalysts," *Journal of Molecular Catalysis A: Chemical*, vol. 229, 2005, pp. 31-37.

[10] R. D. Aher, M. H. Gad, R. S. Reddy, and A. Sudalai, "CuII-exchanged montmorillonite k10 clay-catalyzed dried carboxylation of terminal alkynes with carbon dioxide," *Indian Journal of Chemistry*, vol. 51, 2012, pp. 1325-1329.

[11] A. Darehkordi, S. S. Hosseini, and M. Tahmooresi, "Montmorillonite modified as an efficient and environment friendly catalyst for one-pot synthesis of 3,4-dihydropyrimidine-2(1H)ones," *Iranian Journal of Materials Science & Engineering*, vol. 9, 2012, pp. 49-57.

[12] J. Sun, T. Gan, H. Zhu, Z. Shi, and Y. Liu, "Direct electrochemical sensing for oxytetracycline in food using a zinc cation-exchanged montmorillonite," *Applied Clay Science*, vol. 101, 2014, pp. 598-603.

[13] N. N. Biniha, P. P. Silija, V. Suraj, Z. Yaakob, and S. Sugunan, "Samarium Ion exchanged montmorillonite for high temperature

cumene cracking reaction," *IOP Conference Series: Materials Science and Engineering*, vol. 17, 2011, pp. 1-8.

[14] A. Jha, A. C. Garade, M. Shirai, and C. V. Rode, "Metal cation-exchanged montmorillonite clay as catalysts for hydroxyalkylation reaction," *Applied Clay Science*, vol. 74, 2013, pp. 141-146.

[15] T. Gan, Z. Shi, J. Sun, and Y. Liu, "Simple and novel electrochemical sensor for the determination of tetracycline based on iron/zinc cations-exchanged montmorillonite catalyst," *Talanta*, vol. 121, 2014, pp. 187-193.

[16] Z. Fang, B. Liu, J. Luo, Y. Ren, and Z. Zhang, "Efficient conversion of carbohydrates into 5-hydroxymethylfurfural catalyzed by the chromium-exchanged montmorillonite K-10 clay," *Biomass and Bioenergy*, vol. 60, 2014, pp. 171-177.

[17] M. Farias, M. Martinelli, and G. K. Rolim, "Immobilized molybdenum acetylacetonate complex on montmorillonite K-10 as catalyst for epoxidation of vegetable oils," *Applied Catalysis A: General*, vol. 403, 2011, pp. 119-127.

[18] K. Song, and G. Sandi, "Characterization of montmorillonite surfaces after modification by organosilane," *Clays and Clay Minerals*, vol. 49, 2001, pp. 119-125.

[19] P. K. Igboke, and F. L. Olebunne, "On the catalytic esterification of acetic acid with ethanol using Nigerian montmorillonite clay: Effect of reaction variables on catalyst efficiency," *Journal of the University of Chemical Technology and Metallurgy*, vol. 46, 2011, pp. 389-394.

[20] F. W. Harun, E. A. Almadani, and S. M. Radzi, "Metal cation exchanged montmorillonite K10 (MMT K10): Surface properties and catalytic activity," *Journal of Scientific Research and Development*, vol. 3, no. 3, 2016, pp. 90-96.

[21] E. A. Almadani, "Metal cation exchanged montmorillonite K10 (M-MMT K10) as heterogeneous catalyst for esterification reaction," Ph.D Thesis. Universiti Sains Islam Malaysia, 2016.

[22] E. A. Almadani, S. M. Radzi, and F. W. Harun, "Stearic acid esters synthesized using iron exchanged montmorillonite K10 clay catalysts," *International Journal of Applied Chemistry*, vol. 12, no. 1, 2016, pp. 62-67.

[23] W. W. Christie, "Preparation of ester derivatives of fatty acids for chromatographic analysis," *Advances in Lipid Methodology*, vol. 2, no. 69, 1993, pp. 111.

[24] K. Saravanana, B. Tyagi, and H. C. Bajaj, "Nano-crysatlline, mesoporous aerogel sulfated zirconia as an efficient catalyst for esterification of stearic acid with methanol," *Applied Catalysis B: Environmental*, vol. 192, 2016, pp. 161-170.

[25] H. Gurav, and V.V. Bokade, "Synthesis of ethyl acetate by esterification of acetic acid with ethanol over a heteropolyacid on montmorillonite K10," *Journal of Natural Gas Chemistry*, vol. 19, no. 2, 2010, pp. 161-164.