*Malaysian Journal of Chemistry, 2022, Vol. 24(2), 177-183*
(Special Issue: *2nd IKM Pahang Branch Symposium 2022 – Sustainability & Diversity Through Chemistry*)

# Effect of Sodium Hydroxide on a Bentonite Support as Catalyst for Transesterification of Waste Cooking Oil into Biodiesel

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Biodiesel consists of the mono-alkyl esters of vegetable oils or animal fats produced by transesterification using a mono-hydric alcohol and a catalyst. In this study, the impregnation approach was used to make a series of bentonite:NaOH catalysts with molar ratios of 1:1, 1:2, 1:3, and 1:4. The synthesized catalysts were characterized using FTIR and XRD analysis. Pre-treatment of the waste cooking oil (WCO) sample was conducted before transesterification. The characteristics of WCO such as free fatty acids (FFAs), saponification, and moisture content were determined. The WCO sample had an FFA value of 0.49 %, a saponification value of 206.70 mg KOH/g, and a moisture content of 0.22 %. Based on the FTIR analysis, the impregnation of NaOH into bentonite was successful, with a band at 3430 cm$^{-1}$ indicating the presence of the Al-O-Na group. XRD analysis also showed changes in peak intensity, indicating the presence of $Na_2O$ crystals. The bentonite:NaOH catalyst with a molar ratio of 1:3 had the best FFA yield (40.7%) at a reaction temperature of 60 °C and reaction time of 195 minutes.

**Key words:** WCO; bentonite:NaOH; transesterification; biodiesel

*Received: December 2021; Accepted: February 2022*

As fossil fuels are non-biodegradable and non-renewable, they will be depleted soon due to population growth, industrialization, and urbanization. Due to rising consumption in many sectors, depletion of petroleum supplies and uncertainty surrounding crude oil market pricing, the sustainability of a petroleum-based fuel supply has drawn widespread attention. Biodiesel, which is described as a fuel made up of mono-alkyl esters of long chain fatty acids generated from vegetable oils or animal fats, is a feasible alternative to petroleum diesel thanks to its renewability, nontoxicity, environmental safety, and biodegradability [1].

Waste cooking oil (WCO) may be considered a possible raw material in biodiesel manufacturing due to its ample availability, which can be attributed to the 11.09 % rise in palm oil use from 2004 to 2014 [2]. The United Kingdom, European Union, and Canada generate 200,000 tonnes, 700,000-1,000,000 tonnes, and 135,000 tonnes of WCO per year, respectively [3]. The utilization of WCO in biodiesel production improves economic feasibility because it is readily available owing to disposal problems [4]. WCO that is improperly disposed of can cause various environmental issues, including water and soil contamination, human health concerns, and disruption of aquatic ecosystems [5].

The manufacture of biodiesel may be done using transesterification in the presence of a catalyst. Homogeneous bases, homogeneous acids, heterogeneous solid catalysts, enzymes, and lipase have been investigated and employed as catalysts for biodiesel generation from various feedstocks [6]. A homogeneous base catalyst has traditionally been utilized in biodiesel manufacturing. The use of this type of catalyst in biodiesel manufacturing has several disadvantages, including product loss due to washing, high energy consumption, and the formation of a large amount of wastewater. The use of homogeneous catalysts also increases the cost of production since the utilized catalysts are difficult to recover [4]. Many researchers have recently been conducting experiments to overcome the disadvantages of employing homogeneous catalysts for transesterification reactions [7].

As a result, heterogeneous catalysts are increasingly favoured over homogeneous catalysts. Heterogeneous catalysts have several advantages, including easy catalyst recovery, easy product purification, lower purification costs, regeneration, and easy glycerol recovery. They also consume less energy and water. Furthermore, greater yields have been obtained when solid alkaline catalysts are used. Base-catalyzed transesterification of vegetable oils

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†Paper presented at the 2nd IKM Pahang Branch Symposium 2022 – Sustainability & Diversity Through Chemistry

was found to be quicker than acid-catalyzed transesterification because it is less corrosive. Although less active than metal alkoxides, alkaline metal hydroxides such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) are cheap and can produce satisfactory results.

Clay materials are abundant in nature and are diverse in composition and particle size, making them ideal adsorbents [7]. NaOH and KOH, which produce high product yields when used as homogenous catalysts during transesterification, can be upgraded into heterogeneous catalysts by impregnating them into a supporting material such as bentonite clay. Due to its easy availability, low cost, eco-friendliness, high selectivity, and specific physical-chemical features, bentonite clay is an ideal supporting material for the preparation of heterogeneous catalysts [8]. Because of these qualities, bentonite clay was chosen as the supporting material in the present study.

The transesterification process of WCO is strongly affected by a few factors, one of which is the molar ratio of homogenous catalyst to the supporting material. It was found that as the weight percent (wt.%) of metal oxide loading increased, so did biodiesel production [1]. However, above a certain weight percent, the output was reduced due to agglomeration of the active metal oxide phase or the covering of the basic sites by excess metal oxide, resulting in a lower surface area of the catalyst and decreased activity [9]. At a weakly active site, the conversion of methanol to methoxy was relatively slow. When metal methoxide interacted with a suitable quantity of metal oxide, the methyl ester concentration rose steadily, resulting in a higher output of biodiesel [10].

In this study, sodium hydroxide supported with bentonite was prepared with different mole ratios. Its catalytic activity was tested in the transesterification of waste cooking oil to fatty acid methyl esters (FAME). The prepared catalysts were characterized using XRD and FTIR.

## MATERIALS AND METHODS

### Materials

Waste cooking oil (WCO) was obtained from a household around Pusat Komersil, Seksyen 7 Shah Alam. The chemically pure commercial bentonite, sodium hydroxide (NaOH), potassium hydroxide (KOH), and methanol were purchased from R&M.

### Feedstock Pre-treatment

The WCO feedstock was treated to ensure its suitability for transesterification. The process involved the removal of impurities, determination of acid value and FFA content, esterification of WCO, determination of saponification value and molecular weight, and determination of moisture content.

### Removal of Impurities

A small amount of used cooking oil was centrifuged for 10 minutes at 4800 rpm. The separated contaminants were removed, and the WCO sample was then processed further.

### Determination of Acid Value and Free Fatty Acids

The number of milligrams of potassium hydroxide required to neutralise the free fatty acid content in one gram of fat is known as the acid value (A.V.). Since free fatty acids are generated during the degradation of triglycerides, it is a relative measure of rancidity. The percentage of free fatty acids is computed as oleic acid due to its abundant amount in the feedstock.

The acid value was calculated using the AOCS Te 1a-64 standard method. In hot neutralised alcohol, 5 g of the oil sample was dissolved. Approx. 75 mL ethanol was heated with a few drops of phenolphthalein in a water bath to make the hot neutralised alcohol. Then, when the solution turned a light pink colour, 0.1 N NaOH was added. The oil and alcohol mixture was then heated for 10 minutes at 60 °C in a water bath, and then titrated against a standardised 0.1 N NaOH solution until a pale or light orange colour solution was observed.

Equations 1 and 2 were used to compute the acid value represented as oleic acid and the proportion of free fatty acids (percent FFA) respectively. The acid value should be less than 1.0 %; if it is higher, the sample should not be transesterified as it would disrupt the process by forming soap. If the calculated acid value is more than 1.0 %, the WCO must be neutralised using the acid esterification method.

$$\text{A.V.} = \frac{\text{volume of NaOH (mL)} \times \text{normality of NaOH (N)} \times 40.1}{\text{weight of sample (g)}} \tag{1}$$

$$\%\text{FFA} = \frac{\text{acid value}}{2} \tag{2}$$

### Determination of Saponification Value and Molecular Weight

The number of milligrams of potassium hydroxide (KOH) or sodium hydroxide (NaOH) necessary to saponify one gram of fat under the conditions indicated is referred to as the saponification value or saponification number (SV or SN). The AOAC standard method 920.160 was used to calculate the saponification value. In a 1000 mL volumetric flask, 40 g KOH and 45 g CaO were combined to make ethanolic KOH. The mixture was shaken for 5 minutes after adding distilled water to the mark. The solution was left overnight before filtering. Approx. 5 g of filtered WCO was added to an Erlenmeyer flask containing 50 mL ethanolic KOH, and the solution was refluxed until the fat was totally saponified. The cooled mixture was titrated against a standardised 0.5 M HCl solution with phenolphthalein as indicator. A blank experiment was carried out, in which the same amount of alcoholic potassium hydroxide solution without oil was handled the same way as the actual experiment.

The molecular weight of WCO is a function of its saponification and acid values [11]. The molecular weight of a material must be determined to find out how many grams are present in one mole of that substance. Equations 3 and 4 were used to calculate the saponification value and the average molecular weight of the oil [12].

$$\text{S.V.} = \frac{(V_{\text{HCl}}\text{ blank (mL)} - V_{\text{HCl}}\text{ sample (mL)}) \times 28.05}{\text{weight of oil (g)}} \tag{3}$$

$$\text{Average molecular weight} = \frac{56.1 \times 1000 \times 3}{\text{S.V.} - \text{A.V.}} \tag{4}$$

### Reduction of Free Fatty Acid Content

WCO should be esterified to lower its acid value to less than 1.0 %. The oil is esterified using a traditional reflux technique [13,14]. About 100 g WCO and 2.5 wt% $H_2SO_4$ in methanol were placed in a two-neck round bottom flask with a reflux condenser, temperature indicator, and magnetic stirrer (methanol to oil molar ratio of 6:1). The mixture was then stirred at 60 °C for 1.5 hours at 1400 rpm. After cooling to room temperature, the mixture was separated overnight into two layers in a separating funnel. The methyl ester in the bottom layer was purified, and the aqueous solution at the top, which included excess methanol and catalyst, was discarded. The methyl ester was purified using hot distilled water (80 °C). These steps were repeated six times, three times without shaking and three times with shaking. The oil was then heated for 90 minutes at 90 °C to eliminate any leftover moisture. Equations 1 and 2 were used to get the new acid value and FFA value, respectively.

### Determination of Moisture Content

The moisture content of the WCO was measured by heating a known amount of sample on a hotplate at 90 °C for 30 minutes. Equation 5 was used to compute the moisture content, where

$$\text{Moisture content} = \frac{\text{B - C}}{\text{B - A}} \times 100 \tag{5}$$

A: mass of flask (g)
B: mass of flask + WCO (before heating) (g)
C: mass of flask + WCO (after heating) (g)

### Catalyst Preparation

The method used to modify the bentonite clay was impregnation [6,7]. Prior to the impregnation process, the bentonite was activated by heating it in a muffle furnace at 500 °C for 3 hours. The catalyst was prepared with different molar ratios of bentonite clay and NaOH (1:1, 1:2, 1:3, and 1:4). The preparation of the catalyst was carried out in a two-neck round bottom flask equipped with a reflux condenser, temperature indicator, and mechanical stirrer. The mixture of bentonite and NaOH was heated at 60 °C for 6 hours with continuous stirring at 1500 rpm. Later, the sample was subjected to heating at 60 °C for 21 hours, and then heated in a muffle furnace at 300 °C for 3 hours to activate the catalyst.

### Catalyst Characterization

X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) were used to analyse the catalysts. Powder XRD patterns were captured with a PANalytical X'Pert HighScore Plus instrument that used Cu Kα radiation with a 0.01° step size and a 2° to 90° range [6]. The functional groups in the compounds were identified using FTIR. The absorption of IR radiation by each bond in the molecule was evaluated using infrared spectroscopy, which produces a spectrum that typically measures percent transmittance against wavenumber ($cm^{-1}$) [15]. The samples were analysed at wavenumbers ranging from 370 to 4000 $cm^{-1}$ [16] to detect the presence of new functional groups after the impregnation process.

## Transesterification of Waste Cooking Oil

The transesterification of WCO was accomplished using the standard reflux process. A two-neck round bottom flask with a condenser, temperature indicator, and magnetic stirrer was filled with 6 wt.% of the prepared catalyst, methanol (methanol: oil = 9:1) and treated WCO, and then the mixture was heated at 60 °C for 195 minutes. The catalyst was separated by centrifugation at 4800 rpm for 10 minutes. The glycerol of the upper layer was removed, and the biodiesel in the bottom layer was purified. Biodiesel was purified with hot water (80 °C) until it turned neutral (pH 7). The volume of biodiesel and the amount of water used for washing was 1:1. The biodiesel was then heated at 90 °C for 10 minutes on a hot plate to eliminate moisture [2].

After the acid value of the product was determined using Equation 1, the FFA conversion was calculated using Equation 6, where $A.V_f$ and $A.V_p$ are the acid value of the feedstock and product, respectively.

$$\text{FFA conversion (\%)} = \frac{A.V_f - A.V_p}{A.V_f} \times 100 \tag{6}$$

**Table 1.** Pre-treatment process results

| Properties | Unit | Value | ASTM D6751 Standard |
|---|---|---|---|
| Acid value | mg KOH/g | 0.71 | Max 1.0 |
| FFAs | wt.% oleic acid | 0.35 | Max 0.5 |
| Moisture content | wt.% | 0.22 | Max 1.0 |
| Saponification value | mg KOH/g | 206.70 | * |
| Molecular weight | g/mol | 817.03 | * |

** Not specified*

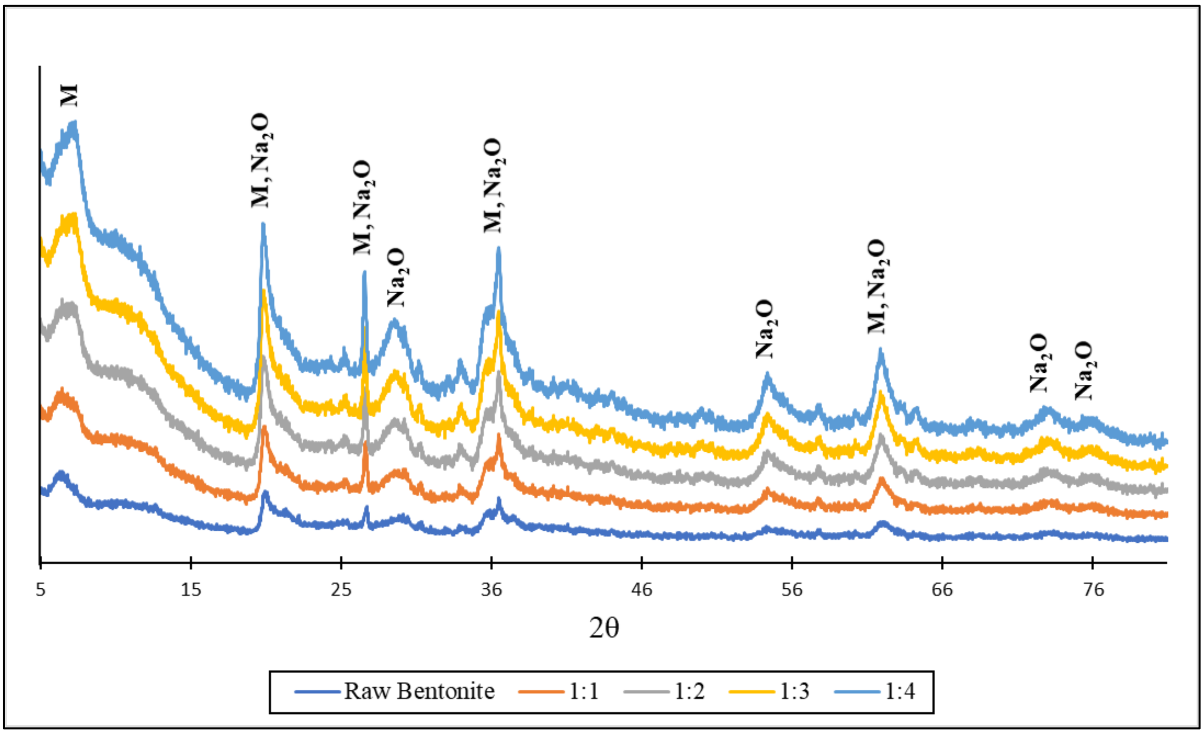

**Figure 1.** XRD patterns of the NaOH/bentonite catalysts and raw bentonite.

## RESULTS AND DISCUSSION

### Feedstock Analysis

The acidity of the starting material can significantly influence the % FAME of the product. The acid value is connected to the FFA value because the acid value increases when the fatty acids break down into shorter chain acids [17]. The acid value was determined to be 0.98 mg KOH/g, while the proportion of FFAs was found to be 0.49 wt.% after pre-treatment of the feedstocks. The results of the pre-treatment process can be seen in Table 1.

### Catalyst Characterization

### XRD Analysis

Sodium hydroxide was converted into its oxide form ($Na_2O$) and other impurities such as $Na_2O_2$ during the calcination process. XRD analysis was used to determine the presence of $Na_2O$. Figure 1 shows the XRD patterns of both the catalyst and raw bentonite.

As shown in Figure 1, the XRD patterns of raw bentonite had typical diffraction peaks at $2\theta = 7°, 20°, 27°, 37°$, and 62° which confirmed the presence of montmorillonite (M) as a major phase in bentonite. The XRD patterns of the raw bentonite and bentonite:NaOH were very similar. However, the formation of a new phase, $Na_2O$, was clear [7]. The peaks at $2\theta = 20°, 27°, 29°, 54°, 62°, 73°$ and 75° indicated the presence of $Na_2O$ crystals formed during the calcination of NaOH/bentonite.

The addition of NaOH and calcination changed the crystallinity of raw bentonite, as shown by the XRD pattern of the composite catalysts. Due to the dispersion of NaOH, the original phases of raw bentonite, as shown in the Figure 1, are also present, with different diffraction peak values and crystal structures [18]. The formation of $Na_2O$ in the composite catalysts was responsible for their high catalytic activity and basicity, while those afore-mentioned metals in their oxide forms dominated the XRD patterns of the catalyst samples [11].

### FTIR Analysis

The FTIR spectrum of raw bentonite (Figure 2) revealed the presence of functional groups such as Al(Mg)-O-H (a, ~3620 $cm^{-1}$), H-O-H (c, ~1650 $cm^{-1}$), Si-O-Si (d, ~1040 $cm^{-1}$), and Si-O (e, ~790 $cm^{-1}$). FTIR analysis also showed that the addition of NaOH affected the structure of the bentonite network. The intensity of the Al(Mg)-O-H stretching band slightly decreased with the addition of NaOH and there was a slight shift in the absorption band of this group from ~3620 $cm^{-1}$ to ~3430 $cm^{-1}$, indicating the presence of a new functional group in the catalysts. The peak at about 3430 $cm^{-1}$ (b) indicated the stretching vibration of the Al-O-Na group [18]. The formation of a new functional group confirmed that sodium hydroxide was impregnated on the surface of bentonite [7].

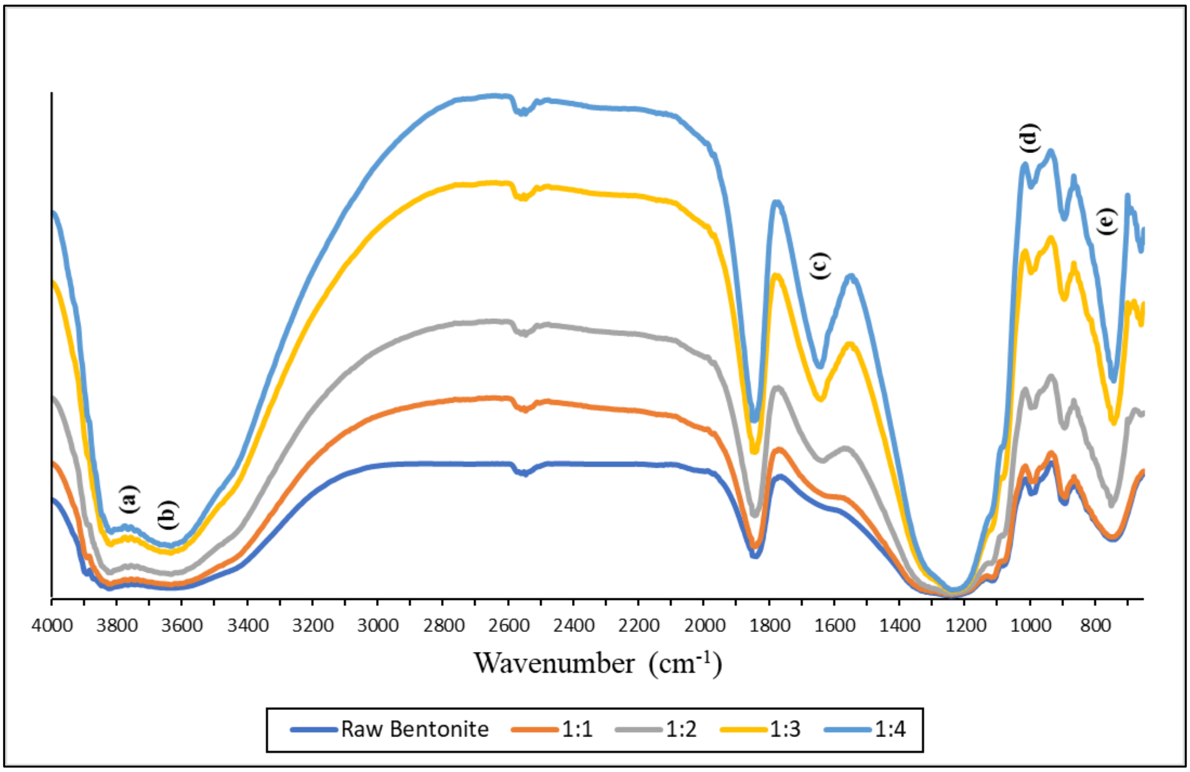

**Figure 2.** FTIR spectra of NaOH/bentonite catalysts and raw bentonite.

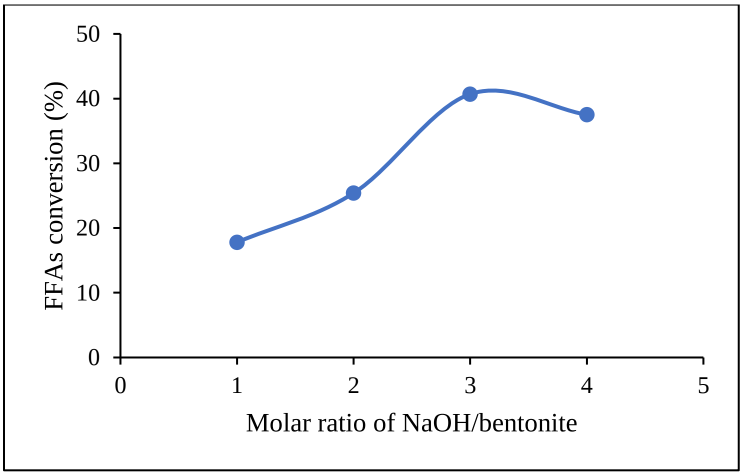

**Figure 3.** FFA conversion values at different NaOH/bentonite molar ratios.

### Catalytic Activity of NaOH/Bentonite

The percentage of free fatty acid conversion was used to study the catalytic effect of NaOH/bentonite loading on transesterification. The amount of catalyst was set at 6% (based on the weight of palm oil), the methanol to oil molar ratio was 9:1, the reaction period was 195 minutes, and the reaction temperature was approx. 60 °C. The results showed that the quantity of NaOH in bentonite impacted the conversion of palm oil to biodiesel. The biodiesel yield was also enhanced by increasing the loading ratio of bentonite:NaOH from 1:4 to 1:1.

The NaOH/bentonite 1:3 ratio produced the best yield (40.7%) with a standard deviation of 9.94. The number of $Na_2O$ active sites in the catalyst rose when the NaOH loading increased, resulting in an increase in biodiesel production. Further increases in NaOH loading, however, resulted in a lower biodiesel output, as can be seen in Figure 3.

## CONCLUSION

A series of NaOH/bentonite catalysts were successfully produced, as evidenced by XRD and FTIR analyses. A maximum biodiesel yield of 40.7 % was obtained with the catalyst having a 1:3 molar ratio of bentonite:NaOH. Overall, this catalyst has the potential to be important in biodiesel generation. However, further studies on the optimal conditions for transesterification are necessary to fully exploit this catalyst.

## ACKNOWLEDGEMENTS

The authors would like to acknowledge the FRGS project funding (FRGS1/2019/STG07/UiTM/02/23) from the Research Management Centre (RMC) and Universiti Teknologi MARA (UiTM). The authors declare that they have no conflict of interest.

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