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Article

Modification of Montmorillonite K10 with Al^{3+} and its Potential in Biodiesel Production

Siti Mariam Muhamad Sabri[1,a], Syahirah Yahya[1.b], Farah Hanis Razali[1,c], Farah Wahida Harun[2]

[1]*Faculty of Science and Technology, Universiti Sains Islam Malaysia (USIM), Bandar Baru Nilai, 71800 Nilai, Negeri Sembilan, Malaysia.*
E-mail: [a]mariamsabri96@gmail.com, [b]syahirahyahya03@gmail.com, [c]farahhanisrazali@gmail.com

[2]*Frontier Materials Research Group, Universiti Sains Islam Malaysia (USIM), Bandar Baru Nilai, 71800 Nilai, Negeri Sembilan, Malaysia.*
E-mail: farahw@usim.edu.my

***Abstract*— Biodiesel is a green fuel diesel, which is used to fuel compression-ignition engines, same as petroleum diesel. By using waste cooking oil (WCO) as raw material, the production of biodiesel requires two-steps esterification-transesterification reactions involving acid catalyst and basic catalyst, respectively. Most researchers used strong acid (i.e. H_2SO_4) followed by a strong base (i.e. NaOH) to enhance the biodiesel products. However, apart from corrosion potential, these homogeneous catalysts also take extra time and cost for the purification process. To overcome this problem, a bi-functional catalyst is required so that the reactions can undergo simultaneously. In this research, WCO for the production of biodiesel was characterized. A bi-functional catalyst was produced by modification of montmorillonite K10 (MMT K10) clay with Al^{3+} ion creating Al-MMT K10 catalyst, followed by characterization of Al-MMT K10 using temperature-programmed desorption of ammonia (TPD-NH_3) and scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM/EDX). Lastly, the catalytic activity was examined by producing biodiesel known as fatty acid methyl ester (FAME) with conditions 10:1 to 14:1 (mol ratio of methanol : WCO), 2 to 4 wt. % of catalyst loading, 4 to 6 hours reaction time and 90 to 130 °C reaction temperature using GC-FID. After modification, the weight percentage of Al in MMT K10 was increased by 0.8 % and the acidity was increased by 1200.97 µmol/g NH_3. By optimizing the parameters using 6 % Al-MMT K10 at 110 °C with 12:1 (methanol:WCO) within 6 hours reaction, 42.47 % acid conversion and 40 % of FAME yield was achieved. It is expected that up to 80 % of biodiesel can be achieved by optimizing the Al composition in MMT K10 clay. In conclusion, Al-MMT K10 was successfully acted as bi-functional catalyst for esterification and transesterification of WCO in biodiesel production.**

***Keywords*— Waste cooking oil; Biodiesel; Al-Montmorillonite K10.**

I. INTRODUCTION

Currently, natural gas, coal and petroleum are the main sources in petrochemical reservoirs to meet the requirements of energy throughout the world. Due to the continuously increasing demand on energy, the sustainability was concerned towards alternative fuels. Year by year, petroleum supplies were slowly depleted and became the factor of arising in price [1]. Instead of unsustainable characteristic, there are about 85 % of floating particulates generated from fossil fuel combustion [2]. This phenomenon does not only affect the environment, but also harmful to human health.

This issue digged an interest among researchers to find an effective way to produce renewable fuels [3]-[4]. An alternative energy that not only environmental friendly, but also renewable and economic are essential to overcome the energy crisis regarding the use of petroleum rather than ensuring the sustainability of the resources. Recently, the worldwide interested in the development of biodiesel due to global warming effect, fossil fuel diminishing reserves and expensive petroleum [1]. Biodiesel is considered as a potential fuel to substitute the petro-diesel fuel. Hence, today biodiesel has been extensively produced and commercialized as biofuel because its properties are close to diesel [5]. Biodiesel is a promising alternative to petroleum-based fuels because it is produced from renewable sources, biodegradable, non-toxic and emits less polluting gases during combustion [6].

The development of biodiesel makes it ranked among the fastest developing alternative to petroleum in many developing countries. For example, US government and most of EU countries had successfully implemented the uses of B100 in their countries [7] while our neighbour country, Indonesia utilized B20. President Joko Widodo has given a mandatory to make use the biodiesel blended fuels for all vehicles and heavy machinery starting on 1 September 2018 [8]. Unfortunately, Malaysia is still using a B5 combination of fossil fuels, which is too far behind compared to other countries. This occurred due to the expensive raw material; palm oil [9].

Instead of palm oil, biodiesel is produced via esterification and transesterification of a mixture of alkyl esters of fatty acid obtained from renewable bio-resources like rapeseed oil [10], jatropha oil [11], vegetable oil [12], palm oil [13], corn oil [14], coconut oil [15], soybean oil [16] and waste cooking oil (WCO) [17]. Among of these raw materials, WCO is the most cost-effective to be used in biodiesel production because it is easy to get and economic to be acquired either from domestic or restaurants. However, WCO from different sources give different characteristics and properties. For examples, the acid value of fast-food origin oil was higher (17.85 mg KOH/g) than those from hospitals (1 mg KOH/g) [18].

In order to produce biodiesel, many researchers converted the WCO via two steps esterification-transesterification reactions [19]-[20]. However, this method is less efficient since it requires two types of catalysts; acid and base and two consecutive steps, which take a long period to complete the reactions. Aside from that, the high value of free fatty acid (FFA) gives high risk to saponification if a base catalyst is used. This leads to low yield of biodiesel. Most researchers used strong acid such as sulphuric acid followed by a strong base such as sodium hydroxide to enhance the activity. Besides their corrosive potential, these homogeneous catalysts take extra time and cost for the purification process [21]-[23]. Hence, the efficient way to use WCO as the feedstock in biodiesel production, a bi-functional catalyst that has no hydroxyl group is recommended.

Therefore, in this study, WCO obtained from several restaurants were taken into consideration to be converted into biodiesel. The characteristics and properties of WCO were analysed prior further reaction. In order to speed up the reaction, montmorillonite K10 (MMT K10) clay as catalyst was modified with Al^{3+} to produce Al-MMT K10. Al had been chosen due to the high density cation thus acidity can be imparted in the clay [24]. Al-MMT K10, which consists both Lewis and Bronsted acid sites, was expected can undergo esterification-transesterification simultaneously without any soap burden. In addition, this heterogeneous catalyst can be separated easily without leaching in the sample product.

II. MATERIALS AND METHODS

A. Materials

Samples of WCO were collected from several local restaurants near Universiti Sains Islam Malaysia (USIM). The samples from different restaurants were mixed thoroughly prior to further analysis. Montmorillonite K10 and $AlCl_3.6H_2O$ were purchased from Sigma-Aldrich and Fisher Scientific, respectively.

B. Methods

1) WCO Characterization: The saponification value (SV) and acid value (AV) of WCO were determined according to Knothe and Odoom [24], who followed AOCS Methods Cd 3-25 and EN 14104 respectively [25]. From the results obtained, SV and AV were used to calculate ester value (EV) [26] and MW [27] while the % FFA was obtained from half of AV [28]. Water and sediment contents were determined according to Hasan et al. [5] by heating and filtering methods and the density was calculated by dividing the mass of WCO to its volume.

2) Modification of Catalyst: 30 g of MMT K10 was stirred with 480 ml of 1 M $AlCl_3.6H_2O$ at 80 °C for 7 h. Then, the covered mixture was left at room temperature for overnight, followed by filtering and washing with distilled water to remove excess ions. The sample was dried at 100 °C for overnight before being calcined at 300 °C for 6 h [21].

3) Catalyst Characterization: SEM/EDX for MMT K10 and Al-MMT K10 were analysed by using Hitachi SU 1510. The morphology was analysed with magnification 1500x at 15 kV. For acidity, the desorption of NH_3 has been analysed by using TPD/R/O Puls Chemisorptionsent 1100. The pretreatment stage was done by using N_2 gas with flow rate 20 cm^3/min and the oven temperature starting at 50 °C, 10 °C/min ramp, hold for 20 min and stop at 150 °C. The analysis stage was done by using He gas with flow rate 30 cm^3/min and oven temperature starting at 50 °C, 10 °C/min ramp, hold for 30 min and stop at 950 °C.

4) Catalytic Activity: The esterification-transesterification reaction of WCO with methanol was carried out by reflux at varied conditions: 10:1 to 14:1 (methanol:WCO mole ratio); 90 °C to 130 °C; 2 to 6 wt. % catalyst loading; and 4 h to 8 h reaction time at fixed agitation; 300 rpm.

Percentage acid conversion was determined by titration method and calculated as in Equation 1 while the FAME product was analyzed by using Gas Chromatography with Flame Ionization Detection (GC-FID) and the percentage yield (% yield) was calculated as in Equation 2.

$$\% \, Acid \, Conversion = \frac{AV_i - AV_f}{AV_i} \, X \, 100 \qquad (1)$$

Where AV_i for initial acid value before reaction while AV_f for final acid value after reaction.

$$\% \text{ yield} = m_{FAME} / m_{WCO} \text{ X } 100 \, \% \qquad (2)$$

Where m_{FAME} is mass of FAME obtained from GC-FID while m_{WCO} is mass of WCO measured before reaction.

III. RESULTS AND DISCUSSION

A. WCO Characterization

Table 1 shows the results of acid value (AV), saponification value (SV), ester value (EV), molecular weight (MW), % free fatty acid (FFA), density, water and sediment contents of WCO.

TABLE I
CHARACTERISTICS OF WCO

Properties of WCO	**Value**
AV (mg of KOH/g)	8.70 ± 0.03
SV (mg of KOH/g)	204.74 ± 0.2
EV (mg of KOH/g)	196.04
MW (g/mol)	858.50
% FFA (%)	3.97 ± 0.01
Density at 20 °C (g/ml)	0.91 ± 0.0002
Water content (%)	0.14 ± 0.0061
Sediment content (%)	2.86 ± 0.01

According to Table 1, it was found that the SV of WCO was 204.74 ± 0.2 mg KOH/g oil while AV was 8.70 ± 0.03 mg KOH/g. Considering that SV and AV were correlated to MW and EV, so the results were calculated theoretically producing 858.5 g/mol and 196.04 mg KOH/g respectively, while % FFA was determined by half AV producing 3.97 ±

0.01 %. The identification of FFA content become one of the most important steps in this study since FFA content will affect the transesterification process [11]. Moreover, the number of AV is important to determine the process takes place and the type of catalyst required to produce biodiesel. It is worthy to evaluate the ester value of a sample because it indicates the actual quantity of glycerides that contained in it. Aside from that, density of raw materials also gives impact to the product specification. For example, Chhetri et al. [29] found that the density of WCO (90 g/cm^3) resulting to 87 g/cm^3 biodiesel and met the ASTM specification. Any used cooking oil should contained moisture and insoluble sediments, which came from the food fried. According to Table 1, water and sediment contents found at 0.14 % and 2.86 % respectively. These contaminants must be eliminated by heating and filtering before any further reaction.

B. Catalyst Characterization

The SEM micrograph of the MMT K10 and Al-MMT K10 with 1500x magnification at 15 kV are shown in Fig. 1. The morphologies obviously show that the surface of Al-MMT K10 has non-aggregated morphology [30]. By comparing both surfaces, the morphology of modified clay not really changed the original surface. Instead of the readily exist in MMT K10 reason, Al was undergone homogenisation process with the MMT K10 due to high temperature effect during calcination step [31]. According to a previous study, Almadani et al. [21] also found that the morphology of modified MMT K10 has not really changed the original surface after being exchanged with Al^{3+}.

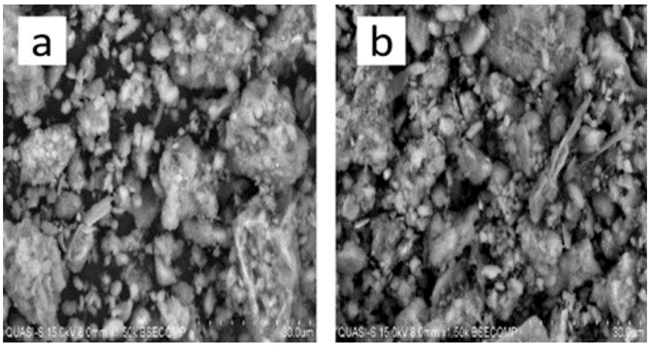

Fig. 1 SEM images of a) MMT K10 and b) Al-MMT K10

Fig. 2 shows the elements presented in both MMT K10 and Al-MMT K10. The weight percentage of Al increased from 4.41 % in MMT K10 to 5.84 % in Al-MMT K10 and this proved that metal cation is exchanged in the modified MMT K10. The decreasing of K and Fe elements indicating ions that successfully exchanged with Al^{3+} to balance the charge.

As the composition of Al differed from the original MMT K10, the acidity also differed. Even though Al carries Lewis acid characteristics [24], the addition of Al composition not only affected the weak acid site but also strong acid sites (Table II). All of the acid sites getting increased, thus raising the amount of NH_3 desorption by 1200.97 µmol/g. In contrast, Luna et al. [32] who modified MMT with Al found that the NH_3 desorption was increased by 436 µmol/g from the original MMT. The difference in modification by pillaring method was detected while the calcination temperature was higher (500 °C) compared to this study (300 °C).

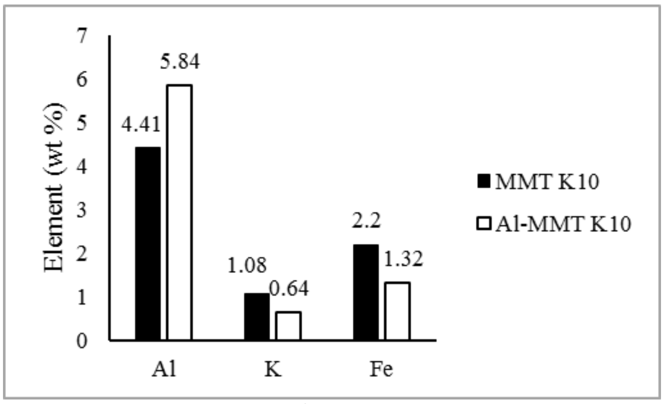

Fig. 2 Element (wt %) of MMT K10 and Al-MMT K10.

TABLE II
DISTRIBUTION OF ACTIVITY IN MMT K10 CATALYST USING TPD-NH_3 ANALYSIS

Type of Catalyst	**NH_3 desorption (µmol/g)**			**Total NH_3 Desorption (µmol/g)**
	Below than 200 °C	**Moderate**	**Above than 600 °C**	
	Weak Acidity	**Moderate Acidity**	**Strong Acidity**	
MMT K10	89.62	-	426.89	516.51
Al-MMT K10	583.36	-	1134.12	1717.48

C. Catalytic Activity

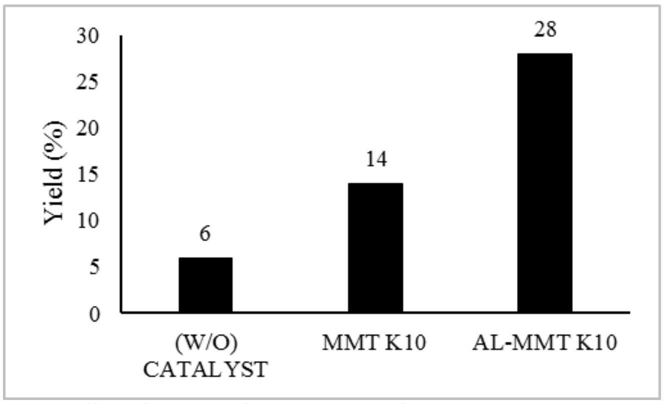

Fig. 3 Effect of absence of catalyst, unmodified MMT K10 and Al-MMT K10 on biodiesel production.

The activity of Al-MMT K10 was studied by comparing its efficacy with unmodified MMT K10 and reaction without catalyst. The results at fixed condition (110 °C, 4 wt%, 12:1, 6 h) were compared and summarized in Fig. 3. It can be concluded that the reaction still occurred in the absence of catalyst and unmodified MMT K10, however, lower result were obtained compared to Al-MMT K10, which were 6 %, 14 % and 28 % respectively. It proved that modification of MMT K10 with Al^{3+} ion gave an improvement impact towards esterification-transesterification reaction.

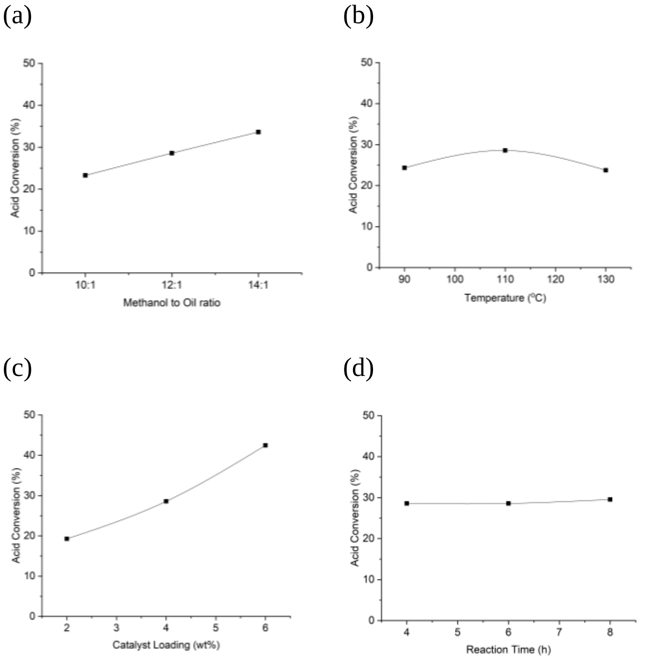

Fig. 4 Effect of (a) mole ratio; (b) temperature; (c) catalyst loading and (d) reaction time on % acid conversion.

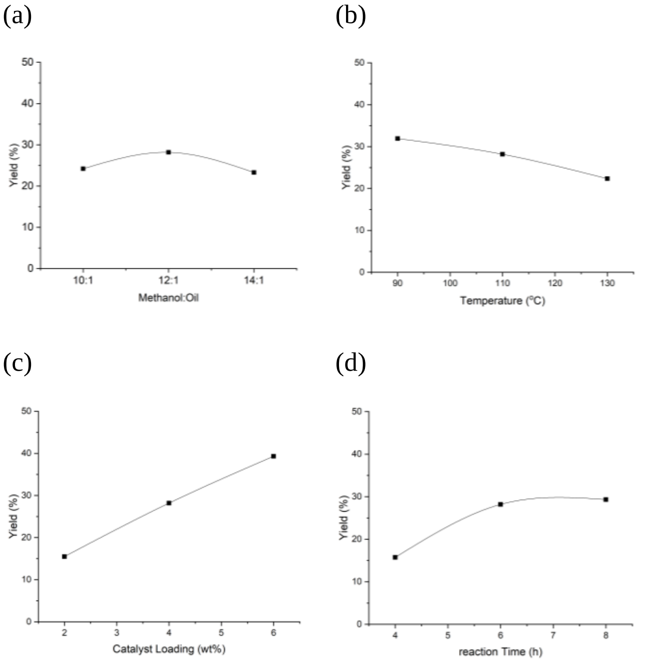

Fig. 5 Effect of (a) mole ratio; (b) temperature; (c) catalyst loading and (d) reaction time on %yield of biodiesel.

In order to study the optimum activity of Al-MMT K10, the influence of methanol to oil ratio, reaction time, temperature and catalyst loading on the % acid conversion and % yield were investigated and the results were illustrated in Fig. 4 and Fig. 5. From Fig. 4, it was observed that the maximum acid conversion was 42.47 % from 8.70 % FFA content in WCO using 6 wt% Al-MMT K10. It was only a small contribution towards biodiesel product while the remaining yield was expected obtained from triglyceride conversion.

From the results, it shows that the temperature not really gave the significant effect on acid and triglyceride conversion to produce biodiesel yield. This was probably due to the optimum temperature and reaction time was already achieved. In comparison, Silva et al. [33] found that the optimum temperature of MMT K10 in catalytic acetylation was 120 °C. Negm et al. [34] used sulphonated phenyl silane MMT K10 to produce biodiesel from jatropha oil. It was found that the conversion increased to 76.5 % at 90 °C and continuously increased up to 98 % at 110 °C before fluctuated to 93.5 % at 120 °C.

In contrast, catalyst loading seemed to give a significant effect towards acid and triglyceride conversion when the results keep increasing without shifting. It was assumed that the high % acid conversion and % yield probably produced in the presence of high amount of catalyst. This could be explained by the increasing number of active sites available for forward reaction.

Individually, methanol to oil ratio was more significant to the acid conversion compared to the yield production. This was probably due to the more solubility of FFA in methanol compared to triglyceride. The rich methanol medium could increase the solubility of FFA in methanol to allow more contact surface between reactants consequently accelerating the reaction rate [35]. Reaction time was not very significant to acid conversion due to the small content of FFA in WCO. The reverse reaction took place immediately after a while. Contrary to the yield percentage, which mainly contributed by triglyceride. More reaction period required to complete the triglyceride conversion.

IV. CONCLUSIONS

The presence of the Al-MMT K10 as heterogeneous catalyst contributed to the effectiveness as bi-functional catalyst of biodiesel production from WCO. The value of % FFA or acidity of WCO are no barrier to produce biodiesel because Al-MMT K10 able to undergo both esterification and transesterification reactions simultaneously. However, higher yield up to 80% is believed can be produced by optimizing the Al^{3+} exchanged during MMT K10 modification process. Hence, it is recommended to increase the concentration of Al^{3+} as well as the period of ion-exchange so that more Al^{3+} ion can exchange into the MMT K10. The higher amount Al^{3+} exchanged in the MMT K10 can increase the acidity effect. Moreover, the optimization of biodiesel can also be done by altering the parameter range. Kulkarni and Dalai [38] studied a review about economical source (WCO) for biodiesel production and found that the favourable conditions in the production of biodiesel from WCO using Lewis acid catalyst were 1:12 (WCO:methanol), temperature ranged 200 °C to 250 °C with pressure 400 psi to 600 psi within 200 minutes and the product could achieved around 87 % to 94 %. Hence, it is recommended to conduct the reaction in a reactor to withstand the conditions as well as activate the Lewis acid site in order to promote transesterification reaction. Otherwise, the reaction can also be conducted by microwave irradiation as done by Ramesh et al. [39]. It is expected that by optimizing the MMT K10 modification and method of biodiesel production can optimize yield up to more than 80 %.

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