Malaysian Journal of Chemistry, 2024, Vol. 26(5), 315-326
(Special Issue: *4th IKMPB Online Symposium 2024 - Development of Chemistry to Accomplish a Sustainable World*)

Synthesis and Characterization of KOH/Bentonite Catalyst for Transesterification of Waste Cooking Oil into Fatty Acid Methyl Esters

Nur Ain Sharina Shukor[1], Izyan Yusof[1], Wan Zurina Samad[3], Sabiha Hanim Saleh[1,2] and Noraini Hamzah[1,2]*
[1]School of Chemistry and Environment, Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor
[2]Industrial Waste Conversion Technology, Research Intensive Group, Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor
[3]Department of Chemistry, Kulliyyah of Science, International Islamic University Malaysia (IIUM Kuantan Campus), Jalan Sultan Ahmad Shah, Bandar Indera Mahkota, 25200 Kuantan, Pahang
*Corresponding author (e-mail: pnoraini@uitm.edu.my)

Fatty acid methyl ester, also known as biodiesel, is a sustainable and clean-burning fuel that can be a substitute for conventional diesel. However, the production of biodiesel requires higher costs compared to conventional diesel. The cost of production can be reduced by using waste cooking oil (WCO) as feedstock. In this study, biodiesel production was carried out via transesterification using WCO as feedstock, and potassium hydroxide (KOH)/bentonite catalyst was used as a heterogeneous catalyst. Different molar ratios of KOH/bentonite catalysts (1:2, 1:3, 1:4, 1:5, and 1:6) were prepared by the impregnation of bentonite with KOH at 60 °C for 6 h. Both raw bentonite and KOH/bentonite catalyst were characterized using thermogravimetric analysis (TGA), Brunauer-Emmett-Teller (BET) surface analysis, X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, and scanning electron microscopy (SEM). The decrease of BET surface area in raw bentonite and KOH/bentonite catalyst and the presence of potassium oxide phase in the XRD pattern showed that KOH was successfully impregnated into the pores of bentonite. Moreover, SEM analysis indicated that the granular size of KOH/bentonite was higher than raw bentonite due to aggregation. A high free fatty acid (FFA) conversion of 27.55% was obtained at an optimum molar ratio of KOH/bentonite of 1:5 under the reaction parameters of methanol-to-oil molar ratio of 6:1, reaction temperature of 60 °C, catalyst concentration of 3 wt.%, and reaction time of 3 h. The reusability test determined that the performance of the KOH/bentonite catalyst decreased from 27.55% to 13.73% in FFA conversion. This research reveals that KOH/bentonite catalyst has great potential to produce biodiesel using of WCO as feedstock.

Keywords: Fatty acid methyl ester; Bentonite; waste cooking oil; reusability

Received: January 2024; Accepted: July 2024

The global economy nowadays depends entirely on petroleum fuel as a source of energy. Most countries such as Australia, China, the United States, Russia, India, Indonesia, Singapore, Thailand, the Philippines, and Malaysia continue to rely extensively on fossil fuels as their primary source of power, accounting for more than 79% of total power consumption [1]. According to [2], non-renewable petroleum fuel is a major source of carbon dioxide (CO_2) emissions. Statistically, petroleum fuel burning contributes to approximately 52% of the total CO_2 emissions that are caused by human activities. Moreover, overexploitation of this fuel has a negative impact on the global temperature level, resulting in global warming [3]. Therefore, a renewable energy source, such as biodiesel, is a promising alternative to petroleum fuel.

Biodiesel can be a substitute for fossil fuel and is being studied by researchers due to its advantages, including better lubrication, biodegradability, non-toxicity, carbon neutrality, reducing pollution, and renewability [4]. According to [3], biodiesel releases low emissions of carbon monoxide, particulate matter, and unburned hydrocarbons. Fatty acid methyl ester, also known as FAME, is the chemical term for biodiesel, and it can be produced through transesterification [5]. explained that biodiesel can be synthesized by reacting fatty acids that can be found in vegetable oils or animal fats with a catalyst and an alcohol (methanol or ethanol) that acts as a solvent.

Many types of catalysts can be used to produce biodiesel, which are homogeneous, heterogeneous,

---

†Paper presented at the 4th IKMPB Online Symposium 2024 – Development of Chemistry to Accomplish a Sustainable World

and enzymatic catalysts. Due to its low energy consumption and simplicity, homogeneous-catalyzed transesterification is the most efficient technique and is widely used in biodiesel production. However, homogeneous catalysts are not biodegradable and are hard to separate after the transesterification process [6]. Therefore, heterogeneous catalysts can be used to replace homogeneous catalysts. [7] stated that heterogeneous catalysts have many advantages over homogeneous catalysts, including easier separation of biodiesel and glycerol. According to [8], heterogeneous catalysts allow for easier separation, have longer life and reduced corrosion, and can also be recycled.

In this study, different concentrations of potassium hydroxide (KOH) were impregnated with bentonite clay to produce heterogeneous catalysts for biodiesel production from waste cooking oil (WCO). The prepared KOH/bentonite catalyst was characterized to evaluate its physicochemical properties. Moreover, the effect of molar ratio and the reusability of the KOH/bentonite catalyst were also investigated.

EXPERIMENTAL

Chemicals and Materials

Waste cooking oil was obtained from the surrounding area of UiTM Shah Alam. Commercial bentonite, KOH, and methanol were purchased from R&M Chemicals. Sulfuric acid (H_2SO_4) was acquired from Merck. The materials required in gas chromatography analysis were obtained from Sigma-Aldrich, which are the reference standards of methyl palmitate, methyl laurate, methyl myristate, methyl stearate, and methyl linoleate, and also an internal standard of methyl heptadecanoate.

Preparation of KOH/Bentonite Catalyst

The catalyst was prepared using the impregnation method [9] of bentonite and KOH. First, bentonite was activated at 500 °C for 3 h in a furnace. Then, different molar ratios of KOH and bentonite clay were prepared, which were 1:2, 1:3, 1:4, 1:5, and 1:6. This impregnation procedure was conducted in a 500 mL two-neck round-bottom flask equipped with a reflux condenser, a temperature indicator, and a mechanical stirrer. The process was carried out at a temperature of 60 °C for 6 h under continuous stirring. After impregnation, excess KOH was removed from the catalyst. After that, the catalyst was dried at 60 °C for 24 h in an oven. After the catalyst was dried, it was calcined at 500 °C in a muffle furnace for 3 h.

Catalyst Characterization

The KOH/bentonite catalyst was characterized using thermogravimetric analysis (TGA), Brunauer-Emmett-Teller (BET) surface analysis, X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, and scanning electron microscopy (SEM). The purpose of the characterization of the catalyst is to identify which molar ratio of the catalyst has the optimum potential as a catalyst. Table 1 lists the function of each instrument used for the characterization of the KOH/bentonite catalyst.

Pretreatment of WCO

Waste cooking oil contains contaminants and moisture that need to be eliminated. First, WCO was filtered using a cloth strainer to separate solid contaminants from the oil. Then, the WCO was once again filtered using filter paper. The properties of WCO, including moisture content, acid value, and saponification value, were determined.

The water content of WCO was removed by heating 20 g of oil sample at 90–100 °C, which is the boiling point of water, for 3 h on a hot plate. Then, the oil sample was cooled to room temperature. The weight of the sample was recorded, and the moisture content (MC) was calculated using Equation (1).

$$MC = \frac{Wb - Wa}{Wb} \times 100\% \qquad (1)$$

Where W_a is the final weight of WCO and W_b is the initial weight of WCO.

Table 1. The function of each catalyst characterization.

Instrument	Function
TGA	To analyze the thermal stability and decomposition nature of the catalyst.
BET	To determine the surface area, pore size distribution, pore volume, and pore radius of the catalyst.
XRD	To determine the crystallinity and purity of the catalyst.
FTIR	To identify the functional groups present in the structure of the catalyst.
SEM	To determine the surface morphology of the catalyst.

The acid value (AV) of the WCO sample was determined using the standard titration method. This method was conducted by pouring 50 mL of 70% ethanol and a few drops of phenolphthalein into a conical flask. Next, 0.1 N KOH was added to the solution until a faint pink color appeared. Then, the solution was added to a flask containing 10 g of WCO sample. The mixture was boiled using the hot plate until the mixture dissolved completely. Following that, a few drops of phenolphthalein were added to the mixture, which was then titrated against standardized 0.1 N KOH until the solution turned brown. The initial and final volumes of KOH were recorded. The AV and free fatty acid percentage (%FFA) were calculated using Equations 2 and 3, respectively.

The WCO sample is not suitable for transesterification if the AV exceeds 0.5 wt.%. This is because it will undergo saponification. Therefore, the most favorable AV should be less than 0.5 wt.%.

About 500 mL of ethanolic KOH was prepared by mixing 20 g of KOH, 22.5 g of calcium oxide (CaO), and ethanol. First, KOH pallets were crushed using a pestle and mortar. Crushed KOH and CaO powder were diluted with a portion of 500 mL ethanol and poured into a 500 mL flask. The flask was shaken for about 5 min. After that, the flask was left overnight while topped with an inverted beaker. The flask was shaken occasionally during the day.

The following day, the ethanolic KOH mixture was filtered and placed in a glass bottle. The blank sample involved the ethanolic mixture, where 50 mL of ethanolic KOH was transferred into a round-bottom flask and placed in a reflux set apparatus. The solution was brought to a boil for 30 min. The oil sample mixture was prepared by mixing 5 g of oil and 50 mL of ethanolic KOH in a round-bottom flask. The flask was also placed in a reflux apparatus and brought to a boil for 30 min. The boiling process was stopped when all the oil had dissolved. The boiling time for both oil and water must be the same. The boiling time of water can be increased if needed.

The mixture was then cooled slightly, and the phenolphthalein indicator was added. The solution was titrated against standardized 0.5 N hydrochloric acid (HCl) until the blank and oil samples appeared clear and yellow, respectively. The initial and final volumes of HCl were measured, and Equations 4 and 5 were used to calculate the saponification value (SV) and molecular weight (MW), respectively.

Esterification of WCO

The esterification of WCO needs to be conducted if the AV obtained from the sample exceeds 0.5 wt.%. First, 3.5 wt.% H_2SO4 and methanol (at a 6:1 methanol-to-oil molar ratio) mixture was heated in a water bath to 62 °C. After reaching the desired temperature, 150 g of WCO was added to the mixture, and the mixture was stirred at 700 rpm for 3 h. After the reaction was completed, the mixture was allowed to separate in a separatory funnel for 3 h. Next, the lower layer of the mixture was discarded, and the upper layer containing WCO was washed using hot distilled water several times. The AV was calculated again using Equation 2.

Transesterification of WCO

The transesterification of WCO was carried out using the conventional reflux method [10]. A two-neck round-bottom flask was equipped with a condenser, a temperature indicator, and a magnetic stirrer. The flask was filled with 20 g of sample and 3 wt.% catalyst in methanol at a methanol-to-oil molar ratio of 6:1. The mixture was refluxed at 60 °C for 3 h at a mixing speed of 1,000 rpm. Later, the catalyst was separated by centrifugation. The glycerol and excess methanol in the upper layer were removed, and the biodiesel in the bottom layer underwent a purification process. The purification of biodiesel was carried out using hot distilled water (70 °C) with three-times washing. The ratio between the volume of biodiesel and water for washing is 1:1. The purified biodiesel was then heated on the hot plate at 110 °C for 10 min to remove any remaining moisture.

$$Acid\ Value\ = \frac{Volume\ of\ KOH\ (mL) \times Normality\ of\ KOH \times 56.1}{Weight\ of\ sample\ (g)} \tag{2}$$

$$\%FFA = \frac{Acid\ value}{2} \tag{3}$$

$$SV = \frac{28.05 \times \left(Volume\ HCl\ (blank) - Volume\ HCL\ (oil)\right)(mL)}{Weight\ of\ oil\ (g)} \tag{4}$$

$$Average\ MW\ = \frac{56.1 \times 1{,}000 \times 3}{SV - AV} \tag{5}$$

Catalyst Reusability

One of the advantages of a heterogeneous catalyst is its reusability. For evaluating the reusability of the catalyst, the KOH/bentonite catalyst was collected and washed with n-hexane to remove any residue. Then, the catalyst was filtered using filter paper, followed by drying in the oven for 1 h at 60 °C. Next, the KOH/bentonite catalyst was calcined in the furnace at 300 °C for 5 h. The transesterification process was repeated using the recycled catalyst.

Biodiesel Analysis Using Gas Chromatography-Flame Ionization Detector

For biodiesel analysis, the FAME composition of the biodiesel produced from the transesterification of WCO can be analyzed using a gas chromatography-flame ionization detector (GC-FID). First, 20 mg of FAME mix (C8–C24) was diluted with 10 mL of hexane to produce a 2,000 ppm stock solution. The internal standard was prepared by dissolving 1 g of methyl heptadecanoate in 1,000 mL of hexane. Then, 5 mL of FAME stock with 5 mL of methyl heptadecanoate was mixed together and injected into the GC-FID. The response factor (RF) of each methyl ester was calculated using Equation 6.

In the analysis, 800 µL of methyl heptadecanoate and 200 µL of biodiesel sample were mixed to obtain five dilution factors according to the dilution factor selected so that the total volume is 1 mL. The mixture was injected into the GC-FID, and the percentage yield of biodiesel was calculated using the following steps.

Step 1: Calculate the concentration of each individual FAME in ppm using Equation 7.

Where Conc. IS is the concentration of internal standard (ppm), Area IF is the area of individual FAME obtained from the GC-FID, Area IS is the area of internal standard (ppm), and RF is the response factor.

Step 2: Convert the concentration of each individual FAME (ppm) to weight (mg) using Equation 8.

Where Conc. IF is the concentration of individual FAME and V is the volume of biodiesel with internal standard (mL).

Step 3: Convert the unit of individual FAME weight from mg to g using Equation 9.

Where Individual FAME weight is obtained from Equation 7 and DF is the dilution factor.

Step 4: Convert the unit of individual FAME weight from g to mol using Equation 10.

Table 2 lists the MW of individual FAME presence in the biodiesel sampel.

$$RF = \frac{Area\ of\ internal\ std. \times Conc.of\ reference\ std.}{Area\ of\ reference\ std. \times Conc.of\ internal\ std.} \quad (6)$$

$$Conc.of\ Individual\ FAME = \frac{Conc.IS \times Area\ IF \times RF}{Area\ IS} \quad (7)$$

$$Weight\ (mg) = \frac{Conc.IF \times V}{1{,}000} \quad (8)$$

$$FAME\ (g) = \frac{Individual\ FAME\ weight\ (mg) \times DF \times Volume\ of\ biodiesel}{1{,}000} \quad (9)$$

$$mol = \frac{Weight\ of\ individual\ FAME\ (g)}{MW\ of\ individual\ FAME\ (g/mol)} \quad (10)$$

Table 2. Molecular weight of individual FAME.

Individual FAME	MW (g/mol)
Methyl myristate	242.39
Methyl palmitate	270.45
Methyl stearate	298.51
Methyl oleate	296.49
Methyl linoleate	294.84

$$Theoretical\ mol\ = \frac{Weight\ of\ WCO\ used\ in\ experiment}{MW\ of\ oil} \times 3 \tag{11}$$

$$Biodiesel\ yield\ (\%)\ = \frac{\sum mol\ of\ individual\ FAME}{Theoretical\ mol\ of\ FAME}\ \times\ 100\% \tag{12}$$

Step 5: Calculate the theoretical mol of FAME using Equation 11.

Step 6: Calculate the yield of biodiesel using Equation 12.

RESULTS AND DISCUSSION

Pretreatment of WCO

The pretreatment of WCO consists of the determination of the MC, SV, AV, and FFA value, and the results are shown in Table 3. The pretreatment step is important because WCO contains a lot of moisture from cooking, which leads to the hydrolysis of triglycerides and the formation of FFAs [11]. High FFA content can affect biodiesel yield. The MC and %FFA obtained from the WCO are 0.9701% and 0.6061%, respectively. The % FFA can be considered low; hence, esterification of WCO is not required.

Moreover, the SV obtained is 190.2969 mg KOH/g. According to the literature, the SV of WCO should be in the range of 177–200 mg KOH/g, and it indicates the quantity of KOH required to saponify 1 g of oil [12]. From the AV and SV, the MW of WCO can be determined, and the MW obtained is 890.0768 g/mol.

Characterization of KOH/Bentonite Catalyst

Thermogravimetric Analysis

Thermogravimetric analysis was conducted to evaluate the thermal stability of raw bentonite and the KOH/bentonite catalyst. The TGA curves of raw bentonite and KOH/bentonite catalyst in Figure 1 show a sharp mass loss at a temperature below 200 °C, which corresponds to the dehydration of water on the parent clay surface [13]. Between 450 and 650 °C, raw bentonite exhibits mass loss due to the dihydroxylation of montmorillonite with a high iron concentration [14]. According to the TGA curve of the KOH/bentonite catalyst, the mass loss decreased gradually at 200–500 °C, followed by a drop between 500 and 1,000 °C due to sample decomposition [13]. The formation of the endothermic peak on the differential scanning calorimetry (DSC) curves for both raw bentonite and KOH/bentonite catalyst indicates the water loss, dehydroxylation, and decomposition of the samples [14].

Table 3. The properties of WCO.

Properties	Value
MC (%)	0.9701
AV (mg KOH/g)	1.2121
FFA value (%)	0.6061
SV (mg KOH/g)	190.2969
MW (g/mol)	890.0768

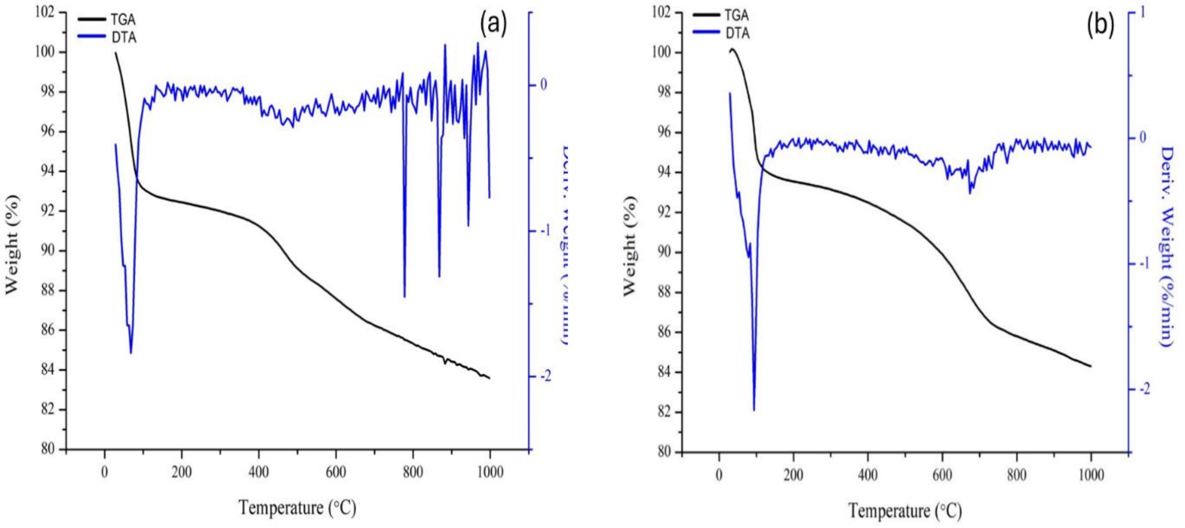


Figure 1. TGA and DSC curves of (a) raw bentonite and (b) KOH/bentonite catalyst (1:5).

Table 4. The properties of raw bentonite and KOH/bentonite catalysts.

Catalyst	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (nm)
Raw bentonite	31.400	0.0754	12.482
KOH/bentonite (1:2)	13.810	0.052	17.254
KOH/bentonite (1:3)	8.750	0.042	19.737
KOH/bentonite (1:4)	5.360	0.027	22.275
KOH/bentonite (1:5)	4.830	0.025	23.682
KOH/bentonite (1:6)	2.530	0.016	34.172

BET Analysis

The BET surface area, pore volume, and pore size of the catalyst can be obtained through BET analysis. Based on the results of BET analysis in Table 4, raw bentonite has a larger BET surface area and pore volume than the KOH/bentonite catalyst, which are 31.40 m^2/g and 0.07537 cm^3/g, respectively. Moreover, the increase of the molar ratio of the catalyst from 1:2 to 1:6 decreased the BET surface area and pore volume. This is because as bentonite is impregnated with KOH, the KOH molecules enter the pores of bentonite, and the increase in the concentration of KOH leads to more KOH molecules filling the empty pores in bentonite. Hence, the BET surface area of the catalyst decreases [9]. Furthermore, the presence of KOH molecules expands the interstitial space of bentonite, consequently reducing the pore volume of the catalyst [15].

According to the IUPAC classification, the structure of raw bentonite and KOH/bentonite is mesoporous because the pore diameter of both materials is in the range of 2–50 nm [16]. Figure 2 shows the BET isotherm linear plot of raw bentonite and KOH/bentonite catalysts with different molar ratios. It can be observed that the hysteresis curve of the adsorption isotherm between raw bentonite and KOH/bentonite catalysts becomes flattened, indicating that the pore structure of bentonite changes from a mesoporous material to a non-porous structure due to the impregnation process [9].

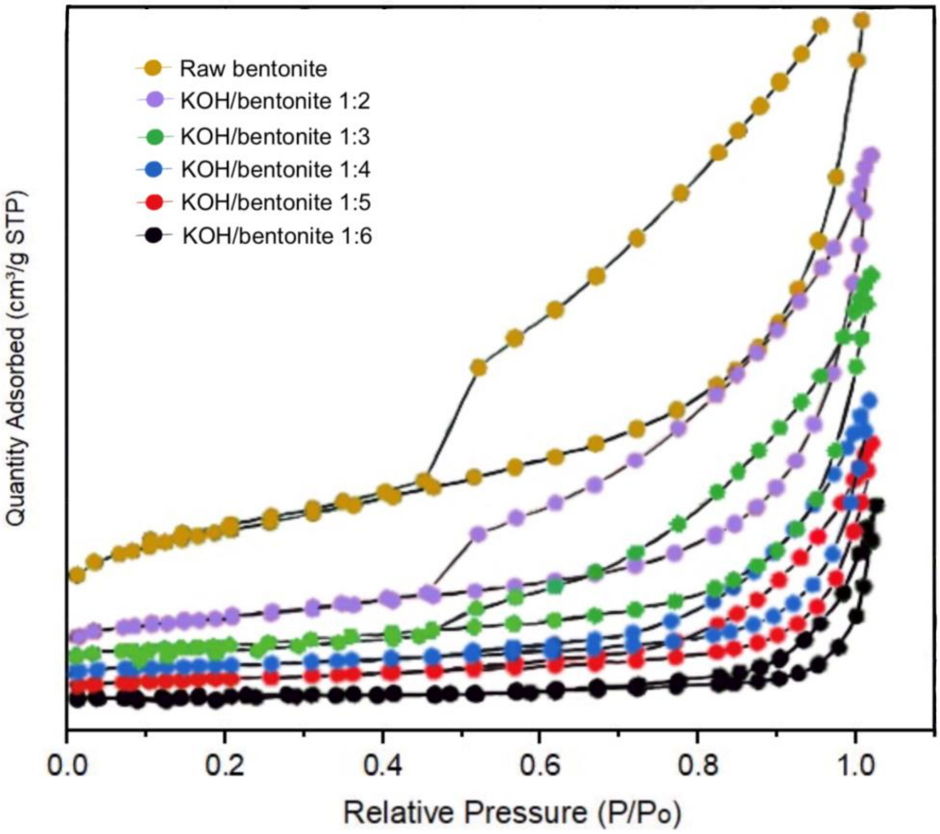


Figure 2. Nitrogen sorption isotherms of bentonite and KOH/bentonite catalysts.

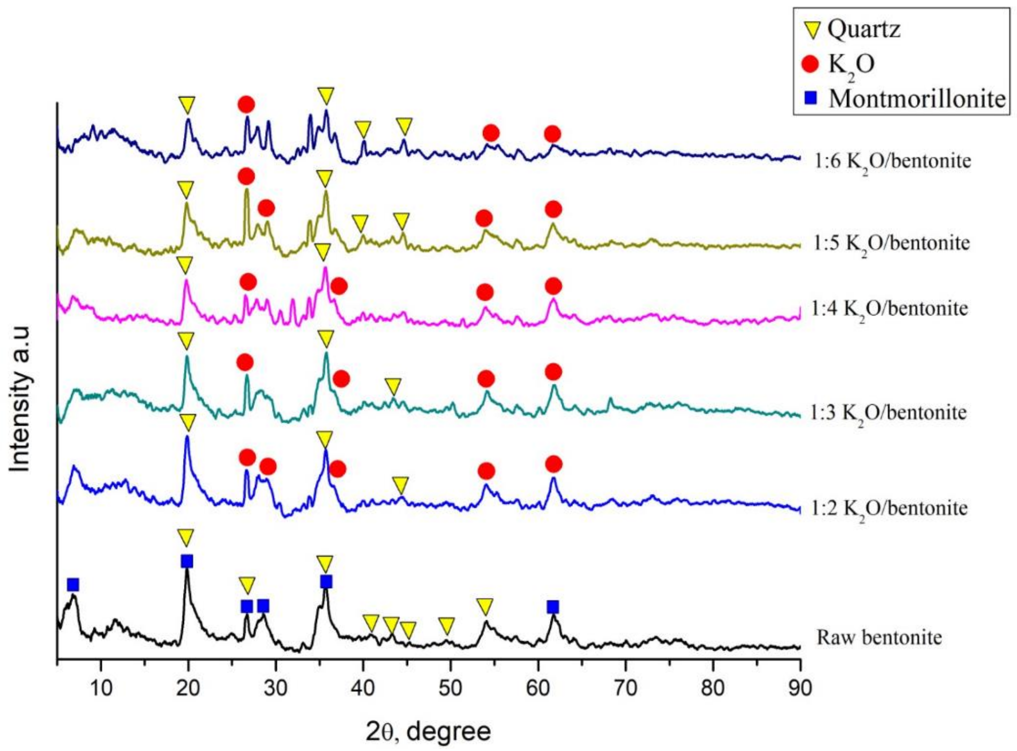


Figure 3. XRD patterns of bentonite and KOH/bentonite catalysts with different molar ratios.

XRD Analysis

X-ray diffraction analysis is used to determine the crystallinity of the catalyst. Figure 3 shows the XRD patterns of raw bentonite and KOH/bentonite catalysts with different molar ratios. Raw bentonite is mainly composed of montmorillonite, and the diffraction peaks are shown at $2\theta = 7°$, 20°, 27°, 29°, 36°, 57°, and 62° [15]. The calcination of the KOH/bentonite catalyst at 500 °C converts KOH to potassium oxide (K_2O), and the presence of K_2O phase in the XRD pattern indicates that there is a process of KOH impregnated with bentonite. The presence of this phase is important because it can improve the performance of the catalyst. The K_2O phase in the XRD pattern can be observed at $2\theta = 27°$, 31°, 39°, 57°, and 62° (JCPDS 23-493) [9] & [17]. When the molar ratio of the catalyst increases, the crystallinity of the catalyst decreases. According to [15], the increase in KOH concentration causes the layers of bentonite to be physically adjusted to expose and adsorb more potassium molecules on the surface of bentonite.

FTIR Analysis

The infrared spectra of raw bentonite and KOH/bentonite catalysts with different molar ratios are shown in Figure 4. The main bentonite peak can be observed at 3618 cm^{-1}, indicating that Al–OH stretching is present. In the KOH/bentonite catalyst spectra, the absorption band of the Al–OH group shifted to a higher wavenumber. This is due to the presence of a new functional group in the catalyst, which is Al–O–K, at a wavelength of 3433 cm^{-1} [9]. The presence of the water content of bentonite was detected at two different wavelengths of 3447 cm^{-1} (H–O–H stretching) and 1637 cm^{-1} (H–O–H bending). Moreover, a strong peak at 1040 cm^{-1} corresponds to the functional group of Si–O–Si [18].

SEM Analysis

The morphology of the activated raw bentonite and KOH/bentonite catalyst can be determined using SEM, as shown in Figure 5. The scans were carried out at 1,000× and 2,000× magnification. The raw bentonite seems to have a smoother surface with porous grain compared to the KOH/bentonite catalyst, which seems to have a rougher surface with porous grain. This is due to the uniform distribution of KOH on the bentonite surface [19]. This distribution was proved by BET analysis, where the surface area of KOH/bentonite decreased. After bentonite was impregnated with KOH, the particle size of the catalyst increased. Figures 5(a) and (c) indicate that the granular size of raw bentonite is within the range of 121 × 129 µm, whereas the granular size of KOH/bentonite catalyst is within the range of 145 × 137 µm, respectively. This might be because the granules of KOH and bentonite form aggregates, thus increasing the granular size [15] & [17]. Furthermore, K_2O was present on the surface of the particle as active sites, as proven by XRD analysis.

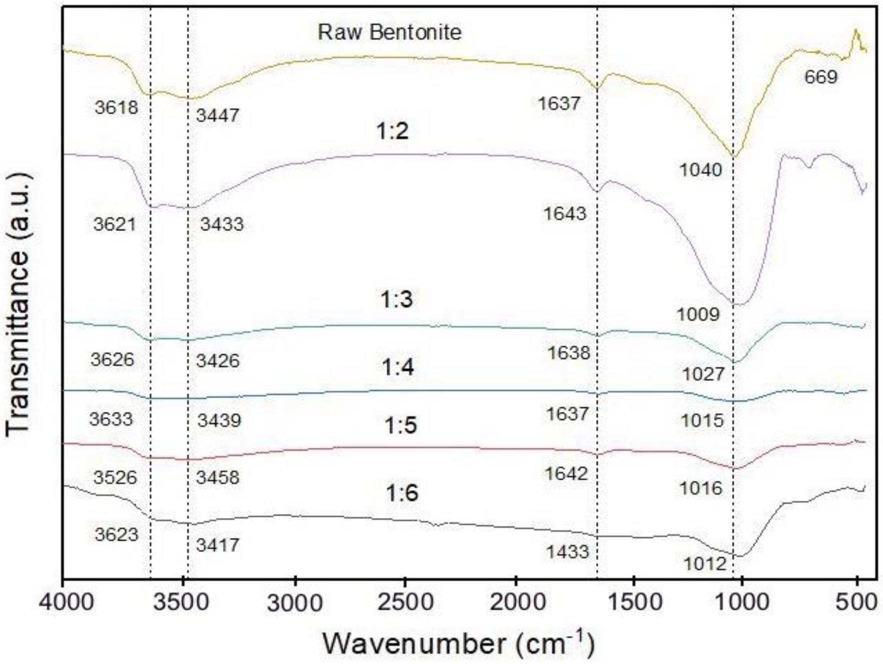
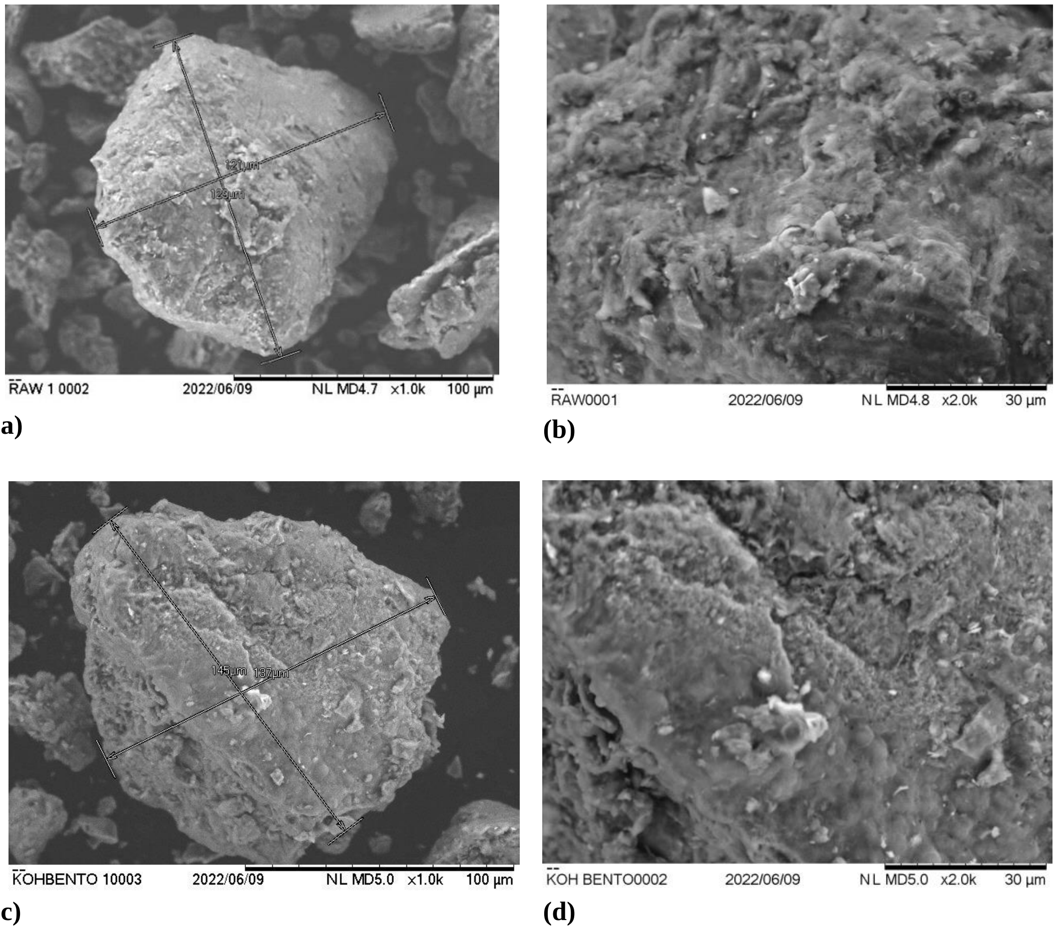


Figure 4. FTIR spectra of bentonite and KOH/bentonite catalysts with different molar ratios.



(a) (b)

(c) (d)

Figure 5. SEM images of (a) raw bentonite at 1,000× magnification, (b) raw bentonite at 2,000× magnification, (c) KOH/bentonite catalyst (1:5) at 1,000× magnification, and (d) KOH/bentonite catalyst (1:5) at 2,000× magnification.

Table 5. The percentage of FFA conversion with catalysts at different molar ratios.

Catalyst Molar Ratio	RT (°C)	CC (wt.%)	M:O	RP (h)	FFA Conversion (%)
1:2	60	3	6:1	3	8.24
1:3	60	3	6:1	3	17.04
1:4	60	3	6:1	3	20.98
1:5	60	3	6:1	3	27.55
1:6	60	3	6:1	3	8.16

RT = Reaction temperature, CC = catalyst concentration, M:O = methanol-to-oil ratio, RP = reaction period

Effect of Molar Ratio of KOH/Bentonite Catalysts

The effect of the molar ratio of KOH/bentonite catalysts was determined from the percentage of FFA conversion obtained from the transesterification of WCO. The transesterification process was conducted under the parameters of the reaction temperature of 60 °C, reaction time of 3 h, catalyst concentration of 3 wt.%, and methanol-to-oil molar ratio of 6:1. Based on the results in Table 5, the amount of KOH concentration affected the conversion of WCO into biodiesel. According to [17], the interaction between KOH and the internal layer of bentonite strengthens with a high concentration of KOH.

As shown in Figure 6, the percentage of FFA conversion increased when the molar ratio of the catalyst increased from 1:2 to 1:5, and the highest conversion of FFA was obtained at the catalyst molar ratio of 1:5, which is 27.55%. The increase in FFA conversion might be due to the increase in the total basicity of active sites (KOH) as the molar ratio increases [15]. However, the percentage of FFA conversion decreased when using a higher catalyst molar ratio, which is 1:6. This is due to agglomeration, which occurs when excess KOH causes a decrease in the surface area of the catalyst, lowering its catalytic activity. Furthermore, the high concentration of catalyst resulted in the formation of a new phase, which is Al–OK, as proven by FTIR analysis. This new phase has lower alkalinity and catalytic activity compared to K_2O [17].

Reusability of Bentonite/KOH Catalyst

The reusability of a catalyst needs to be determined in order to observe its activity and stability [20]. It is also one of the advantages of using heterogeneous catalysts in biodiesel production. In this study, the optimum molar ratio of the catalyst was used, which is 1:5. The XRD patterns of fresh and reused catalysts are shown in Figure 7. It can be observed that the XRD patterns for both catalysts are similar, highlighting the stability of the catalysts.

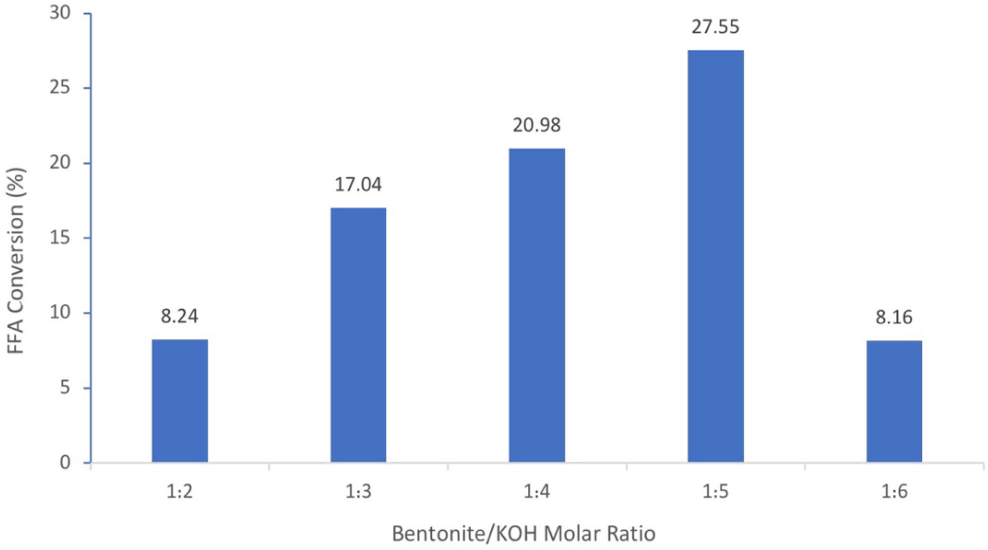


Figure 6. Percentage of FFA conversion with catalysts at different molar ratios.

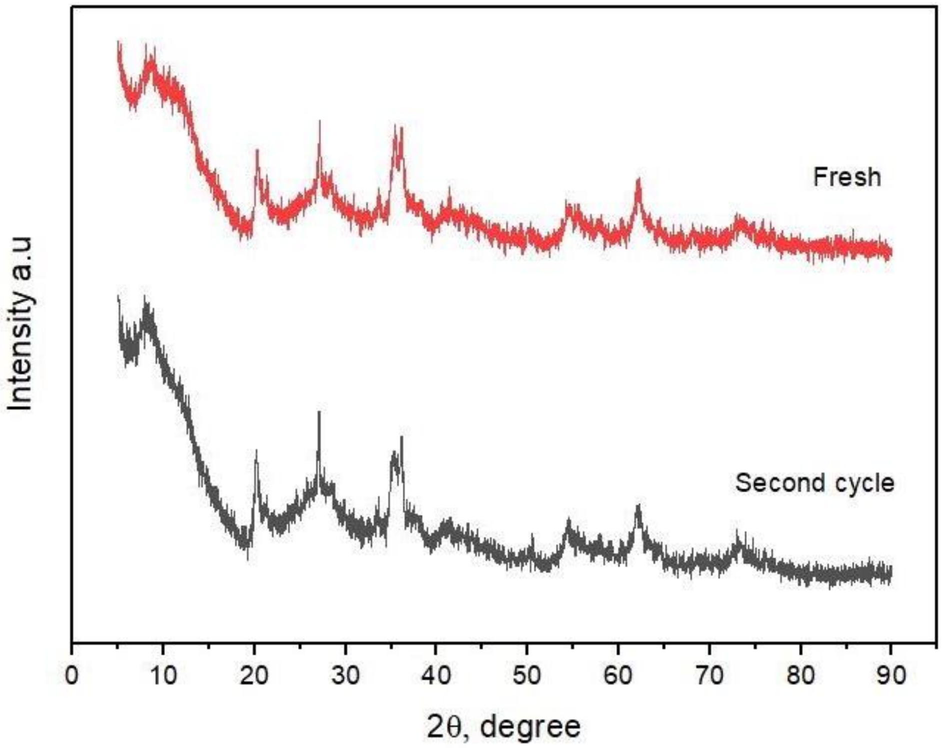


Figure 7. XRD patterns of fresh and reused catalysts (KOH/bentonite 1:5).

The FFA conversion for the reused catalyst is lower than the fresh catalyst. According to Figure 8, the percentage of FFA conversion for the second cycle of the conversion dropped from 27.55% to 13.73%. This is because the catalytic active sites of the catalyst decrease. According to [9], the basic sites of the catalyst were deactivated, and some of the basic sites were poisoned during the transesterification reaction, thereby lowering the reaction rate of the catalyst.

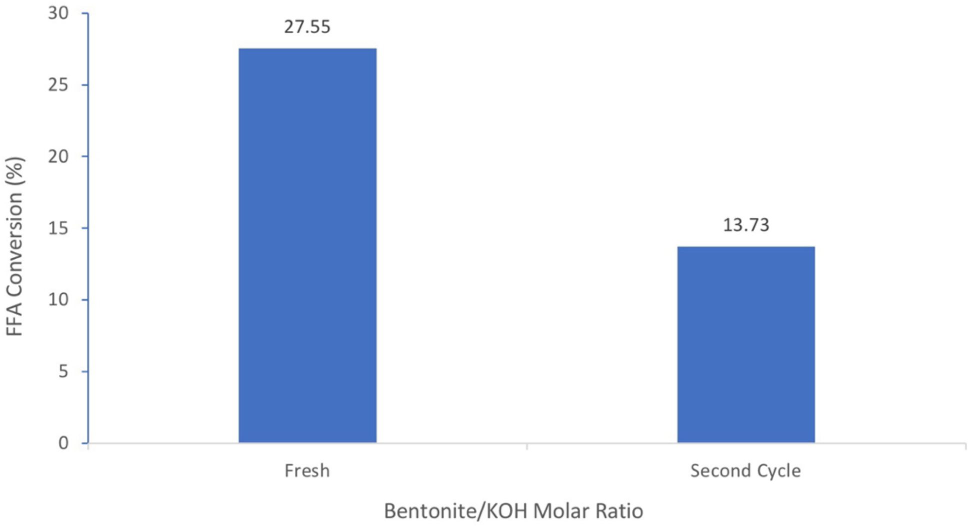


Figure 8. Reusability of the catalyst (KOH/bentonite 1:5).

CONCLUSIONS

In conclusion, KOH/bentonite catalyst can be used as a heterogeneous catalyst in the production of biodiesel from WCO. Different molar ratios of KOH/bentonite catalysts were successfully synthesized, and the catalysts were characterized using TGA, BET, XRD, SEM, and FTIR. The thermal stability of the raw bentonite and KOH/bentonite catalyst showed that the catalyst could be prepared at higher temperatures up to 500 °C. The decrease in the BET surface area and the presence of a K_2O phase in the XRD patterns confirmed the impregnation of KOH into the pores of bentonite. Moreover, the impregnation process also increased the particle size of the catalyst.

Furthermore, the catalyst with a 1:5 molar ratio resulted in the highest percentage of FFA conversion of 27.55%, which was carried out at the reaction temperature of 60 °C, reaction time of 3 h, catalyst concentration of 3 wt.%, and methanol-to-oil molar ratio of 6:1. Moreover, the catalyst could be reused, and the stability of the catalyst was proven by the XRD pattern. However, due to the decrease in catalytic activity, the percentage of FFA conversion using the recycled catalyst was lower than the fresh catalyst, which dropped from 27.55% to 13.73%.

ACKNOWLEDGEMENT

The authors are grateful to Universiti Teknologi MARA, Malaysia for the financial support provided for this research by the Ministry of Higher Education, Malaysia with grant number FRGS/1/2019/STG 07/UITM/02/23.

REFERENCES

1. Latif, S. N. A., Chiong, M. S., Rajoo, S., Takada, A., Chun, Y. Y., Tahara, K. & Ikegami, Y. (2021) The trend and status of energy resources and greenhouse gas emissions in the Malaysia power generation mix. *Energies*, **14(8)**. https://doi.org/10.3390/en14082200

2. Faruque, M. O., Razzak, S. A. & Hossain, M. M. (2020) Application of heterogeneous catalysts for biodiesel production from microalgal oil—a review. In *Catalysts*, **10(9)**, 1–25. MDPI. Doi: https://doi.org/10.3390/catal10091025

3. Jha, A. & Das, S. (2017) Waste Cooking Oil-Revolution in Biodiesel Production. *Fermentation Technology,* **06(02)**. Doi: https://doi.org/10.4172/2167-7972.1000143

4. Jayakumar, M., Karmegam, N., Gundupalli, M. P., Bizuneh Gebeyehu, K., Tessema Asfaw, B., Chang, S. W., Ravindran, B. & Kumar Awasthi, M. (2021) Heterogeneous base catalysts: Synthesis and application for biodiesel production – A review. In *Bioresource Technology*, *Elsevier Ltd.*, **331**. Doi: https://doi.org/10.1016/j.biortech.2021.125054

5. Hamza, M., Ayoub, M., Shamsuddin, R. bin, Mukhtar, A., Saqib, S., Zahid, I., Ameen, M., Ullah, S., Al-Sehemi, A. G., & Ibrahim, M. (2021). A review on the waste biomass derived catalysts for biodiesel production. In *Environmental Technology and Innovation*, **21**. Doi: https://doi.org/10.1016/j.eti.2020.10120

6. Mohiddin, M. N. bin, Tan, Y. H., Seow, Y. X., Kansedo, J., Mubarak, N. M., Abdullah, M. O., Chan, Y. S. & Khalid, M. (2021) Evaluation on feedstock, technologies, catalyst and reactor for sustainable biodiesel production: A review. In *Journal of Industrial and Engineering Chemistry, Korean Society of Industrial Engineering Chemistry*, **98**, 60–81. https://doi.org/10.1016/j.jiec.2021. 03.036

7. Amani, H., Ahmad, Z. & Hameed, B. H. (2014) Highly active alumina-supported Cs-Zr mixed oxide catalysts for low-temperature transesterification of waste cooking oil. *Applied Catalysis A: General*, **487**, 16–25. https://doi.org/10.1016/j.apcata.2014.08.038

8. Gaur, A., Mishra, S., Chowdhury, S., Baredar, P. & Verma, P. (2020) A review on factor affecting biodiesel production from waste cooking oil: An Indian perspective. *Materials Today: Proceedings*, **46**, 5594–5600. doi: https://doi.org/10.1016/j.matpr.2020.09.432

9. Soetaredjo, F. E., Ayucitra, A., Ismadji, S. & Maukar, A. L. (2011) KOH/bentonite catalysts for transesterification of palm oil to biodiesel. *Applied Clay Science*, **53(2)**, 341–346. Doi: https://doi.org/10.1016/j.clay.2010.12.018

10. Da Costa, J. M. & de Andrade Lima, L. R. P. (2021) Transesterification of cotton oil with ethanol for biodiesel using a KF/bentonite solid catalyst. *Fuel*, **293**. Doi: https://doi.org/10.1016/j.fuel.2021.120446

11. Karmakar, B. & Halder, G. (2019) Progress and future of biodiesel synthesis: Advancements in oil extraction and conversion technologies. In *Energy Conversion and Management*, **182**, 307–339. Doi: https://doi.org/10.1016/ j. enconman.2018.12.066

12. Aworanti O. A., Ajani A. O., Agarry S. E., Babatunde K. A., Akinwumi O. D. (2019) Evaluation of Process Parameters for Biodiesel Production from Vegetable and Palm Waste Frying Oils Using a Homogeneous Catalyst. *International Journal of Energy Engineering*, **9(2)**, 25-35. doi: 10.5923/j.ijee.20190902.01.

13. Kurniawan, Y. S., Imawan, A. C., Stansyah, Y. M. & Wahyuningsih, T. D. (2021) Application of activated bentonite impregnated with PdO as green catalyst for acylation reaction of aromatic compounds. *Journal of Environmental Chemical Engineering*, **9(4)**. Doi: https://doi.org/10.1016/j.jece.2021.105508

14. Moraes, D. S., Miranda, L. C. R., Angélica, R. S., Rocha Filho, G. N. & Zamian, J. R. (2018) Functionalization of bentonite and vermiculite after the creation of structural defects through an acid leaching process. *Journal of the Brazilian Chemical Society*, **29(2)**, 320–327. https://doi.org/10.21577/0103-5053.20170143

15. Intarapong, P., Jindavat, C., Luengnaruemitchai, A. & Jai-In, S. (2014) The transesterification of palm oil using KOH supported on bentonite in a continuous reactor. *International Journal of Green Energy*, **(9)**, 987–1001. https://doi.org/10.1080/15435075.2013.829477

16. Wang, Y., Muhammad, Y., Yu, S., Fu, T., Liu, K., Tong, Z., Hu, X. & Zhang, H. (2022) Preparation of Ca-and Na-Modified Activated Clay as a Promising Heterogeneous Catalyst for Biodiesel Production via Transesterification. *Applied Sciences (Switzerland)*, **12 (9)**. Doi: https://doi.org/10.3390/app12094667

17. Utubira, Y., Wijaya, K., Triyonol & Kunarti, E. S. (2018) Kalium hydroxide/zirconia pillared bentonite for palm oil transesterification. *Oriental Journal of Chemistry*, **34(3)**, 1484–1491. Doi: https://doi.org/10.13005/ojc/340339

18. Taher, T., Mohadi, R., Rohendi, D. & Lesbani, A. (2017) Kinetic and thermodynamic adsorption studies of congo red on bentonite. *AIP Conference Proceedings*, **1823**. Doi: https://doi.org/10.1063/1.4978101

19. Naik, B. D. & Meivelu, U. (2020) Experimental studies on sodium methoxide supported bentonite catalyst for biodiesel preparation from waste sunflower oil. *Environmental Progress and Sustainable Energy*, **39(4)**. https://doi.org/10.1002/ep.13390

20. Hossain, M. N., Bhuyan, M. S. U. S., Alam, A. H. M. A. & Seo, Y. C. (2019) Optimization of biodiesel production from waste cooking oil using S–TiO2/SBA-15 heterogeneous acid catalyst. *Catalysts*, **9(1)**. Doi: https://doi.org/10.3390/catal9010067