

# MODIFIED MESOPOROUS $\gamma$ -ALUMINA FROM KANO KAOLIN IN HETEROGENEOUS TRANSESTERIFICATION OF RICE BRAN OIL

Abdu Muhammad Bello<sup>a,b</sup>, Abdul Rahim Yacob<sup>a\*</sup>, Kamaluddeen Suleiman Kabo<sup>a,b</sup>

## Article history

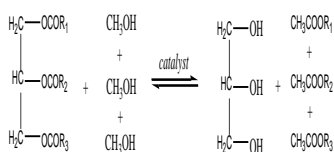
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\*Corresponding author  
manrahim@kimia.fs.utm.my

<sup>a</sup>Department of Chemistry, Faculty of Science, University of Technology Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

<sup>b</sup>Department of Chemistry, School of Natural and Applied Sciences, Sa'adatu Rimi College of Education Kumbotso, PMB 3218, Kano State, Nigeria

## Graphical abstract



## Abstract

The environmental problems caused by the excessive usage of fossil fuel, prompted the need for an alternative source of energy. Renewable energy from biodiesel is one of the most promising substitutions of fossil fuel due its environmental-friendliness. In the present work NaOH-modified  $\gamma$ -alumina heterogeneous base catalysts were prepared using wet impregnation method, and characterized by Nitrogen Adsorption Analysis (BET), Fourier Transform Infra-Red (FTIR), X-Ray Powder Diffraction (XRD), basic back titration, and Temperature Programmed Desorption-CO<sub>2</sub> (CO<sub>2</sub>-TPD). The catalysts were tested for the transesterification of rice bran oil with methanol, and the biodiesel product characterized by Fourier Transform Infra-Red-Attenuated Total Reflection (FTIR-ATR) and Nuclear Magnetic Resonance Spectroscopy (NMR) analyses. Catalyst synthesise with 50% NaOH was found to have the highest basic sites and when applied for the transesterification of rice bran oil it gave the highest yield of 81.2%. The high catalytic activity is attributed to the formation of NaAlO<sub>2</sub> that is believed to contribute to the basicity of the catalyst.

Keywords: Mesoporous, heterogeneous, catalyst, biodiesel, transesterification

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## 1.0 INTRODUCTION

The growing increase in the environmental problems experienced as a result of excessive usage of fossil fuel prompted the need for an alternative energy source. Renewable energy from biodiesel is one of the most promising substitutions of fossil fuel due to its environmental-friendliness combined with the positive engine properties similar to those of petroleum-derived diesel. Rudolf Diesel proposed vegetable oil as an engine fuel over 100 years ago [1]. However, due to high viscosity of vegetable oils its utilization as fuel for diesel engines became practically unacceptable [2]. Chemical or physical modifications viz; pyrolysis, micro-emulsification,

dilution, and transesterification have been attempted to overcome this problem. Transesterification is the most common method used to reduce the viscosity of vegetable oils due to the fact that other methods are associated with problems such as carbon deposition and contamination. The transesterification products are collectively termed 'biodiesel' because they can be used either neat or blended with the petro-diesel (petroleum diesel) [3, 4]. Biodiesel has the advantage of being biodegradable, as a result the carbon dioxide emissions can be recycle, this greatly reduce the emission of green-house gases [5].

The oil crises of the 1970s initiated the biofuels development so as to moderate the price hike, over dependent and harmful effects of fossil fuel [6]. Industrial production process of biodiesel was first patented by a Brazilian scientist, Expedito Parente, but the commercial production of biodiesel has suffered a setback as a result of increasing subsidy in the petroleum market. However, due to the growing concerns about the environmental sustainability, many European countries have started constructing biodiesel plants in the late 1990s, which open the door for commercial production of biodiesel [4].

Rice bran oil is extracted from rice bran, but, currently only small amount of it is being used to produce oil [7]. Rice bran is a thin outer layer covering the surface of rice seeds and its oil content is about 13.5%, this make it an interesting candidate as biodiesel substrate [8]. In some African countries like Nigeria there is a high production of rice, but the husk and bran are thrown away. Using rice bran oil for biodiesel production will encourage farmers to utilize the rice bran thereby improving their incomes, at the same time reducing environmental problem.

Homogeneous catalysts including strong acidic solutions such as hydrochloric acid and sulphuric acid and strong basic solutions such as sodium hydroxide, sodium methoxide and potassium hydroxide where initially used in transesterification reaction [9]. High energy consumption and costly separation of homogeneous catalyst from the reaction mixture make the process uneconomical. There is also the problem of soap formation through neutralization of FFAs or saponification of triglycerides.

Heterogeneous catalysts are developed to overcome the problem associated with homogeneous catalysts. Heterogeneous catalysts can eliminate the corrosion problem and consequent environmental hazards posed by the homogeneous catalysts [10]. Solid heterogeneous catalysts have the advantage of reusability which makes continuous fixed-bed operation possible. Such continuous process can minimize product separation and purification costs, which will make it economically viable to compete with commercial petroleum-based diesel fuel [9].

Alumina has been widely used as a support in catalysis processes owing to its extremely thermal and mechanical stability, high specific surface area, as well as large pore size and pore volume. Supports should be modified during preparation of catalysts to anchor catalytic species and obtain reusability. MgO, CaO, ZnO and Al<sub>2</sub>O<sub>3</sub>, are used as supports, however, alumina is the most popular support due to the aforementioned advantages, coupled with transition crystalline phases that exist in a wide temperature range. Both acid and base can be supported on alumina, most super basicity sources can be well dispersed on the alumina support in the form of a monolayer at a low loading [11]. Alkaline and alkaline earth metals in the metallic form or as various ionic forms of hydroxide, halide, carbonate

and nitrate are used as active species of supported catalyst for biodiesel synthesis due to their super basicity. For example in KNO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst, K<sup>+</sup> ions replaced proton of isolated hydroxyl groups to form Al-O-K groups, the Al-O-K groups and K<sub>2</sub>O derived from KNO<sub>3</sub> are the basic species. The basic strength is influence by KNO<sub>3</sub> loading and calcination temperature. Result showed that catalyst prepared using 35% KNO<sub>3</sub> and calcined at 500 °C has the highest basicity, but, when calcined at 700 °C it possessed highest stability [11].

Numerous studies were reported in the literature using alumina as catalyst support for the production of biodiesel [12-16]. However, all these catalysts used commercial alumina as support, as such little is known on the catalytic activities of mesoporous alumina synthesized from kaolin, especially one obtained from Kano Nigeria. Utilization of kaolin, which is abundant, inexpensive and non-toxic, as precursor for the synthesis of mesoporous  $\gamma$ -alumina will result in chemical processes that are clean, energy efficient, intrinsically safe and responsive to market needs, this will lead to achievement of the requirements for generation of nearly zero waste chemicals, less energy consumption and use of less hazardous chemicals. In the present work, different amount of sodium hydroxide were supported on mesoporous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, the synthesis procedure for the alumina was reported in our previous work [17]. The synthesized NaOH/Al<sub>2</sub>O<sub>3</sub> catalysts were applied for the transesterification of rice bran oil in the present of methanol to assess their catalytic activities.

## 2.0 EXPERIMENTAL

### 2.1 Materials

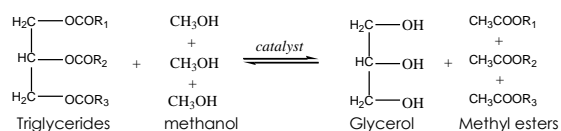
The kaolin was obtained from Getso town, Kano state, Nigeria, rice bran oil from Jusco Super Market, Skudai, Malaysia, hydrochloric acid (HCl) with purity 37%, sodium hydroxide (NaOH) and methanol purity > 99% were purchased from QRëC™, while 99.8% deuterated chloroform was supplied by Merck, Germany for NMR analysis. All chemicals were of analytical grade and used without further purification.

### 2.2 Wet Impregnation

0.2 g NaOH (10 wt% base on Al<sub>2</sub>O<sub>3</sub>) was dissolved in 25 mL distilled water, the solution then added to 2 g of Al<sub>2</sub>O<sub>3</sub>, stirred for 1 h and allowed to stay for 3 h at room temperature. After evaporation the product was dried overnight at 120 °C, followed by calcination at 500 °C for 3 h. 15, 20, 30, 40 and 50 wt% were prepared using same procedure. The catalysts were denoted X-NaOH/Al<sub>2</sub>O<sub>3</sub>, where, X is 10%, 15%, 20%, 30%, 40% and 50%, respectively.

### 2.3 Transesterification Reaction

5 wt% of the catalyst, based on oil, was added to 4.2 mL of methanol in a 250 ml double necked round bottom flask fitted with condenser and thermometer, the mixture was stirred for 20 mins at 67 °C in a paraffin oil bath, then 11 mL of rice bran oil was added and the reaction maintained at the same temperature for 3 hrs with stirring (oil: methanol is 1:9). After the completion of the reaction the products were allowed to settle overnight and centrifuged at 3000 rpm for 15 mins. Three layers were observed; the small upper layer of excess methanol was removed, while the middle layer of biodiesel and the lower layer which contained glycerol and settled catalyst were separated using separating funnel. Figure 1 depicts the schematic equation for the transesterification reaction.



**Figure 1** General equation for transesterification reaction

### 2.4 Characterization of the Catalyst and Biodiesel

Micromeritics PulseChemiSorb 2705 (USA) was used to determine the surface area based on the principle of nitrogen gas adsorption-desorption on the porous surfaces of the sample. 10 mg of each sample was placed in a tube and degassed for 1 hr at 473 K under nitrogen gas flow condition. The tube containing the sample was then evacuated to  $10^{-2}$  Torr and immersed in liquid nitrogen. Perkin Elmer 1650 Infra-Red Spectrometer (USA) was used for FTIR analysis of samples in the range of  $4000\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$ . Structural phase analysis was carried out on a Bruker D8 having Siemens Diffractometer D5000 (USA) with Cu-K $\alpha$  radiation (40 kV, 40 mA,  $\lambda = 1.5406\text{ \AA}$ ). Temperature Programmed Desorption- $\text{CO}_2$  ( $\text{CO}_2$ -TPD) analysis was performed on a micromeritics AutoChem 2920 Chemisorption Analyzer (USA), 3-4 mg sample was degassed by heating in a flow of helium gas from room temperature to  $600\text{ }^\circ\text{C}$  at a rate of  $10\text{ }^\circ\text{C}/\text{min}$  and maintained at  $600\text{ }^\circ\text{C}$  for 2 hrs. Adsorption of  $\text{CO}_2$  gas occurred at  $100\text{ }^\circ\text{C}$ , the physically adsorbed  $\text{CO}_2$  gas was purged by a helium flow at  $45\text{ }^\circ\text{C}$  for 2 hours. The basic strength of the catalysts was determined using basic back titration method. Perkin Elmer 1650 FTIR (USA) Spectrometer-Frontier fitted with universal attenuated total reflection (ATR) sampling accessory was used for the analysis of the products of the transesterification reaction in the wave number range of  $4000$  to  $600\text{ cm}^{-1}$ . The spectra were obtained using 16 scans at spectral resolution of  $2\text{ cm}^{-1}$ . The NMR spectra of biodiesel samples were

obtained using Bruker 400 (USA) to determine the percentage conversion of the biodiesel [12, 18, 19].

## 3.0 RESULTS AND DISCUSSION

### 3.1 BET Surface Area

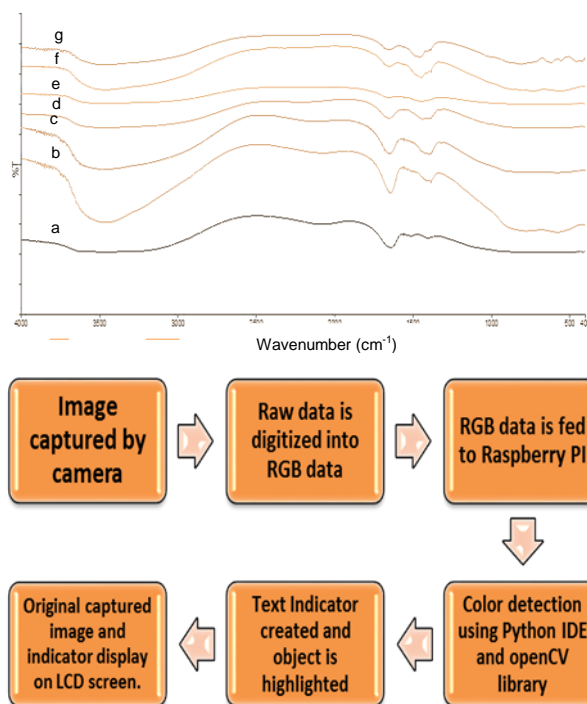
From the BET result presented in Table 1, the surface area was found to decrease with increasing loading of NaOH. The lowering of the alumina surface area after supporting NaOH is due to fact that the surface and pores of alumina were covered by sodium compound. Same observation was reported by other researchers [12, 13, 15]. The lower surface area of catalyst loaded with 40% NaOH compared with that of 50% may be due to the conversion of more NaOH to  $\text{NaAlO}_2$  in the later as indicated by the FTIR and XRD results.

**Table 1** Surface area of catalysts

CATALYSTS	SURFACE AREA ( $\text{m}^2/\text{g}$ )
0% NaOH/ $\text{Al}_2\text{O}_3$	222.7
10% NaOH/ $\text{Al}_2\text{O}_3$	193.4
15% NaOH/ $\text{Al}_2\text{O}_3$	136.3
20% NaOH/ $\text{Al}_2\text{O}_3$	73.7
30% NaOH/ $\text{Al}_2\text{O}_3$	21.4
40% NaOH/ $\text{Al}_2\text{O}_3$	4.0
50% NaOH/ $\text{Al}_2\text{O}_3$	6.1

### 3.2 Fourier Transform Infra-Red (FTIR)

Figure 2 depicts the FTIR spectra of the NaOH-modified  $\gamma\text{-Al}_2\text{O}_3$ . All the peaks present in the as-synthesized alumina were also present in the modified one. New peaks appeared around  $1394$  to  $1460\text{ cm}^{-1}$  and they became more and more intense and shift to higher wavelength with increasing amount of NaOH loading. These peaks are associated with the anti-symmetric vibration of carbonate [20-22], which indicate increasing basic sites with increasing amount of NaOH loading. The carbonate is formed as a result of chemisorption of  $\text{CO}_2$ , an acidic probe molecule that is used to assess the basic sites of a compound [23]. Three more peaks appeared in the 50% NaOH/ $\text{Al}_2\text{O}_3$  spectrum at  $457.5$ ,  $556.9$  and  $623.8\text{ cm}^{-1}$ , these peaks may be due to the present of  $\text{NaAlO}_2$  whose peaks are very well pronounced in the XRD pattern of the 50% NaOH/ $\text{Al}_2\text{O}_3$ .



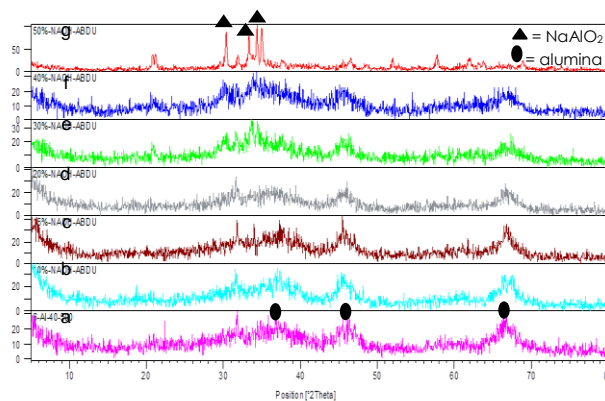
**Figure 2** FTIR spectra of a. 0% NaOH/Al<sub>2</sub>O<sub>3</sub>, b. 10% NaOH/Al<sub>2</sub>O<sub>3</sub>, c. 15% NaOH/Al<sub>2</sub>O<sub>3</sub>, d. 20% NaOH/Al<sub>2</sub>O<sub>3</sub>, e. 30% NaOH/Al<sub>2</sub>O<sub>3</sub>, f. 40% NaOH/Al<sub>2</sub>O<sub>3</sub> and g. 50% NaOH/Al<sub>2</sub>O<sub>3</sub>

### 3.3 X-Ray Diffraction Analysis (XRD)

At lower loading of NaOH on alumina, 10%, 15% and 20%, the characteristic peaks of the alumina remain almost unchanged in the XRD patterns presented in Figure 3, indicating good dispersion of NaOH on the alumina support [24]. With increasing amount of NaOH loading to 30% and 40% several diffraction peaks due to the present of NaAlO<sub>2</sub> appeared as a result of a reaction between NaOH and Al<sub>2</sub>O<sub>3</sub>, the peaks became very sharp when the loading reached 50%, indicating very high crystallinity and basicity of the 50% NaOH/Al<sub>2</sub>O<sub>3</sub> catalyst compared with the rest. This affirms the observation in the FTIR analysis that attributed the appearance of new peaks to the formation of NaAlO<sub>2</sub>. Alumina reacts with sodium hydroxide according to the following equation;



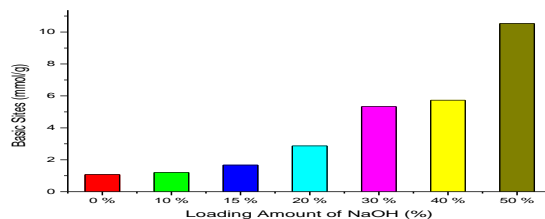
The formation of the sodium aluminate originates the stronger basic sites of the catalyst [25].



**Figure 3** XRD pattern of a. 0% NaOH/Al<sub>2</sub>O<sub>3</sub>, b. 10% NaOH/Al<sub>2</sub>O<sub>3</sub>, c. 15% NaOH/Al<sub>2</sub>O<sub>3</sub>, d. 20% NaOH/Al<sub>2</sub>O<sub>3</sub>, e. 30% NaOH/Al<sub>2</sub>O<sub>3</sub> f. 40% NaOH/Al<sub>2</sub>O<sub>3</sub> and g. 50% NaOH/Al<sub>2</sub>O<sub>3</sub>

### 3.4 Basic Back Titration Analysis

Basic strength of the unsupported and supported alumina were determined using basic back titration method and the results are presented in Figure 4, the basic sites were found to be 1.07 mmol/g for the unmodified alumina and 1.20, 1.67, 2.87, 5.33, 5.73 and 10.53 mmol/g for 10%, 15%, 20%, 30%, 40% and 50% NaOH/Al<sub>2</sub>O<sub>3</sub> catalysts, respectively. This confirm the deduction made from FTIR and XRD results indicating that 50% NaOH/Al<sub>2</sub>O<sub>3</sub> have very high amount of basic sites.

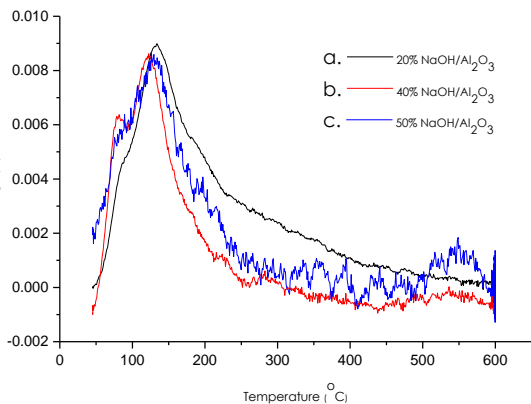


**Figure 4** Basic sites of the synthesized catalysts

### 3.5 Temperature Programmed Desorption-CO<sub>2</sub> (CO<sub>2</sub>-TPD)

The 20%, 40% and 50% NaOH/Al<sub>2</sub>O<sub>3</sub> catalysts were selected and analyzed using temperature programmed desorption of CO<sub>2</sub> in order to ascertain the result obtained from basic back titration analysis, the TPD spectra are presented in Figure 5. The 20% NaOH/Al<sub>2</sub>O<sub>3</sub> catalyst gave only one desorption peak at 126.3 °C, which is assigned to weak basic sites, while the spectrum of 40% NaOH/Al<sub>2</sub>O<sub>3</sub> showed three desorption peaks, two at 78.8 °C and 130.4 °C that are attributed to weak basic sites and the other one at higher temperature, 582.2 °C, that is assigned to a strong basic sites. Regarding the 50% NaOH/Al<sub>2</sub>O<sub>3</sub>, apart from the broad desorption band at lower temperature, 129.5 °C, corresponding to weak basic sites, it showed two small desorption peaks at high temperature, 586.5 °C and 599.0 °C that point to a

strong basic sites. Desorption peaks at temperature below 300 °C, 320-570 °C and 550-700 °C are assigned to weak, medium and strong basic sites respectively [12,26-28]. This observation corroborates the findings in the FTIR, XRD and basic back titration that identified 50% NaOH/Al<sub>2</sub>O<sub>3</sub> as one with the highest basic sites.



**Figure 5** TPD-CO<sub>2</sub> spectra of a) 20% NaOH/Al<sub>2</sub>O<sub>3</sub>, b) 40% NaOH/Al<sub>2</sub>O<sub>3</sub> and c) 50% NaOH/Al<sub>2</sub>O<sub>3</sub> catalyst

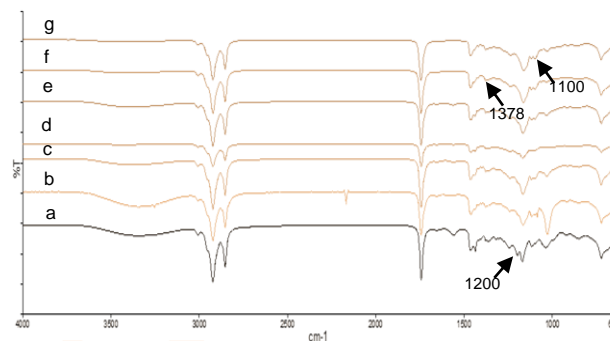
### 3.6 Biodiesel Analysis

The catalytic activities of the synthesized catalysts were determined using transesterification reaction of rice bran oil with methanol, and the biodiesel obtained was characterized by FTIR-ATR and NMR analysis.

#### 3.6.1 Fourier Transform Infra-Red Analysis/Attenuated Total Reflection (FTIR-ATR)

The FTIR spectra of biodiesel produced in the present of un-modified Al<sub>2</sub>O<sub>3</sub> and the NaOH modified Al<sub>2</sub>O<sub>3</sub> catalysts are presented in Figure 6. Due to the high chemical similarities between methyl ester and triglycerides the spectra of biodiesel and oil are similar [12]. However some characteristic absorption frequencies can be used to detect the formation of FAME from the triglyceride. For instance the peak around 1100 cm<sup>-1</sup> assigned to the C-CH<sub>2</sub>-O vibration present in TG is observed to be decreased on the formation of FAME and almost became absent in the biodiesel produced using 50% NaOH/Al<sub>2</sub>O<sub>3</sub> catalyst indicating high conversion. The absorption peak at 1200 cm<sup>-1</sup> attributed to O-CH<sub>3</sub> stretching vibration in methyl ester is only present in the spectra of biodiesel produced with 20% NaOH/Al<sub>2</sub>O<sub>3</sub> and 50% NaOH/Al<sub>2</sub>O<sub>3</sub> catalysts, however, it is very small in the former and sharp in the later, pointing to a high conversion in the case of 50% NaOH/Al<sub>2</sub>O<sub>3</sub> catalyst [29,30].

The absorption peak at 1378 cm<sup>-1</sup> characteristic of the terminal CH<sub>3</sub> and OCH<sub>2</sub> in a glycerol can also be used to monitor the formation of FAME, since the conversion of TG to FAME involves the loss of glycerol [31]. This peak was found to decrease drastically in the spectrum of the biodiesel produced using 50% NaOH/Al<sub>2</sub>O<sub>3</sub> catalyst. This finding supports the results for the characterization of the catalysts that attributed highest basic sites to the 50% NaOH/Al<sub>2</sub>O<sub>3</sub> catalyst.



**Figure 6** FTIR-ATR spectra of biodiesel using a. 50% NaOH/Al<sub>2</sub>O<sub>3</sub> b. 40% NaOH/Al<sub>2</sub>O<sub>3</sub>, c. 30% NaOH/Al<sub>2</sub>O<sub>3</sub>, d. 20% NaOH/Al<sub>2</sub>O<sub>3</sub>, e. 15% NaOH/Al<sub>2</sub>O<sub>3</sub>, f. 10% NaOH/Al<sub>2</sub>O<sub>3</sub> and g. 0% NaOH/Al<sub>2</sub>O<sub>3</sub>

#### 3.6.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

The percentage conversions of the biodiesel produced with different catalysts were determined by <sup>1</sup>H NMR spectroscopy. The ratio of peak area of the methoxy protons from methyl esters (singlet) at 3.7 ppm and that of  $\alpha$ -carbonyl methylene groups from fatty ester at 2.3 ppm (triplet) were used in the calculation of the percentage conversion of biodiesel. The relationship is presented below;

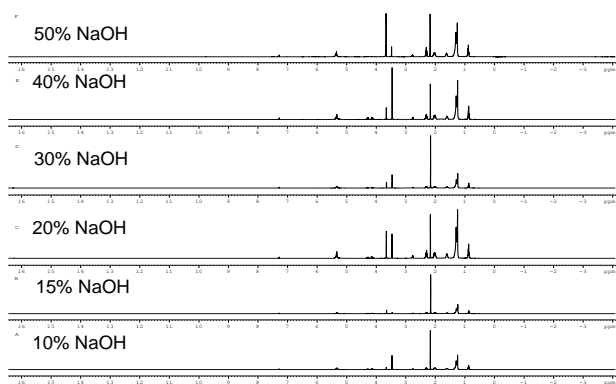
$$\text{Percentage conversion} = \frac{2A_1}{3A_2} \times 100$$

Where, A<sub>1</sub> and A<sub>2</sub> are the areas of the methoxy and the methylene protons, respectively [32].

The percentage conversions of oil to biodiesel using different catalysts are depicted in Table 2, and to highlight the reliability of NMR analysis as a method for determining the conversion of oil to biodiesel the present work is compared with other results from literature in Table 3. From the NMR spectra in Figure 7, peak due to glyceride proton at 4.3 ppm can be observed in all the biodiesel products indicating an incomplete conversion, however for the biodiesel produced using 50% NaOH/Al<sub>2</sub>O<sub>3</sub> the peak is very small supporting the high conversion observed with this catalyst.

**Table 2** Percentage conversion of oil to biodiesel

Catalyst	Conversion (%)
0% NaOH/Al <sub>2</sub> O <sub>3</sub>	1.41
10% NaOH/Al <sub>2</sub> O <sub>3</sub>	14.2
15% NaOH/Al <sub>2</sub> O <sub>3</sub>	23.4
20% NaOH/Al <sub>2</sub> O <sub>3</sub>	46.1
30% NaOH/Al <sub>2</sub> O <sub>3</sub>	29.9
40% NaOH/Al <sub>2</sub> O <sub>3</sub>	23.3
50% NaOH/Al <sub>2</sub> O <sub>3</sub>	81.2

**Figure 7** NMR spectra of biodiesel from different NaOH modified alumina

The respective high and moderate conversion observed when 50% NaOH/Al<sub>2</sub>O<sub>3</sub> and 20% NaOH/Al<sub>2</sub>O<sub>3</sub> catalyst were used, as well as the low conversion for the rest of catalysts agreed very well with the observation from the FTIR spectra of the biodiesel where the absorption peak at 1200 cm<sup>-1</sup> due to O-CH<sub>3</sub> was observed only in the 20 and 50% NaOH/Al<sub>2</sub>O<sub>3</sub>.

The findings from the biodiesel characterizations corroborate the results obtained from the catalysts characterizations that point to a high basicity of the 50% NaOH/Al<sub>2</sub>O<sub>3</sub> in comparison with the remaining catalysts. The low conversion from 40% NaOH/Al<sub>2</sub>O<sub>3</sub> despite its high basicity may be attributed to low BET surface area 4.00 m<sup>2</sup>/g, since activity of a catalyst also depends on surface area. The low surface area may be the reason for low amount of desorbed CO<sub>2</sub> (0.04152 mmol/g), which when compared with 20% NaOH/Al<sub>2</sub>O<sub>3</sub> although the desorption peak was observed at low temperature, however the amount of CO<sub>2</sub> desorbed was 0.28917 mmol/g and could be the reason for the moderate conversion of TG to FAME in its present.

**Table 3** Comparison of biodiesel conversion using different method

Catalyst	Conversion (%)	Reference
NaOH/Al <sub>2</sub> O <sub>3</sub>	81.2	This study
NaOH/Al <sub>2</sub> O <sub>3</sub>	99	[12]
CaO/KI/Al <sub>2</sub> O <sub>3</sub>	95	[13]
KF/Al <sub>2</sub> O <sub>3</sub>	99.6	[15]
KF & NaNO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	80 & 87	[18]
Na/NaOH/γ-Al <sub>2</sub> O <sub>3</sub>	83	[23]
NaOH/Al <sub>2</sub> O <sub>3</sub>	86	[24]
KI/Al <sub>2</sub> O <sub>3</sub>	96	[33]

## 4.0 CONCLUSION

Different amounts of sodium hydroxide were supported on synthesized mesoporous alumina using wet impregnation method. FTIR, XRD, back titration and TPD-CO<sub>2</sub> analyses were used to probe the basicity of the catalysts. From the results obtained, 50% NaOH/Al<sub>2</sub>O<sub>3</sub> catalyst was found to have the highest basic sites and when applied for the transesterification of rice bran oil it gave the highest conversion of 81.2%. Although other workers reported higher conversion, as presented in Table 3, however, they used optimized reaction conditions. It is expected to get much higher conversion after optimizing the reaction parameters. It can be concluded that mesoporous alumina synthesized from Kano kaolin can serve as a good catalyst support. This can be attributed to its high surface area and very good thermal stability as reported in our previous work [17].

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