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Conversion of Waste Cooking Oil to Biodiesel Catalysed by ZnAl Layered Double Hydroxide

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In this study, the catalyst ZnAl layered double hydroxides (LDH) were successfully being synthesised with molar ratios 4:1 and 3:1 via free-alkali method by using ammonia solution instead of sodium hydroxide. The catalyst has been characterised before and after calcination by using XRD, TGA, SEM, BET and FT-IR. Based on the XRD result, the crystalline peak was successfully obtained and collapsed into mixed oxides of zinc oxide after the calcination. The carbonate decomposition was analysed by TGA to confirm the decomposition temperature of carbonate anions which is 250 °C. The surface area performed by BET showing an increasing from 213 m^2/g to 224 m^2/g on ZnAl LDH. Carbonate anions were confirmed by FT-IR result which are at 1390 cm^{-1} and 856 cm^{-1}. 1 wt% of calcined ZnAl LDH catalyst has been used in the transesterification reaction using waste cooking oil (WCO). The compositions of biodiesel that has been detected using GC-FID are laurate, myristate, palmitate, linoleate, and stearate.

Keywords: alkali-free; ZnAl layered double hydroxide; waste cooking oil; transesterification

I. INTRODUCTION

An alternative fuel is very essential in today's industrial scenario due to the concern towards environmental health and safety. In the new global economy, fuel oil has become the central issue for steep market prices. Unfortunately, the fossil fuel keeps declined and predicted to be depleted soon (Aarøen *et. al.,* 2021; Deng *et al.,* 2020). This issue should require better alternative energy (Gaurav *et al.,* 2016). The biodiesel production from vegetable oil is relatively easy and possess various environmental enhancements (Sahar *et al.,* 2018). However, the major problem with this kind of oil is the high cost due to demand has increased massively (Keller *et al.,* 2020).

The most ubiquitous technique used for production of biodiesel is transesterification reaction (Sahar *et al.,* 2018). Biodiesel production by transesterification catalysed by homogeneous (acid and alkali) or heterogeneous catalyst (acid, alkali and enzyme) (Bukhtiyarova, 2019). Homogeneous catalysts can be base catalysts, such as sodium hydroxide (NaOH) and potassium hydroxide (KOH), or acid catalysts, such as sulphuric, sulphonic and phosphoric. Base catalysts reaction are preferable due to its higher catalytic activity and lower cost. However, base catalyst can react with free fatty acid (FFA) present in the feedstock during the transesterification which lead to the formation of soap by saponification. Therefore, the catalyst may be consumed and reduce its efficiency (Cao *et al.,* 2016). Waste cooking oils (WCO) is one of the alternative ways to decrease biodiesel production cost (Gaurav *et al.,* 2016).

Nevertheless, catalyst with alkali consumption can be difficult when the free fatty acid (FFA) content is high, despite the biodiesel yield and purity of the product is elevated (Bukhtiyarova, 2019). The challenge of high FFA content can be removed by esterification using sulphuric acid and methanol (Shan *et al.,* 2018). In this process, heterogeneous catalysts that plays vital role to avoid saponification process occur and to prevent from massive from corroding the reactor. Consequently, heterogeneous catalysts such as metal oxides, mixed oxides, supported alkali metals, zeolites and hydrotalcites have been widely

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studied to replace homogeneous bases due to their less corrosion, easy separation and low environmental pollution.

Hydrotalcite is one of the heterogeneous catalysts, also known as layered double hydroxide (LDH) and belongs to a class of anionic clays (Figure 1). The general formula of hydrotalcite is $[M(II)_{1-x}\ M(III)_{x}\ (OH)_{2x+}\ (A^{n-}{}_{x/n})$. mH2O (Bujok *et al.,* 2020) (Liu *et al.,* 2015), where MII and MIII resemble the divalent and trivalent metal cations (Elhalil *et al.,* 2018). The formula A^{n-} in the interlayer is indicated as the intercalation anions, which is to stable the excess positive charges (Liu *et al.,* 2015). In the interlayer space, carbonate is located in it which to balance the anions charge (Liu *et al.,* 2015). Divalent and trivalent cations can be used in their synthesis, e.g. Zn^{2+}/Al^{3+}, and x, trivalent cation degree of substitution can take values in the range $0.2 \leqslant x \leqslant 0.33$ (Woodford *et al.,* 2012). Co-precipitation is the most common technique used to prepare the hydrotalcite which involve the pH regulators. Recently, alkali-free method is introduced in the preparation of hydrotalcites to avoid alkali-contaminant and sodium entrain in the catalyst backbones (A.Tajuddin *et. al.,* 2018; Tajuddin *et al.,* 2019). In this method, ammonia and ammonium carbonate have been used instead of sodium hydroxide.

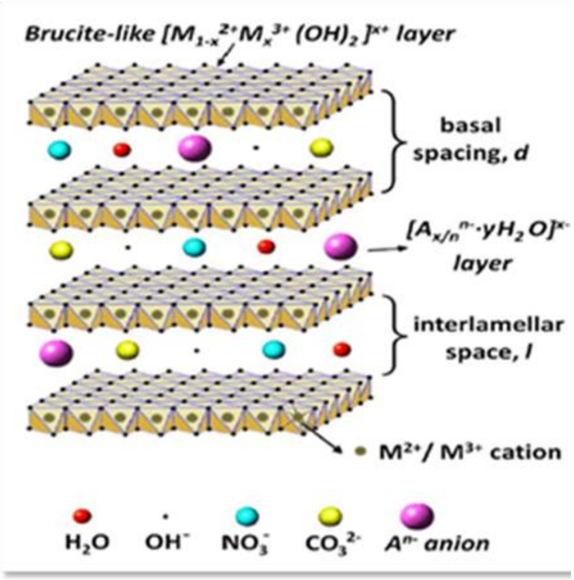

Figure 1. Cross-section of layered double hydroxide structure adapted from (Liu *et al.*, 2015).

The LDHs structure can be improved through rehydration process known as "the memory effect" (Elhalil *et al.,* 2018) when it is exposed to water as the hydroxide anions replace carbonate in the interlayer space. LDHs have many attractive properties such as flexibility, anion exchangeability and biocompatibility (Theiss *et al.,* 2016). Among them, one of the most important properties for LDH is their excellent anion exchangeability. The aim of this study is to design an alkali-free heterogeneous catalyst mainly Zn Al hydrotalcite and to be exposed in transesterification reaction of waste cooking oil.

II. MATERIALS AND METHOD

A. Catalyst Synthesis

LDHs was prepared with addition of mixed metal solutions of 29.75 g zinc nitrate ($Zn(NO_3)_2.6H_2O$) and 37.52 g of aluminium nitrate nonahydrate ($Al(NO_3)_3.9H_2O$) in 100 mL of volumetric flasks and was labelled as solution A (3:1 ratio) (Mahjoubi *et al.,* 2017). 19.22 g of ammonium carbonate $(NH_4)_2CO_3$ was dissolved in 100 mL of distilled water. The pH 10 was kept constant by the addition of 0.5 M buffer ammonium carbonate $(NH_4)_2CO_3$. The final products were washed several times with distilled water and then dried for 5h at 100 °C. Parts of the synthesised products was calcined at 250 °C for 5h and was cooled under a flowing stream of wet nitrogen (100 ml min^{-1}, relative humidity 95%) before catalyst testing (Zhao *et al.,* 2016). The similar steps has been taken to synthesise 4:1 Zn:All ratio except the weight of Zn and Al has been adjusted to fit this particular ratio.

B. Catalyst Characterisation

X-ray diffraction (XRD) was used to obtain information on crystalline structure on the catalyst. The XRD measurements were performed on Philips X'Pert Pro Super X-ray diffractometer equipped with and X'Celerator detection system and CuK alpha radiation (40 kV and 30 mA) was used as the X-ray source. Scans were performed over the 2° range of 10° - 80°.

Thermal gravimetric analysis (TGA) was conducted on the as-synthesised catalyst to obtain the temperature of carbonate anions started to decompose. The temperature was raised from 25°C to 300°C with a heating rate of 10°C per minutes. TGA analysis was performed in an oxidative atmosphere (inert gas mixtures) with a linear temperature ramp.

A scanning electron microscope (SEM) was conducted on the catalyst fresh and calcined catalyst to obtain the morphology of the catalyst. The SEM images were obtained from a JSM-6700F field emission (FE) microscope operating at 15kv which fitted with Energy Dispersive X-Ray Spectroscopy (EDX). Brunauer–Emmett–Teller (BET) analysis provide precise specific surface area of the ZnAl LDH catalyst by nitrogen multilayer adsorption measured as a function of relative pressure using a fully automated analyser. LDHs was degassed at 100 °C and 300 °C for 2h, respectively. The formation of channels and pores are due to water and carbonate anions removal during the calcination process which give the access of N_2 molecules therefore, increase the surface area of the catalyst (Boukhalfa *et al.,* 2017). The infrared spectra were obtained on Jasco FT-IR-460 spectrometer in range of 4500-900 cm^{-1} using KBR pellet technique.

C. Biodiesel Production

1. Pretreatment of waste cooking oil (WCO)

Waste cooking oil was treated to get rid of the impurities such as free fatty acid (FFA) water (Abdul Raqeeb, 2015). Saponification can be formed when water is presence in the oil and a high FFA content (Gebremariam & Marchetti, 2018). This will cause catalyst consumption and the production of biodiesel will be low (Abdul Raqeeb, 2015). The treatment of WCO was started with centrifuge then filtered to remove the cooked food. Next, determination of acid value by acid base titration and moisture content of the waste cooking oil were obtained.

To determine the free fatty acid (FFA) content, 1 g of oil was dissolved in 25mL of ethanol and 25 mL of diethyl-ether with a few drops of phenolphthalein was added as indicator. The titration process was stopped when the solution turned into light pink colour. The acid value (AV) was calculated using the equation:

$$\text{AV (mg KOH/g)} = \frac{56.1 \times C(KOH) \times V(KOH)}{\text{Mass of oil}}$$

Where: 56.1 is the MW of the KOH

V(KOH) is volume of KOH consume during titration

C(KOH) is the concentration of KOH

2. Transesterification Process

25 g of waste cooking oil was poured in a three-necked round bottom flask equipped with a reflux condenser and cool-water chiller. The waste cooking oil was heated at 100˚C for 30 min to remove traces of water. Mixture of methanol to oil ratio used for this process was 15:1 with 5 % base catalyst were added and reaction was ran at 65 ˚C at 24 h. The reaction mixture was transferred into the separating funnel. The biodiesel from the upper layer was collected and the bottom layer of oil was discarded. The rotary evaporator was used to completely remove the glycerol leaving only biodiesel. The final product which is biodiesel was characterised by using Gas Chromatography (Agilent Technologies 6890N) equipped with Flame Ionisation Detector (FID) and 30m x 250 µm HP5-MS capillary column. The injection port was furnished with split mode (40:1) with 250 °C injection port temperature. The column temperature was initially set at 100 °C and increased until 290 °C at 40 °C min^{-1}. The carrier gas flow was 30 ml s^{-1} and the detector temperature was fitted at 250 °C.

III. RESULT AND DISCUSSION

A. Catalyst Characterisation

Thermal stability before calcination of the ZnAl LDH catalyst was first investigated to the determine the right temperature of decomposition of CO_3^{2-} on LDH sample. Figure 2 shows the TG-DTG curves obtained for the ZnAl LDH of molar ratio 4:1 which indicating two main weight loss stages. The first transition associated with the loss of water (dehydration) that occurs around 100-150 °C. Meanwhile, a second transition was observed around 250 °C corresponds with the decomposition of the carbonate anions and decarboxylation/dihydroxylation of the LDH sheets with mass loss 84.64 %. This temperature indicates the brucite-like layers start to collapse and CO_3^{2-} interlayer decomposed to yield CO_2. This temperature was used as a key indicator for a right calcination process.

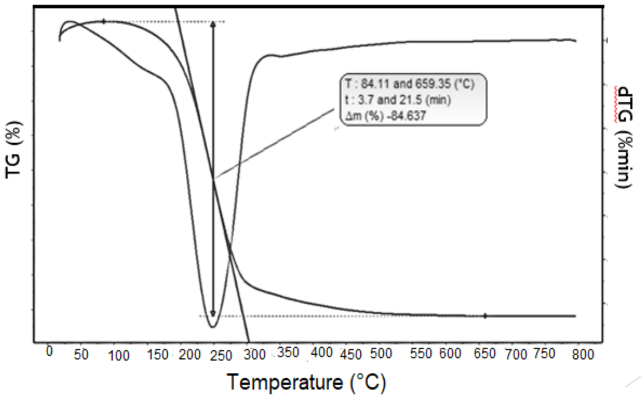

Figure 2. The TGA/dTG profiles during decomposition of ZnAl LDHs 4:1 from 50-800 °C.

The XRD was successfully conducted on catalyst before and after calcinations. Based on the XRD patterns of as-synthesised catalyst shown in Figure 3, the basal planes of (003), (006) and (009) peaks are at low 2θ angles meanwhile the basal plane of (101), (015), (0012) (110) and (113) planes are at high 2θ angles (Seftel *et al.,* 2018). This shows that the catalyst are highly crystalline materials since the peaks are relatively sharp.

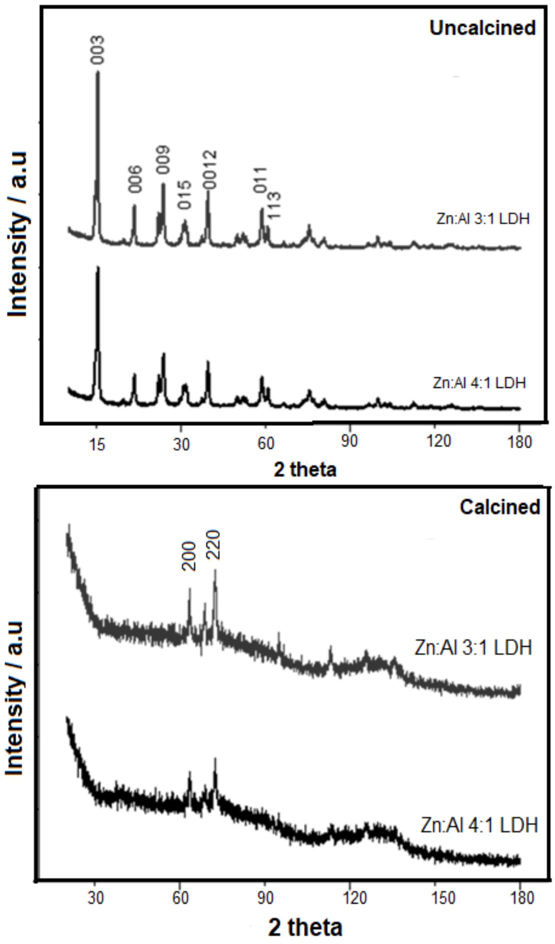

Figure 3. The XRD patterns of uncalcined and calcined ZnAl LDHs with ratio spanning from 3:1 to 4:1, respectively.

The unit cell parameters and the crystallite size for the ZnAl LDH were obtained, and the result are listed in Table 1. The c parameter corresponds to three times the distance between adjacent brucite-like layers, and the parameter is almost the same as that of brucite for which a = 3.10 Å. The basal spacing corresponds to CO$_3^{2-}$ containing LDHs. These values are in the literature range (Starukh *et al.,* 2016). ZnAl LDH was calcined in air at 250 °C for 4 h to obtain a mixture of zinc and aluminium oxides. The XRD patterns of calcined ZnAl LDH shows formation of metal oxides ZnO and ZnAl$_3$O$_4$ corresponding to 200 and 220 reflections (Boukhalfa *et al.,* 2017).

Table 1. Structural parameters of ZnAl LDHs

Parameters	**Value**
Lattice parameter a = $2d_{110}$, Å	3.074
Lattice parameter c = $3d_{003}$, Å	22.8
Basal spacing d003, Å	7.60
Interlayer distance *a*, Å	2.8
Crystallite size, Å	172

The SEM images of the sample studied are presented in Figure 4 where it shown a structure with irregular edges (Seftel *et al.,* 2018). The calcined ZnAl LDH sample retains platelet shape with exhibited the characteristic hexagonal plate-like of anionic clays. This further demonstrated that amorphous formation of HTs was succefully gained after calcination as proven and aligned with XRD results.

The surface area of ZnAl LDH catalysts were investigated by using the N_2 adsorption/desorption technique. Figure 5 shows the N_2 sorption isotherms of uncalcined and calcined Zn:Al 4:1 LDH. The isotherms represent type IV hysterisis with resembles the mesoporous absorbent and pore wider more than 4 nm. The specific surface area of calcined ZnAl LDH of molar ratio 3:1 and 4:1 increased from 213 m^2/g to 224 m^2/g, respectively.

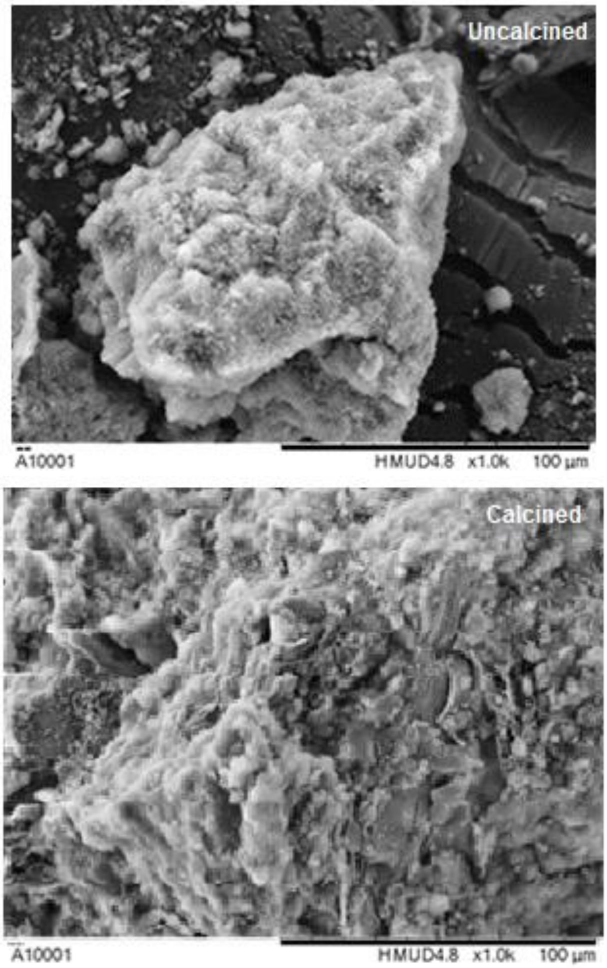

Figure 4. SEM images of Zn:Al 4:1 LDH of uncalcined and calcined at 100 µm magnification.

The formation of channels and pores are due to water and carbonate anions removal during the calcination process which give the access of N_2 molecules therefore, increase the area of the catalyst (Boukhalfa *et al.,* 2017). The presence of carbonate anions in LDH structure can be proved by FT-IR spectroscopy. The IR spectra of the uncalcined ZnAl LDH and its calcined forms are presented at Figure 6. For both spectrums, the broad absorption around 3456 cm^{-1} and 3467 cm^{-1} are assigned to O-H stretching of water molecules in the brucite-like layers (Zhang *et al.,* 2013). The stretching and bending modes of CO_3^{2-} are observed at 1390 cm-1 and 856 cm^{-1} for unclacined LDH. In additions, the peak at 990 cm^{-1} and 639 cm^{-1} can be assigned to the interaction of CO_3^{2-} with the brucite-like layers (Starukh *et al.,* 2016). In the case of calcined LDHs, the bands at 1384 cm^{-1} are due to residue bulk polydentate carbonates. Thus, the crystal-layered structure is destroyed after calcination of LDHs as was confirmed with the XRD patterns as shown in Figure 2.

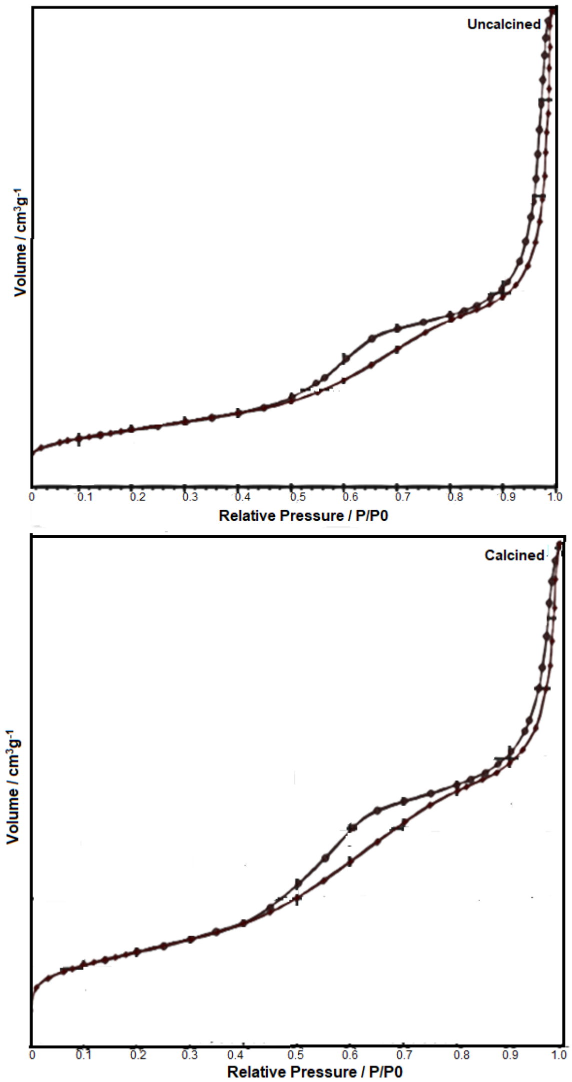

Figure 5. N2 adsorption/desorption of isotherm linear plot of uncalcined and calcined ZnAl 4:1 LDH

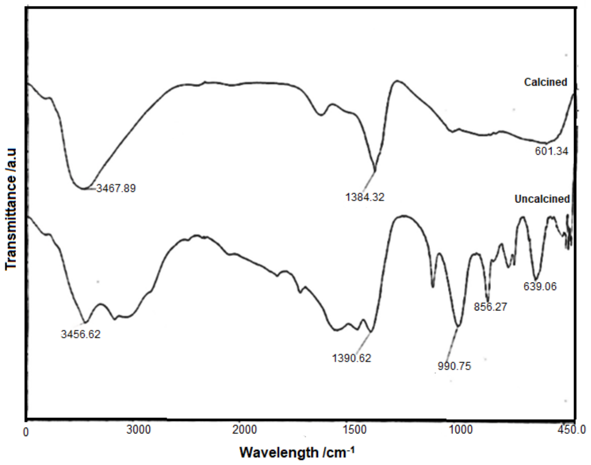

Figure 6. FTIR spectra of calcined and uncalcined Zn:Al 4:1 LDH

B. Biodiesel Production

The transesterification reaction was done by using the calcined ZnAl LDH which react as solid base heterogeneous catalyst. Prior to that, the acid value of the WCO was determined in order to obtain the acid content present in the WCO. The acid value, fatty acid and water content of waste cooking oil sample obtained in acid-base titration was tabulated in Table 2. It shows that the acid value and FFA of untreated WCO obtained were lower than previous study done by Sahar *et al.* (2018) which is 0.9665 mg KOH/g WCO and 0.39% WCO respectively. Therefore, there is no requirement for the two step reaction processes (esterification and transesterification) to be done here, hence can proceed to biodiesel production under tranesterification only.

Table 2. Acid, FFA value and moisture content for untreated waste cooking oil sample

Parameters	**Value**
Acid value	0.967 (mg KOH/g WCO)
Fatty acid value	0.39%
Water content	0.64%

Characterisation of methyl ester compounds in biodiesel samples was analysed using GC-FID. In this study, the standard methyl esters used are methyl palmitate, methyl myristate, methyl stearate and methyl linoleate. Each of the single standard was injected to obtain persistent retention time reading and the result was tabulated in Table 3. The biodiesel was produced by the reaction of 30:1 methanol/oil with 5 wt% of calcined ZnAl hydrotalcite in the transesterification process. The yield of biodiesel for 3:1 and 4:1 Zn:Al ratio were 28.5 %, and 32.7 %, respectively.

Table 3. Retention time of single standard FAME

FAME standard	**Retention time**
Methyl myristate	2.132
Methyl palmitate	2.950
Internal standard (methyl hepta)	3.558
Methyl linoleate	4.094
Methyl stearate	4.355

IV. CONCLUSION

In conclusion, ZnAl LDH catalyst with molar ratios 4:1 and 3:1 have been successfully synthesised via alkali-free method and have been characterised by TGA, XRD, SEM, BET and FT-IR. Based on the TGA decomposition temperature, samples were calcined at 250 °C. In XRD result, it was proved that the uncalcined LDH catalyst consist of crystalline materials since the peaks are relatively sharp and after the calcination, the LDH layer was successfully destroyed and converted to an amorphous material of mixed zinc aluminium oxides since the carbonate anions have been removed. This was further confirmed by SEM images where the crystalline and amorphous structures are clearly seen in uncalcined and calcined samples, respectively.

Meanwhile the surface area of the calcined ZnAl LDH is increasing from 212.9406 m2/g to 224.1770 m2/g, respectively which shows that the calcination give the access of N2 molecule to penetrate into the catalyst due to the removal of interlayer anion. The presence of carbonate anions can be proved from the FT-IR result which occurred at 1390 cm-1 and 1384 cm-1 is the residue bulk polydentate carbonate.

The production of biodiesel using waste cooking oil has been successfully conducted through transesterification reaction since the value of acid value obtained is 0.967 mg KOH/g and further analysed by using GC-FID analysis. The yield of biodiesel for 3:1 and 4:1 Zn:Al calcined ratio were 28.5 %, and 32.7 %, respectively.

As for the recommendation, biodiesel properties should be further study to ensure that the quality meets European Standard of biodiesel (EN4214). Last but not least, the basicity of the catalyst ZnAl LDH should be further investigated to determine the active basic-site of the catalyst itself and compare it with the surface area of the catalyst.

V. ACKNOWLEDGEMENT

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