



ISSN: 2319-5967

ISO 9001:2008 Certified

International Journal of Engineering Science and Innovative Technology (IJESIT)

Volume 9, Issue 3, May 2020

Acid treated attapulgite functionalized with Na-compounds as novel bi-functional heterogeneous solid catalysts for biodiesel production

Sylvia Adipah, Mohammed Takase

Department of Environmental Engineering and Science, Chongqing University, Chongqing, 400044
Department of Environmental Science, Cape Coast University, Ghana

Abstract: *In this study, transesterification reaction of Allanblackia floribunda oil with methanol to biodiesel using attapulgite which was treated with HCl and then functionalized with NaOH and NaCl as solid base catalysts was studied. Having screened the catalytic performance of HCl treated attapulgite functionalized with NaOH at different concentrations, 3M of NaOH was chosen and the performance was compared with 3M of NaCl. The two catalysts were prepared using impregnation method. Following drying (after functionalization) and calcination at 450 °C for 4 h, the catalysts were characterized by means of Hammett indicators, Nitrogen adsorption isotherms, XRD, SEM and TGA. The performance of HCl treated attapulgite functionalized with 3M of NaOH (3NaOH/HCl-Atta-4) was superior to that of NaCl (3NaCl/HCl-Atta-4) and HCl-Atta-4 (control). Maximum yield of 94.7 and 92.2% was obtained by 3NaOH/HCl-Atta-4 and 3NaCl/HCl-Atta-4, respectively. The optimum reaction conditions were methanol/oil ratio of 9:1, catalyst amount of 6wt.%, reaction temperature of 60 °C in 6 h. The catalysts maintained sustained activities after 5 runs of reuse. The properties of the biodiesels were comparable with American and European Union standards and could be rated as realistic fuel alternative to diesel.*

Key words: Biodiesel, Allanblackia floribunda oil, Attapulgite, Heterogeneous catalyst, Na-compounds, Transesterification, Methyl esters.

I. INTRODUCTION

Biodiesel production has become very important due to increase in cost and demand for energy, environmental considerations and reductions in fossil fuel reserves [1, 2]. Commercial production of biodiesel is commonly being carried out using basic homogeneous catalysts such as sodium hydroxide, potassium hydroxide and methoxide. The homogeneous catalysts could produce relatively high yields [3, 4], however, there are several setbacks including corrosion of equipment and the need to deal with waste from the neutralization of acid. Enzymes are also used as catalyst for biodiesel production but the main problem is the high cost and instability of enzymes [5]. Studies indicate that using solid catalysts rather than homogeneous can minimize the cost of producing biodiesel [6, 7]. Heterogeneous solid catalysts offer advantages such as recyclability, easy separation from biodiesel, high quality esters and are also less consumed [8, 9].

Current studies on heterogeneous catalysts are directed towards basic single metal oxides such as strontium, calcium and magnesium oxides [10-13]. To enhance the basicity and yield of fatty acid methyl esters, mixed metal oxides such as Al_2O_3 -SnO, Al_2O_3 -ZnO and Mg-La oxides [14, 15], $Ca_2Fe_2O_5$, $CaZrO_3$ and $CaCeO_3$ [16] have been tested and proven promising.

Studies have however, shown that heterogeneous catalysts functionalized with either sodium or potassium compounds could be feasible for producing biodiesel [17]. The activity of such catalysts depend greatly on the type of the carrier, potassium or sodium loading amount and the conditions of pretreatment [18, 19].

Studies concerning the use of clay minerals as catalysts or catalytic support are gaining prominence. Typical clays such as zeolite, dolomite, kaolin, bentonite and attapulgite are currently used as catalysts or catalyst supports in various applications [18-21]. However, there is only one report available on the use of attapulgite as catalyst support for transesterification reaction [21] despite its industrial application. You et al. [21] used immobilized *Burkholderia cepacia* lipase on modified attapulgite as catalyst for transesterificating jatropha oil to biodiesel and obtained a maximum yield of 94% using 10 g of jatropha oil, 2.4 g methanol (molar ratio of oil to methanol of 1:6.6), 7 wt% water, 10 wt% immobilized lipase at 35 °C for 24 h.



ISSN: 2319-5967

ISO 9001:2008 Certified

International Journal of Engineering Science and Innovative Technology (IJESIT)

Volume 9, Issue 3, May 2020

Attapulgite (Atta, or palygorskite), is a species of hydrated magnesium aluminum silicate non-metallic mineral $[(H_2O)_4(Mg, Al, Fe)_5(OH)_2Si_8O_{20} \cdot 4H_2O]$ with common lath or fibrous morphology which is characterized by porous crystalline structure that contain tetrahedral layers alloyed together along longitudinal chain [22]. Attapulgite is obtained from the weathering of volcanic ash in the presence of water. Depending on the type, attapulgite may have varying elemental compositions such as K, Fe, Mg, Na, Ca, and Al. Attapulgite clay is generally cheap and environmentally friendly. It is widely used in adsorption, adhesion, catalysis/ supports etc [18, 23-25].

In this study, attapulgite functionalized with $C_4H_6O_4KNa$ and $Na_2C_2O_4$ was tested on *Allanblackia floribunda* oil which is a non-edible resource. The plant is commonly grown in Guangdong, Hubei, Shanxi, Qinghai (China) and mild climatic regions in Africa [26]. Despite its attention in medicinal and pharmaceutical research [27, 28], studies indicate that the seeds of the plant contains a lot of oil [29, 30]. Takase et al. [31-33] studies indicate that the seeds contain about 46% of oil. The oil is also abundant in industrial oil production as by-product and not utilized. To fully develop *Allanblackia floribunda* plant, this study was undertaken with the aim of producing biodiesel from the plant's oil using novel bi-functional heterogeneous catalysts. The oil had saponification index of 191.5 mgKOH/g and average molecular weight of 887.9g/mol [31]. The attapulgite was treated with HCl and modified by 4M of $C_4H_4O_6KNa$ or $Na_2C_2O_4$ and subsequently calcined at 450 °C for 4 h. The catalysts were characterized using XRD, FTIR, SEM-EDS, thermo gravimetric analysis and the Hammett indicator methods [34-36]. The yields biodiesel were determined as function of the type and concentration of the Na compound and transesterification reaction conditions.

II. EXPERIMENTAL

A. Materials

Attapulgite was obtained from Soil Science Department, University of Cape Coast, Ghana. *Allanblackia floribunda* seeds were obtained from Rite Aid Chemicals (Ghana). Ammonium hydroxide, sodium oxalate ($Na_2C_2O_4$), hydrochloric acid (HCl), potassium sodium tartrate ($C_4H_4O_6KNa$), methanol, tetradecane and petroleum ether were purchased from Rite Aid Chemicals (Ghana) and were of analytical grade reagent.

B. Extraction of oil

The oil's extraction process was a slight modification of Takase et al. [31, 32]. Briefly, the seeds of *Allanblackia floribunda* were dried at 100 °C for about 10 h in oven in order to remove the excess moisture prior to the extraction. The dried seeds were then ground and weighed. The extraction process was carried out using soxhlet extractor with petroleum ether (60-90 °C) for 8 h. 6 L of petroleum ether per kilogram of *Allanblackia floribunda* seeds was used. The extracted oil was recovered with rotary evaporator and the amount determined using Li et al. [30] method.

C. Catalysts synthesis

The attapulgite was dried at 120 °C for 12 h. About 5 g of the dried attapulgite powder was then treated with 2M of HCl for 1h at 80 °C under magnetic stirring, followed by washing with distilled water until pH of 7 was detected by 0.1 mol/L $AgNO_3$ aqueous solution. Having centrifuged, the treated attapulgite was dried at 120 °C for 12 h to obtain HCl treated attapulgite (HCl-Atta). The HCl treated attapulgite was then modified with ammonium hydroxide solution under constant mechanical stirring at room temperature till pH of the solution, which ranged between 10 and 12 was reached. The resultant precipitate was separated through filtration and washed with distilled water. The treated attapulgite was subsequently soaked in aqueous solution of $C_4H_4O_6KNa$ at varying concentration (1, 2, 3, 4, 5 and 6M) for 24 h. Following drying in vacuum oven at 150 °C for 12 h, the catalysts were calcined at 450 °C for 4 h. The catalyst with the highest yield was then chosen and compared with 4M of $Na_2C_2O_4$. The catalysts samples are referred to on the basis of the concentration of NaOH or NaCl. Thus, 4M of NaOH functionalized with HCl treated attapulgite calcined at 450 °C for 4 h is designated as 3NaOH/HCl-Atta-4 while that of NaCl treated under similar condition is designated as 3NaCl/HCl-Atta-4.

D. Characterization of the catalysts

The characterization of the base strengths of the catalysts was performed by Hammett indicator procedure [34-36]. The indicators used were bromothymol blue (H_{7.2}), phenolphthalein (H_{9.8}), 2, 4-dinitroaniline (H₁₅) and 4-nitroaniline (H_{18.4}). Typically, 250 mg of 4NaOH/HCl-Atta-4 was mixed with 1 ml of solution of Hammett indicators diluted in 10 ml methanol and allowed to settle for 2 h. After equilibration, the color of the



ISSN: 2319-5967

ISO 9001:2008 Certified

International Journal of Engineering Science and Innovative Technology (IJESIT)

Volume 9, Issue 3, May 2020

catalyst was noted. The base strength was taken to be higher than the weakest indicator that underwent a color change and lower than the strongest indicator that underwent no color change. Hammett indicator benzene carboxylic acid (0.02 mol/L anhydrous ethanol solution) titration method was then used to determine the basicity of the catalysts [34-36].

Thermo gravimetric analysis (TGA) of the catalysts were carried out on Netzsch instrument (STA 449C, Netzsch, Seligenstadt, Germany). The programme heating range was between 30 and 800°C at a heating rate of 10°C/min under nitrogen atmosphere. The measurement was done for 6-10 mg samples. Nitrogen adsorption and desorption isotherms were measured at -196°C using NDVA2000e analytical system (Quntachrome Corporation, USA). The specific surface areas were calculated using Brunauer-Emmett-Teller (BET) method while the pore size distribution and pore volumes were calculated using Barrett-Joyner-Halenda (BJH) method. Fourier transformation infrared (FT-IR) spectra of the samples were obtained between 500 and 4000 cm⁻¹ on KBr powder with FTIR spectrometer (AVATAR 360, Nicolet, Madison, USA). A minimum of 32 scans performed indicated average. The resolution of 2 cm⁻¹ was in the range of 500 to 4000 cm. The X-ray diffraction (XRD) patterns of the samples were examined using reflection scan with nickel-filtered Cu K α radiation (D8, Bruker-AXS, Germany) at angular range of between 20 and 80°. Scanning electron microscopy (SEM) images of the catalysts were obtained using 20-kV accelerating voltage field emission scanning electron microscope (S-4800, HITACHI Corp., Tokyo, Japan). The elemental chemical analysis of the catalysts was carried out under energy dispersive X-ray spectroscopy (EDS) technique. Analyses of the raw attapulgite and the catalyst (4NK/HCl-Atta-4) were carried out prior to transesterification.

E. Transesterification of the oil to biodiesel

20 g of the oil with a varied molar ratio (5:1 to 17:1) of methanol to oil and 3NaOH/HCl-Atta-4 or 3NaCl/HCl-Atta-4 in various amounts (2 to 10 wt.%) with reference to the weight of the oil were refluxed together in a 250 ml three-neck reaction flask equipped with a condenser and magnetic stirrer (600 rpm) at different temperatures (40 to 80 °C) and time (1 to 7 h). After completion of the reaction, the mixture was washed with n-hexane to remove any absorbed biodiesel out of the solid catalysts. The mixture was subsequently, centrifuged at 5000 rpm for 10 min to ensure separation of the solid catalysts from the liquid layer containing the biodiesel and n-hexane. The decanted liquid phase was then transferred to a rotary vacuum evaporator to remove the n-hexane and any other by-products from the biodiesel. Each biodiesel sample was then kept in separatory funnel and allowed to stand for 24 h before washing with water for at least three times. Drying and analyses of the biodiesel then followed.

F. Analyses and characterization of methyl esters

The analyses of the biodiesel samples were done using Takase et al. [31] reported method with little modification. Briefly, the analyses were done using 7890A gas chromatograph (Agilent Technology Inc. USA), equipped with a flame-ionization detector (FID) and HP-5 capillary column (30 m × 0.32 mm × 0.25 μm). Helium was used as the carrier gas. The oven temperature was held at 170 °C for 1 min, then increased to 210 °C at 20 °C/min for 2 min and further increased from 210 °C to 215 °C at 0.3 °C/min for 3 min and finally increased to 250 °C at 30 °C/min for 1 min [31, 32]. Hydrogen gas' flow rate was 50 mL/min and that of air was 400 mL/min. Temperature of the injector and detector were 250 °C each. The injection was done in split mode with a split ratio of 70:1. The analysis of each sample was done by dissolving 1 mL of the biodiesel with 5 mL of petroleum ether (30-60 °C) in the presence of tetradecane as the internal standard and 0.5 μL of the solution injected into GC. The yields of the biodiesel samples were determined from the content of the biodiesel using the equation below [37]:

$$\text{Me yield}(\%) = \frac{\% \text{ FAME area from GCMS} \times \text{weight of product}}{\text{weight of oil sample}} \times 100\%$$

The identification of the methyl esters was done using Agilent HP-6890 gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) with a HP-5MS 5% phenylmethylsiloxane capillary column (30 m × 0.25 mm i.d., film thickness 0.25 μm; Restek, Bellefonte, PA). Helium was used as the carrier gas at the flow rate of 1.0 mL/min. 1 μL of biodiesel sample was injected into the column at a split ratio of 40:1. The oven temperature ramp program was done by applying the GC method [31, 32]. The content of the biodiesel was identified by comparing the obtained mass spectra with NIST05.LIB and NIST05s.LIB (National Institute of Standards and Technology) libraries data using AMDIS-Chromatogram (GC-MS system) software. All data points are presented as means of triplicate of both experimental and GC determinations.



ISSN: 2319-5967

ISO 9001:2008 Certified

International Journal of Engineering Science and Innovative Technology (IJESIT)

Volume 9, Issue 3, May 2020

III. RESULTS AND DISCUSSION

A. Oil extraction

Having extracted the oil from the seeds, the amount was calculated using Li et al. [30] method. The content of oil in the seeds (46%) was however, comparable to those of other oils and this indicated that the seeds contain relatively high amount of oil [38]. The presence of high amount of free fatty acid and water content in oils can lead to soap formation and this lowers the yield of biodiesel [39]. Given the fact that the pure attapulgite and the HCl treated one yielded < 10% of biodiesel coupled with the oil's free fatty acid and water content of 0.68% w/w and 0.089 % w/w, respectively (figures below 1.0%), base catalyst (with Na compounds) was chosen.

B. Catalyst characterization

The base strength and catalytic performance of the catalysts are shown in Table 3.1. From the Table, pure attapulgite and the HCl treated one exhibited low activities which were due to their low base strengths. The HCl treated attapulgite functionalized with 3M of NaOH and NaCl recorded the highest base strengths and the corresponding yields were 92.5% and 90.0%, respectively. The results obviously indicated that the performance of the catalysts were dependent on the base strength and the amount of base sites. The acid treated attapulgite functionalized with 1 to 3M of NaOH generated weaker base sites with base strength ranging between 7.2 and 9.8 and yields <20% (Table 1). Considering the base strength and catalytic performance, it was obvious that the performance of 3M of NaOH and NaCl related with their base strengths and yields. For catalytic sites of 3NaOH/HCl-Atta-4, more K_2O species were possibly formed by dehydroxylation of OH groups which could have contributed to catalytic performance of 3NaOH/HCl-Atta-4 more than 3NaCl/HCl-Atta-4 [40]. NaOH can be regarded as the best support for the treated attapulgite. And since the yields of NaOH/HCl-Atta-4 (92.5%) and 3NaCl/HCl-Atta-4 (90.0%) were relatively comparable, the two catalysts were selected for further investigation and their properties and performances were then studied in more detail.

Table 1: Properties and yields of attapulgite and Na-functionalized attapulgite catalyst supports under similar transesterification conditions

Catalyst	Basic strength (H.)	Yield of FAME (%)
Attapulgite	<7.2	< 10
HCl-Atta	<7.2	<20
1NK/HCl-Atta-4	7.2-9.8	14.7
2NK/HCl-Atta-4	7.2-9.8	42.3
3NK/HCl-Atta-4	7.2-9.8	78.9
4NK/HCl-Atta-4	9.8-15	92.5
4NC/HCl-Atta-4	9.8-15	90.0

Transesterification conditions: molar ratio of methanol/oil: 7/1, reaction temperature: 60 °C, reaction time: 6 h, catalyst amount: 6 wt.%, calcination temperature and time: 450 °C and 4 h, respectively.

The effect of calcination temperature on weight loss as indicated by thermo gravimetric analyses of HCl treated attapulgite functionalized with the two Na-compounds (NaOH and NaCl) following calcination at 450 °C for 4 h are indicated in Fig. 1. The weight loss of 3NaOH/HCl-Atta-4 ranges from 100 to 500 °C and 500 to 700 °C. For 3NaCl/HCl-Atta-4, the weight loss ranges from 400 to 700 °C and 700 to 800 °C. From Fig (1a), the weight loss of between 100 and 500 °C (endothermal region) correspond to the loss of adsorbed water and this can be attributed to fragmentation of sodium compounds as well as the loss of other organic matter, while the weight loss at between 500 and 700 °C can represent the transmutation of K_2CO_3 [41]. Similar deductions can be made from the weight loss of 4NC/HCl-Atta-4. Thus weight loss of 400 to 700 °C is attributed to fragmentation of $Na_2C_2O_4$ and loss of some compounds while the loss of weight at 700 to 800 °C can be ascribed to the decomposition of K_2CO_3 . The thermo gravimetric analysis of the catalysts indicate that the Na functionalized with HCl treated attapulgite catalysts exhibit low energy of adsorption [42]. And this presupposes that the pore size distribution of the catalysts could be quite narrow (<0.6 nm). Granados et al. [10] have reported that, the dimensions of methyl oleate (oleic acid methyl ester) and glycerine are around 2.5 nm and 0.6 nm, respectively. It can be deduced that the mean pore size diameter of the catalysts would be occupied by triglycerides which suggest that the triglycerides molecules could easily penetrate into the pores of the catalysts. This therefore indicates that much of the active sites would be utilized during the transesterification process.

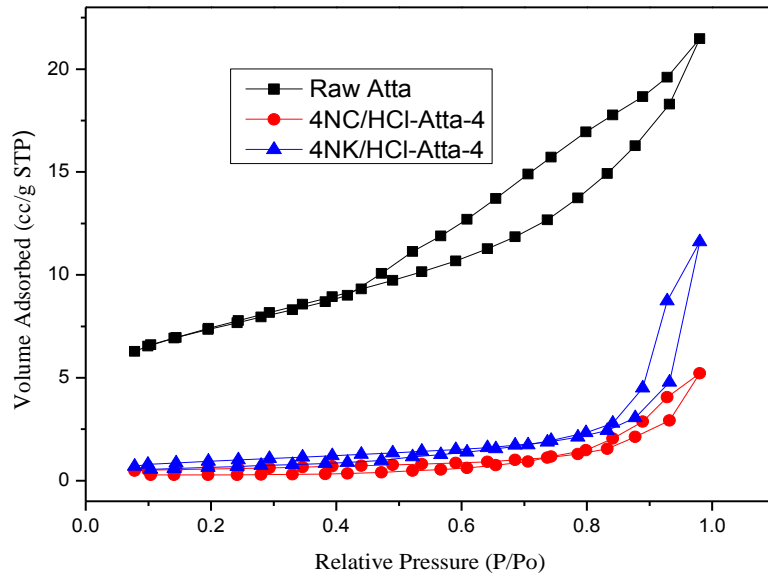


Fig 1: Nitrogen adsorption isotherms of Raw Atta, 4NK/HCl-Atta-4 and 4NC/HCl-Atta-4.

The BET surface area of pure attapulgite was $104.8 \text{ m}^2/\text{g}$. Having functionalized the HCl treated attapulgite with NaOH and NaCl, respectively, the BET surface areas reduced significantly and this was attributed to the covering of the surface and pores of the attapulgite [40]. The BET surface area of 3NaOH/HCl-Atta-4 and 3NaOH/HCl-Atta-4 was 16.2 and $16.8 \text{ m}^2/\text{g}$, respectively. Nitrogen adsorption isotherms of the pure attapulgite and the HCl treated attapulgite functionalized with $\text{C}_4\text{H}_4\text{O}_6\text{KNa}$ and $\text{Na}_2\text{C}_2\text{O}_4$ (3NaOH/HCl-Atta-4 and 3NaOH/HCl-Atta-4) following calcination at $450 \text{ }^\circ\text{C}$ K for 4 h is shown in Fig. 1b. The nitrogen adsorption isotherms of attapulgite show typical Type II isotherm. On the other hand, the nitrogen adsorption isotherms of the synthesized catalysts (3NaOH/HCl-Atta-4 and 3NaOH/HCl-Atta-4) exhibit typical Type III isotherm which indicate that the NaOH and NaCl functionalized on HCl treated attapulgite are macroporous and exhibit low energy of adsorption [43].

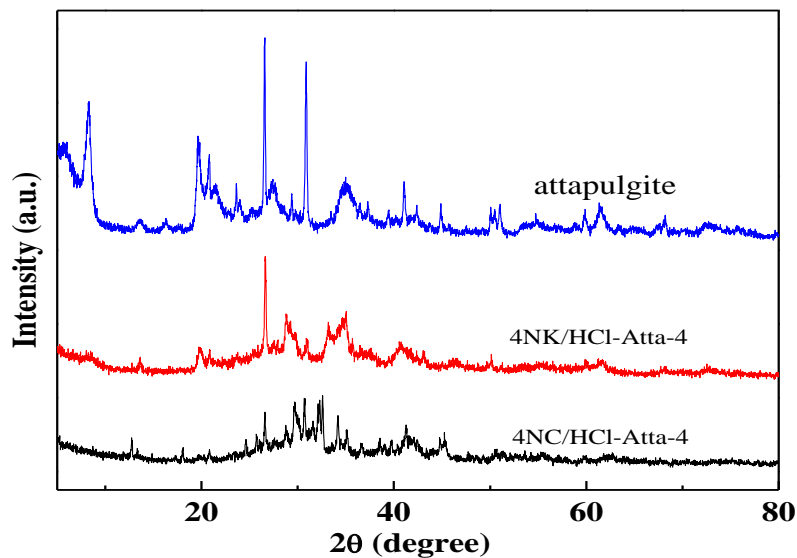
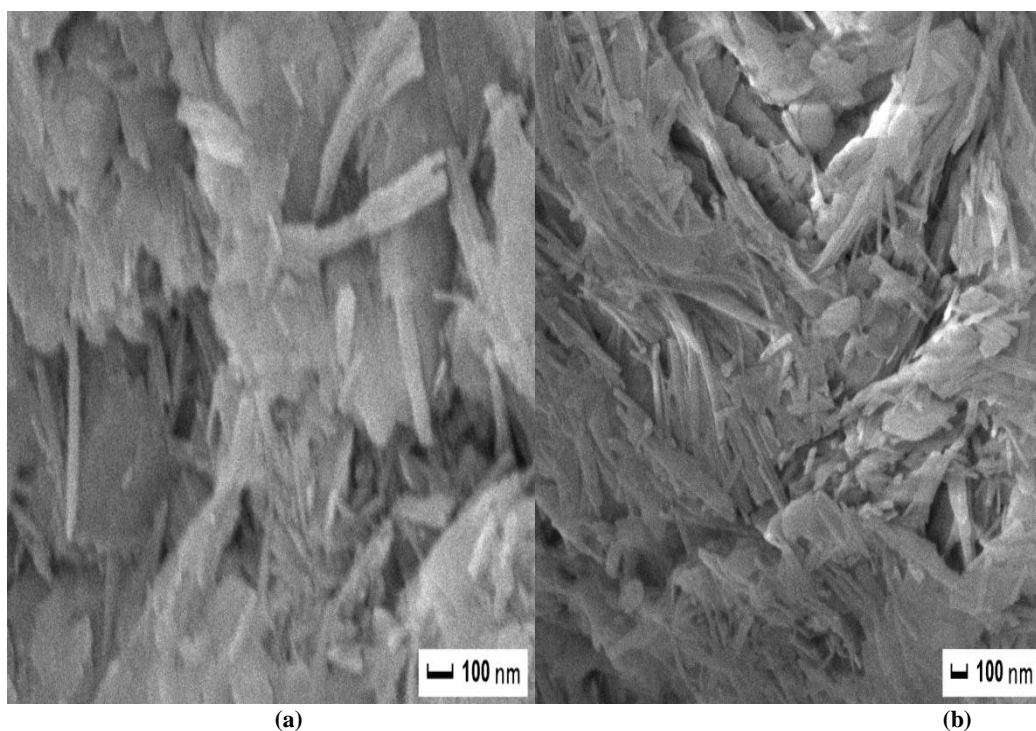
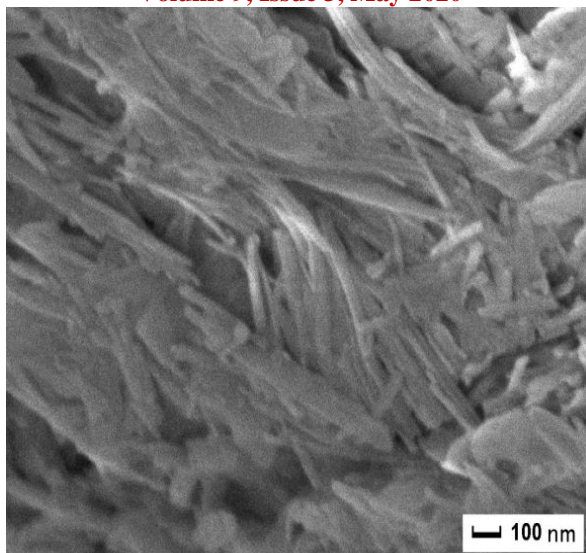


Fig. 2 The XRD patterns of pure attapulgite, 3NaOH/HCl-Atta-4 and 3NaCl/HCl-Atta-4.

Typical diffraction peaks of the pure attapulgite at primarily dioctahedral smectite phase $2\theta = 8.4^\circ, 19.8^\circ, 27.3^\circ$ and 31.9° this corresponds to the fundamental diffraction of (1 1 0), (2 0 0), (0 4 0) and (4 0 0) planes of attapulgite, respectively [44]. The phenomenon however, agree with the crystalline structure [45]. Upon functionalizing the HCl treated attapulgite with NaOH and NaCl, typical NaOH peaks were observed at the Bragg angles, $2\theta = 29.1^\circ, 30.2^\circ, 36.7^\circ, 55.4^\circ, 67.8^\circ$ and 68.1° . In the case of 3NaCl/HCl-Atta-4, typical angles could be observed around $21.5^\circ, 29.2^\circ, 34.5^\circ, 37.2^\circ, 43.2^\circ, 45.1^\circ, 62.5^\circ$, respectively. It was noticed that other clay minerals such as montmorillonite and quartz could be found in the attapulgite [46]. New phases of K_2O of 3NaOH/HCl-Atta-4 appeared clearly in the diffraction peak at $15.6^\circ, 18.9^\circ, 47.5^\circ$ and 53.2° . Meanwhile new phases associated with K_2O for 3NaCl/HCl-Atta-4 appeared at $29.1^\circ, 32.3^\circ$ and $37.2^\circ, 48.4^\circ$. The K_2O phases were the contributors of active sites of the catalysts. Comparing the X-ray diffraction patterns of the pure attapulgite with the synthesized catalysts, it was noted that little difference exist between the peaks of the catalysts indicating that the crystal structure of attapulgite did not completely changed after calcination at $450^\circ C$.

The SEM photographs of pure attapulgite, 3NaOH/HCl-Atta-4 and 3NaCl/HCl-Atta-4 prior to transesterification reaction are shown in Fig. 3. The crystallites particles of attapulgite, 3NaOH/HCl-Atta-4 and 3NaCl/HCl-Atta-4 samples were 100 nm each. Freshly crystalline morphologies could be found on the surfaces of the prepared catalysts. A reduction in particle sizes of 3NaOH/HCl-Atta-4 and 3NaCl/HCl-Atta-4 as a result of functionalizing HCl treated attapulgite with $C_4H_4O_6KNa$ and $Na_2C_2O_4$, respectively could be noticed. However, no significant difference could be observed between the images of the pure attapulgite and the catalysts, suggesting a good dispersion of both NaOH and NaCl on the surface of HCl treated attapulgite. Obviously, having functionalized 3M of NaOH and NaCl on HCl treated attapulgite, the attapulgite retained its structure and this was important for the catalytic performance. K-Na species could be found distributed on the surfaces of the supports. The largest particles were attapulgite while the smallest were K_2O . The observation agrees with the XRD results (Fig. 3(a)). It could also be noticed that 3NaOH/HCl-Atta-4 and 3NaCl/HCl-Atta-4 formed netlike structures of smaller granules of 100 nm which indicates that there was possible increase in contact between the catalysts and the substrates and this might contributed to enhancement in the catalytic performance with increased efficiency of transesterification [47].





(c)

Fig. 3: SEM photographs of (a) raw attapulgite, (b) 3NaOH/HCl-Atta-4 and (c) 3NaCl/HCl-Atta-4.

The EDS analyses of the attapulgite and 4NK/HCl-Atta-4 particles are shown in Table 3.2. The surfaces of the samples were probed at three different locations using SEM-EDS. The reported data in Table 2 are averages from the three locations. From the typical empirical formula of attapulgite $[(H_2O)_4(Mg, Al, Fe)_5(OH)_2Si_8O_{20} \cdot 4H_2O]$ [50], Al, Si, Ca, Mg, K, Ti and Fe were found on EDS data. The K content of the attapulgite was 0.5 wt.%. The content of K on the surface of 3NaOH/HCl-Atta-4 was increased to 51.4 wt.%. This was an indication that the NaOH loading on the HCl treated attapulgite was indeed carried out successfully. The 3NaOH/HCl-Atta-4 particles exhibited increase amount of K when compared with that of the raw attapulgite which indicates that some amount of K_2O might formed at the surface of the catalyst particles which increased the activity of the catalysts [32].

C. Transesterification reaction

Transesterification of *Allanblackia floribunda* oil at four different concentrations (1 to 4M) of NaOH and 4M of NaCl under methanol/oil molar ratio of 7/1, reaction temperature of 60 °C, reaction time of 6 h and catalyst amount of 6 wt.% are shown in Table 1. The biodiesel obtained by 4M of NaOH was higher than the respective yields obtained by 4M of NaCl and the control (only acid treated attapulgite). The yield increased significantly with increased concentration (from 1 to 4M) of $C_4H_4O_6KNa$ and reached optimum (92.5%) at 4M. At 1M concentrations of NaOH and below, there was possible coverage of the active sites of NaOH by the attapulgite in which there was little contribution of the $C_4H_4O_6KNa$ since the yields of the biodiesel were low at those concentrations. The yields of biodiesel however, increased significantly between 1 and 3M of NaOH. The relationship between the yields and the NaOH concentration in this case could be described as proportional since the correlation coefficient for linear regression R^2 , was > 0.95 . The optimum biodiesel yield (92.5%) was however, slightly below the minimum biodiesel requirements of the European EN standard (EN-14103) and ASTM 6751-03 of 96.5% [51]. And since the optimum yield of 4M $C_4H_4O_6KNa$ (92.5%) was less than the required international standard for biodiesel products (96.5%), additional experiments were then carried out at similar concentration (4M) of NaCl.

A major factor to consider is the increase in the basicity with increase concentration of NaOH. Basicity play a significant role on catalytic performance [20]. The increase in the biodiesel yield was most pronounced at 3M of NaOH in which the basicity was significantly greater than the basicity values at low (1 to 3M) NaOH concentrations. The increase in biodiesel yield with increase basicity of catalysts was however, noted in our previous studies [32]. Xie et al. [34] also reported similar observation, thus increase in basicity of catalyst leads to increase in the performance with consequent increase in biodiesel yield. To ascertain the trend and optimum transesterification reaction conditions, methanol to oil ratio, catalyst amount, reaction temperature and time were then investigated at varying levels.



ISSN: 2319-5967

ISO 9001:2008 Certified

International Journal of Engineering Science and Innovative Technology (IJESIT)

Volume 9, Issue 3, May 2020

Table 2: EDS analysis of the raw and 3NaOH/HCl-Atta-4 particles

Element	Weight %	
	Raw Atta	3NaOH/HCl-Atta-4 (fresh)
Mg	18.9	10.1
Al	7.2	1.6
Si	47.6	18.3
K	0.5	51.4
Ca	5.6	1.1
Ti	0.7	0.1
Fe	5.2	0.1

Transesterification conditions: methanol/oil ratio: 9/1, reaction temperature: 60 °C, reaction time: 6 h, catalyst amount: 6 wt. %, calcination temperature and time: 450 °C and 4 h, respectively.

D. Influence of transesterification reaction parameters

1. Influence of methanol to oil molar ratio

Varying each of the reaction parameters in Table 1 (ie. initial molar ratio of methanol/oil of 7/1, reaction temperature of 60 °C, reaction time of 6 h and catalyst amount of 6 wt.%), transesterification was carried out using 3NaOH/HCl-Atta-4, 4NC/HCl-Atta-4 and HCl-Atta-4 (control) in order to determine optimum reaction parameters. Studies have shown that molar ratio of alcohol to oil under heterogeneous catalyses ranges between 5:1 and 275:1 [12, 34-36, 42, 52-54]. The normal stoichiometric ratio of alcohol to oil is 3:1. Excess alcohol (mostly > 6) is used to drive the reaction to the product in order to increase the yield of biodiesel and to also facilitate glycerol separation. In this study, the influence of methanol to *Allanblackia floribunda* oil on the rate of reaction using 3NaOH/HCl-Atta-4, 3NaCl/HCl-Atta-4 and HCl-Atta-4 (control) was investigated by systematically changing the molar ratio of methanol to *Allanblackia floribunda* from 5:1 to 17:1 (reaction temperature of 60 °C, reaction time of 6 h and catalyst amount of 6 wt.%) (Table 1). The results are indicated in Fig. 5a. The Fig. shows that altering methanol/oil molar ratio in the range of 5:1 to 17:1 affect the biodiesel yield. The data reported using triplicates of experimental and GC analyses confirmed that methanol/oil ratio greater than 3:1 did increased the yield of biodiesel since the maximum biodiesel yield of 94.7% was obtained at molar ratio of methanol/oil of 9:1 for 3NaOH/HCl-Atta-4.

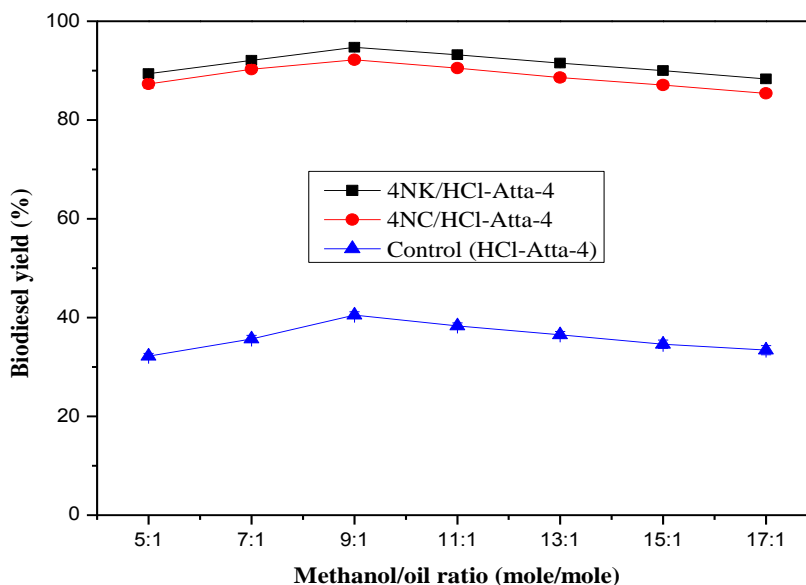


Fig. 5a: Influence of methanol to oil ratio. Transesterification conditions: reaction temperature 60 °C, reaction time 6 h, catalyst amount 6 wt.%, calcination temperature and time 450 °C and 4 h, respectively.

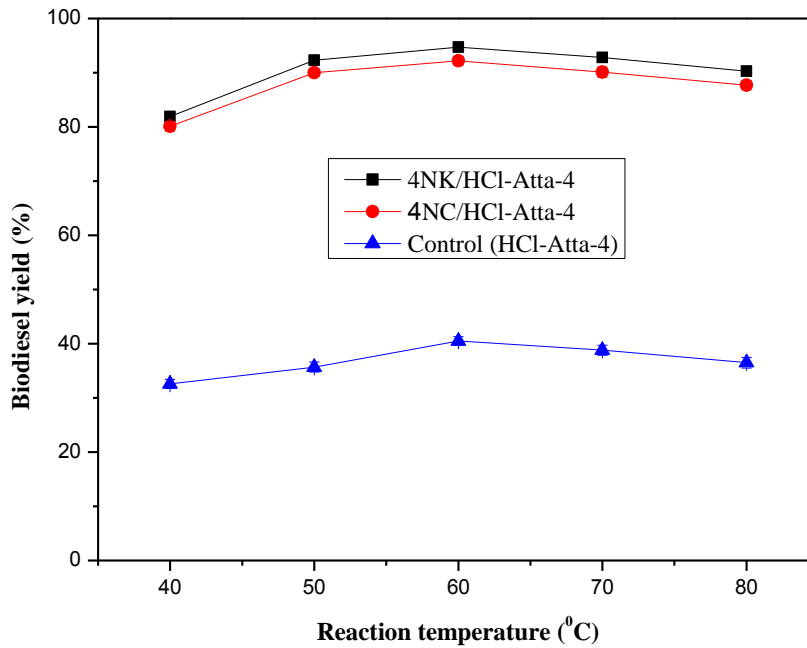


Fig. 5b: Influence of reaction temperature. Transesterification conditions: reaction time 6 h, catalyst amount 6 wt.%, calcination temperature and time 450 °C and 4 h, respectively.

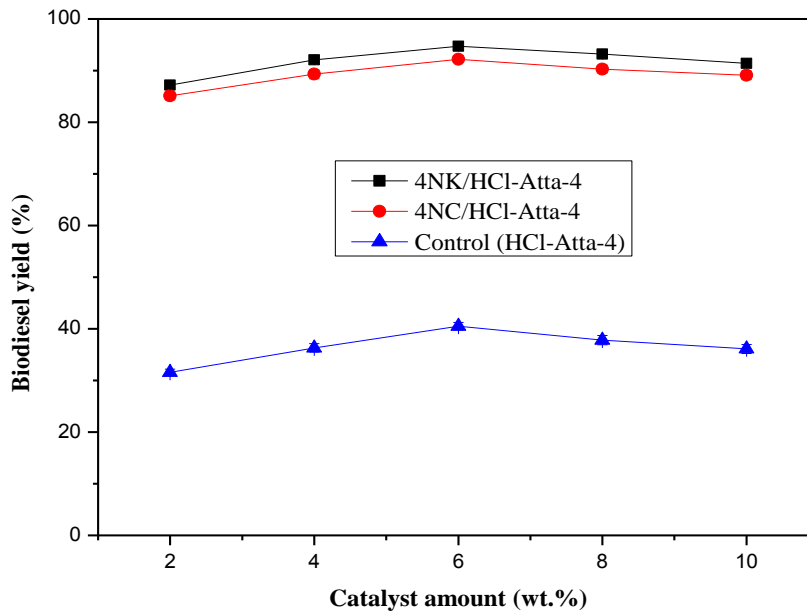


Fig. 5c: Influence of catalysts amount. Transesterification conditions: reaction temperature 60 °C, reaction time 6 h, calcination temperature and time 450 °C and 4 h.

The yields of 3NaCl/HCl-Atta-4 and HCl-Atta-4 (control) were also increased from 90.0% and 35.7 % to optimum at 92.2% and 40.5% respectively. For methanol to *Allanblackia floribunda* oil molar ratio greater than 9:1, further increase in the biodiesel was negligible with slight decrease in yield and this was possibly due to the dilution of the catalyst. Comparatively, methanol to oil molar ratio of 11:1 also resulted in relatively high yields (93.2%-4NaOH/HCl-Atta-4 and 90.5%-4NaCl/HCl-Atta-4) which were closer to those of 9:1. In order to reduce cost of production, ratio of 11:1 could be avoided. The findings of this study agrees with other related studies [55]. Accordingly, the appropriate ratio of methanol to *Allanblackia floribunda* oil was 9:1.

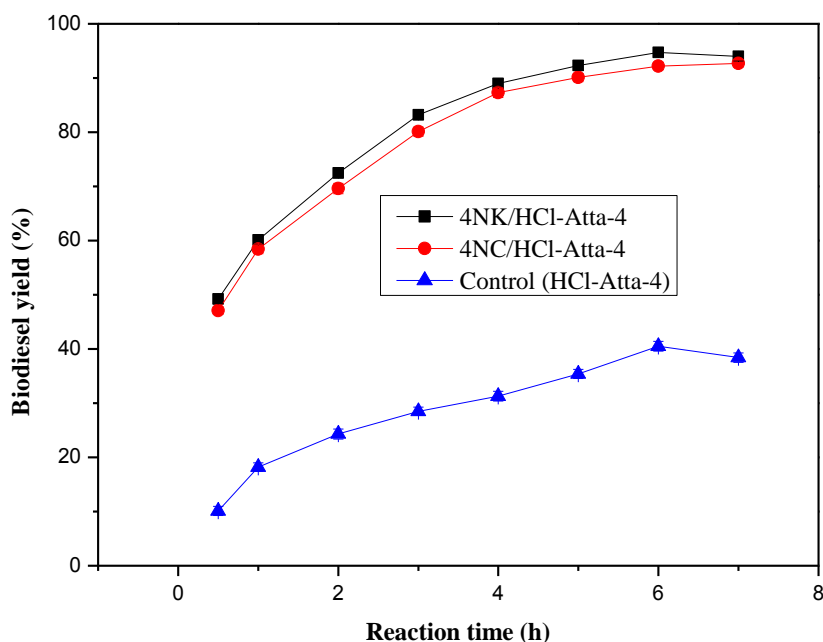


Fig. 5d: Influence of reaction time. Transesterification conditions: reaction temperature 60°C, catalyst amount 6 wt.%, calcination temperature and time 450 °C and 4 h.

2. Influence of reaction temperature

Another important parameter is the reaction temperature. The reaction temperature affects the reaction rate and yield of biodiesel since the intrinsic rate constant depends on the temperature. The influence of the reaction temperature on the yield of biodiesel was studied using 3NaOH/HCl-Atta-4, 3NaCl/HCl-Atta-4 and HCl-Atta-4 (control) at 40, 50, 60, 70 and 80 °C under catalyst amount of 6wt.%, methanol to oil ratio of 9/1 in 6 h. It was noted that the maximum temperature of the reaction (60 °C) coincided with the boiling point of methanol. As shown in Fig. 5b, the rate of reaction was slow at low temperatures using 3NaOH/HCl-Atta-4. Thus at 40 °C the biodiesel yield was 81.9% even after 6 h. The yield however, increased with increased reaction temperature and reached maximum 94.7% at 60 °C. Ideally, a more rapid reaction could be obtained at high temperatures [56]. However, at temperatures of beyond 60 °C (in this study), methanol was possibly vaporized and formed bubbles which might inhibit the reaction on the interface since methanol melts at temperature of between 60 and 65 °C. These findings agree with those of other studies [57-59]. It was also noted that at the yield of 40 °C (81.9%), the reaction was uncompleted even after 6 h, possibly due to the slightly high viscosity of the oil at the low temperature resulting in poor mixing between the oil-catalyst-methanol phases [12]. Similar trend was observed for 3NaCl/HCl-Atta-4 and HCl-Atta-4 (control). Considering the fact that the maximum yields of 94.7%, 92.2% and 40.5% for 3NaOH/HCl-Atta-4, 3NaCl/HCl-Atta-4 and HCl-Atta-4 (control), respectively were obtained at 60 °C, 60 °C was chosen as the optimum reaction temperature.

3. Influence of catalyst amount

The influence of catalyst amount on yield of biodiesel is indicated in Fig. 5c. The catalyst amount which was based on the mass of the oil used for the study was varied in the range of 2 and 10%. High activity of catalyst can be obtained when the base site is strong with optimum base strength. From Fig. 5c, the increase in catalysts amounts (from 2 to 6%) resulted in increase in biodiesel yields (81.9% to 94.7% and 92.2% for 3NaOH/HCl-Atta-4 and 3NaCl/HCl-Atta-4 respectively). The phenomenon could be assigned to the increase in the number of catalysts active sites at 6wt.%. Judging from the yields, it could be deduced that the basicity and the catalytic sites of 3NaOH/HCl-Atta-4 was greater than those of 3NaOH/HCl-Atta-4. Previous studies [32, 60-62] indicated that high concentrations of alkaline catalyst form soap in the presence of high free fatty acids which result in emulsion formation between the soap and water molecules and this consequently reduce yield. However, in this study the oil had low free fatty acids (<0.68%). However, mass transfer limitations of the

reactants might occur in the reaction process which might lead to reduction in yield after the catalyst amount exceeded 6% [55, 61, 63]. Li et al [49] reported similar observation in their study using Na salts loaded on ZrO₂. It was evident that 3NaOH/HCl-Atta-4 was superior to 3NaCl/HCl-Atta-4. The optimum yield of HCl-Atta-4 (control) was 40.5%. On the basis of the yields, catalyst amount of 6wt.% was chosen as the optimum.

4. Influence of reaction time

The dependence of biodiesel yield on the reaction time of is shown in Fig. 5d. The reaction time was varied in the range of 0.5 and 7 h. As can be seen from Fig (5d), the increase in the reaction time led to corresponding increase in the yield till maximum in 6 h for 3NaOH/HCl-Atta-4 and HCl-Atta-4 (control) with yields of with yield of 94.7% and 40.5% respectively and 7 h for 3NaCl/HCl-Atta-4 with yield of 92.2%. It was noted that the reaction was slow at the initial time (especially first 2 h) which could possibly be due to inadequate stirring time to enhance proper mixing and dispersion of methanol and catalyst onto the oil [32]. However, further in the reaction time beyond the optimum, no remarkable increase in the yield was recorded. Rather, excess time beyond 6 h led to slight decrease in the yield and this was due to reversible reaction [64]. The optimum yield (94.7%) was less than yield (98.2%) of Boz et al. [42] at similar reaction conditions; methanol to canola oil ratio of 6:1, reaction temperature of 65 °C in 7 h using KF functionalized with calcium bentonite but slightly higher than yield (94%) of You et al. [21] who used immobilized *Burkholderia cepacia* lipase on modified attapulgitte as catalyst for transesterification of jatropha oil to biodiesel at 2.4 g methanol, 7 wt% water, 10 wt% immobilized lipase, 35 °C of reaction temperature in 24 h. (Sample chromatogram of the optimum reaction conditions of the maximum biodiesel yield of 3NaOH/HCl-Atta-4 and 3NaCl/HCl-Atta-4 are shown in Figs. 6a and b, respectively).

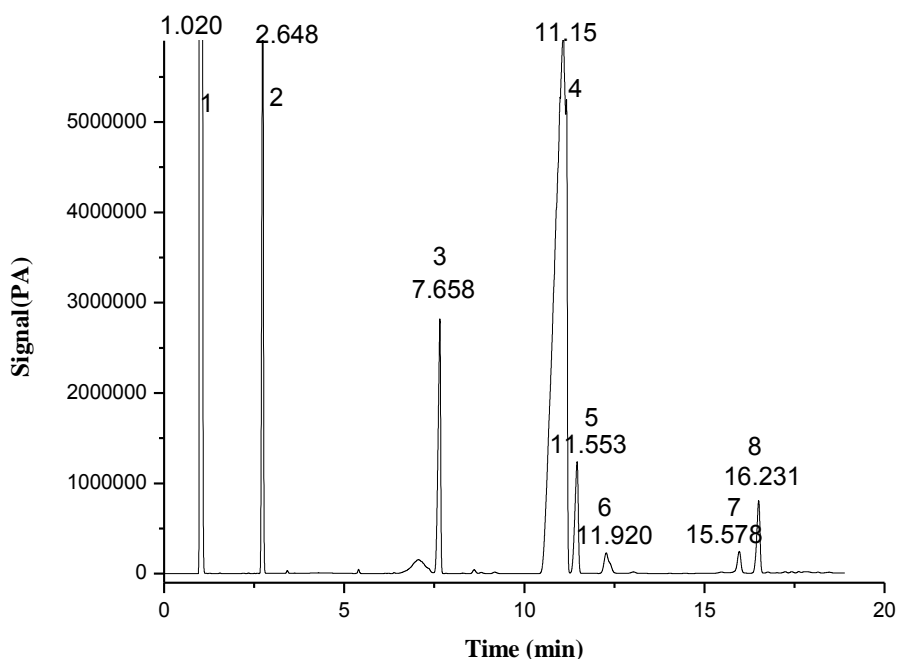


Fig.6: GC Chromatogram of *Allanblackia floribunda* biodiesel using (a) 3NaOH/HCl-Atta-4

E. Recovery and reusability of the catalysts

Reusability of a catalyst is an important determinant in shaping the economics of heterogeneous catalyst. Reusability of 3NaOH/HCl-Atta-4 and 3NaCl/HCl-Atta-4 were tested. This was done by systematically recovering and reusing the catalysts up to five times at methanol/oil molar ratio of 9/1, reaction temperature of 60 °C, catalyst amount of 6wt% and reaction time of 6 h for 3NaOH/HCl-Atta-4 and 7 h for 3NaCl/HCl-Atta-4. Having recovered the catalysts through filtration and washing with n-hexane, the catalysts were dried at 120 °C for 2 h then re-calcined at 450 °C for 4 h for the next reuse (Fig. 7). For each run, freshly prepared methanol and *Allanblackia floribunda* oil was used. Evidently from Fig. 7, the rate of reaction was high in the fresh state. The yields however, reduced from 94.7% to 80.1% for 3NaOH/HCl-Atta-4 and 92.2% to 78.4% for 3NaCl/HCl-

Atta-4 at the end of the 5th reuse. The reductions in the yields upon recycle and reuse are attributed to reduction in the catalysts activities due to leaching of some amount of K and other elements [19, 53]. The slightly high yield of 3NaOH/HCl-Atta-4 (80.1%) as compared to that of 3NaCl/HCl-Atta-4 (78.4%) at the end of the 5th reuse indicates that the surface of 3N/HCl-Atta-4 did not deteriorate much upon successive transesterification.

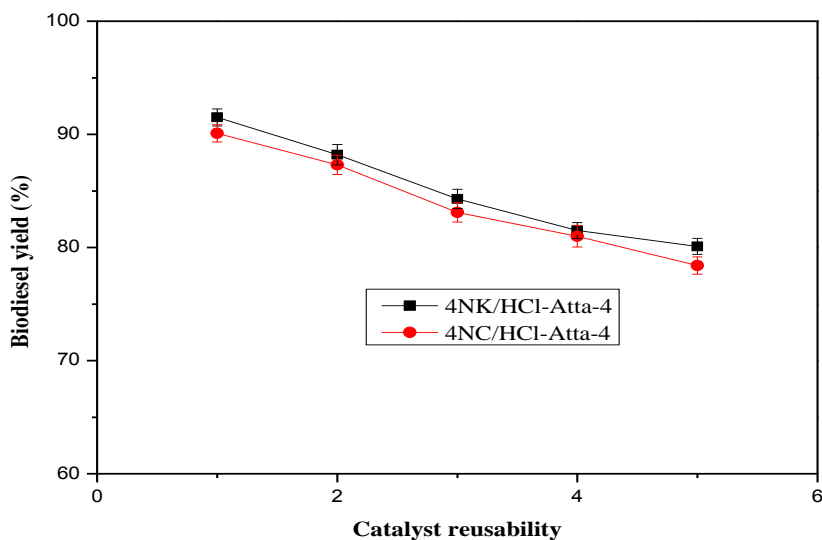


Fig. 7: Catalyst regeneration. Transesterification conditions: reaction temperature 60 °C, reaction time 6 h for 3NaOH/HCl-Atta-4 and 7 h for 3NaCl/HCl-Atta-4, catalyst amount 6 wt.%, calcination temperature and time 450 °C and 4 h respectively.

F. Properties of the biodiesel

The properties of the biodiesels produced were determined and compared with the standards of United States and European Union (Table 3). The properties including density, cetane number, flash point, cloud point, acid number, water content and kinematic viscosity of both 3NaOH/HCl-Atta-4 and 3NaCl/HCl-Atta-4 generally showed many similarities with the international standards and could be rated as realistic fuel alternative for diesel.

Table 3: Comparison of properties of the obtained biodiesel and the standards of Europe and the United States

Item	Method	Biodiesel		USA	ASTMD	EUROPE	EN
		4NK/HCl-Atta-4	4NC/HCl-Atta-4	6751-03	14214		
Cetane number	ASTM D6890	53	51	≥47		≥51	
Density (20 °C)	SH/T0248	877	875	-		860-900	
Flash point (°C)	ASTM D93	149	149	≥93		≥120	
Cloud point (°C)	GB/T510	-3	-3	-		-	
Sulfur content (% w/w)	ASTM D4294	0.002	0.001	≤0.05		0.02	
Acid value (KOH mg/kg)	ASTM D664-01	0.42	0.40	≤0.5		≤0.5	
Water (mg/kg)	ASTM D6304	0.05	0.05	≤0.05		≤0.05	
Total glycerine (% w/w)	EN 14105	0.13	0.14	0.24		≤0.25	
Ash content (% w/w)	GB/T508	0.017	0.018	≤0.02		≤0.02	
Kinematic viscosity (mm ² /s; 40 °C)	ASTM D445	4.1	4.3	1.9-6.0		3.5-5.0	

IV. CONCLUSION

HCl treated attapulgite was modified with ammonium chloride and subsequently functionalized with aqueous solutions of two different sodium compounds (NaOH and NaCl) at concentration of 4M and calcined at 450 °C



ISSN: 2319-5967

ISO 9001:2008 Certified

International Journal of Engineering Science and Innovative Technology (IJESIT)

Volume 9, Issue 3, May 2020

for 4 h. The catalysts were used to transesterificate *Allanblackia floribunda* oil to biodiesel. The reaction conditions which were focused with systematic variations include methanol/oil ratio of 5:1 to 17:1, catalysts amount of 2 to 10wt.%, reaction temperature of 40 to 80 °C and reaction time of 0.5 to 7 h. 3NaOH/HCl-Atta-4 resulted in high biodiesel yield when compared with 3NaCl/HCl-Atta-4 which was possibly due to the high basicity of 4NK/HCl-Atta-4. Relatively high (94.7%) biodiesel yield was obtained using 3NaOH/HCl-Atta-4 at methanol/oil molar ratio of 9:1, catalyst amount of 6wt.%, reaction temperature of 60 °C in 6 h. The yield of 3NaCl/HCl-Atta-4 under similar condition was 92.7%. The maximum yield of 3NaOH/HCl-Atta-4 (94.7%) was close to the standard of European Union EN-14103 (96.5%). The reusability and stability of the catalysts (3NaOH/HCl-Atta-4 and 3NaCl/HCl-Atta-4) indicated relatively modest reduction in biodiesel yields (10 to 14%). The decrease in the yields of the catalysts was attributed to leaching of K and other elements from the catalysts [65]. The properties of the obtained biodiesel were similar to the international standards and could be rated as realistic fuel alternative to diesel.

REFERENCES

- [1] L. Wan, H. Liu, D. Skala, Applied Catalysis B: Environmental 152–153 (2014) 352-359.
- [2] G. Corro, U. Pal, N. Tellez, Applied Catalysis B: Environmental 129 (2013) 39-47.
- [3] M. Agarwal, G. Chauhan, S.P. Chaurasia, K. Singh, Journal of the Taiwan Institute of Chemical Engineers 43 (2012) 89-94.
- [4] Y.-C. Lin, K.-H. Hsu, J.-F. Lin, Fuel 115 (2014) 306-311.
- [5] H. Yun, M. Wang, W. Feng, T. Tan, Energy 54 (2013) 84-96.
- [6] C. Poonjarernsilp, N. Sano, H. Tamon, Applied Catalysis B: Environmental 147 (2014) 726-732.
- [7] X.-F. Li, Y. Zuo, Y. Zhang, Y. Fu, Q.-X. Guo, Fuel 113 (2013) 435-442.
- [8] S. Semwal, A.K. Arora, R.P. Badoni, D.K. Tuli, Bioresource Technology 102 (2011) 2151-2161.
- [9] E. Li, V. Rudolph, Energy & Fuels 22 (2007) 145-149.
- [10] R. Sree, N. Seshu Babu, P. Sai Prasad, N. Lingaiah, Fuel Processing Technology 90 (2009) 152-157.
- [11] A. Kawashima, K. Matsubara, K. Honda, Bioresource Technology 100 (2009) 696-700.
- [12] X. Liu, H. He, Y. Wang, S. Zhu, X. Piao, Fuel 87 (2008) 216-221.
- [13] Y. Asakuma, K. Maeda, H. Kuramochi, K. Fukui, Fuel 88 (2009) 786-791.
- [14] C. Macedo, F.R. Abreu, A.P. Tavares, M.B. Alves, L.F. Zara, J.C. Rubim, P.A. Suarez, Journal of the Brazilian Chemical Society 17 (2006) 1291-1296.
- [15] N.S. Babu, R. Sree, P.S. Prasad, N. Lingaiah, Energy & Fuels 22 (2008) 1965-1971.
- [16] A. Kawashima, K. Matsubara, K. Honda, Bioresource Technology 99 (2008) 3439-3443.
- [17] T.H. Dang, B.-H. Chen, D.-J. Lee, Bioresource Technology 145 (2013) 175-181.
- [18] W. Xie, X. Huang, H. Li, Bioresource Technology 98 (2007) 936-939.
- [19] O. Ilgen, Fuel Processing Technology 92 (2011) 452-455.
- [20] F.E. Soetaredjo, A. Ayucitra, S. Ismadji, A.L. Maukar, Applied Clay Science 53 (2011) 341-346.
- [21] Q. You, X. Yin, Y. Zhao, Y. Zhang, Bioresource Technology 148 (2013) 202-207.
- [22] X. Liang, S. Gao, H. Wu, J. Yang, Fuel Processing Technology 90 (2009) 701-704.
- [23] N. Boz, O. Sunal, Journal of the Faculty of Engineering and Architecture of Gazi University 24 (2009) 389-395.
- [24] O. Ilgen, A.N. Akin, Energy & Fuels 23 (2008) 1786-1789.
- [25] C. Samart, P. Sreetongkittikul, C. Sookman, Fuel Processing Technology 90 (2009) 922-925.
- [26] M. Ahmad, M. Zafar, S. Sultana, A. Azam, M.A. Khan, International Journal of Green Energy 11 (2014) 589-594.
- [27] J.-W. Wu, L.-C. Lin, T.-H. Tsai, Journal of Ethnopharmacology 121 (2009) 185-193.
- [28] J. Doehmer, G. Weiss, G.P. McGregor, K. Appel, Toxicology in Vitro 25 (2011) 21-27.
- [29] N. Ghavami, A. Ramin, Communications in Soil Science and Plant Analysis 39 (2008) 2608-2618.



ISSN: 2319-5967

ISO 9001:2008 Certified

International Journal of Engineering Science and Innovative Technology (IJESIT)
Volume 9, Issue 3, May 2020

- [30] F. Li, L. Yang, T. Zhao, J. Zhao, Y. Zou, Y. Zou, X. Wu, Food and Bioproducts Processing 90 (2012) 87-94.
- [31] M. Takase, W. Feng, W. Wang, X. Gu, Y. Zhu, T. Li, L. Yang, X. Wu, Fuel Processing Technology 123 (2014) 19-26.
- [32] M. Takase, M. Zhang, W. Feng, Y. Chen, T. Zhao, S.J. Cobbina, L. Yang, X. Wu, Energy Conversion and Management 80 (2014) 117-125.
- [33] M. Takase, Y. Chen, H. Liu, T. Zhao, L. Yang, X. Wu, Ultrasonics Sonochemistry 21 (2014) 1752-1762.
- [34] W. Xie, H. Li, Journal of Molecular Catalysis A: Chemical 255 (2006) 1-9.
- [35] W. Xie, H. Peng, L. Chen, Applied Catalysis A: General 300 (2006) 67-74.
- [36] W. Xie, X. Huang, Catalysis Letters 107 (2006) 53-59.
- [37] W.N.N. Wan Omar, N.A.S. Amin, Fuel Processing Technology 92 (2011) 2397-2405.
- [38] S. Benita, Microencapsulation: methods and industrial applications, CRC Press, 2005.
- [39] A. Demirbaş, Energy Conversion and Management 44 (2003) 2093-2109.
- [40] Y.-L. Meng, S.-J. Tian, S.-F. Li, B.-Y. Wang, M.-H. Zhang, Bioresource Technology 136 (2013) 730-734.
- [41] I. Lukić, J. Krstić, D. Jovanović, D. Skala, Bioresource Technology 100 (2009) 4690-4696.
- [42] N. Boz, N. Degirmenbasi, D.M. Kalyon, Applied Catalysis B: Environmental (2013).
- [43] J.B. Condon, in: J.B. Condon (Ed.), Surface Area and Porosity Determinations by Physisorption, Elsevier Science, Amsterdam, 2006, pp. 29-53.
- [44] J.-M. Xu, W. Li, Q.-f. Yin, Y.-L. Zhu, Electrochimica Acta 52 (2007) 3601-3606.
- [45] W. Wu, Q. Fan, J. Xu, Z. Niu, S. Lu, Applied Radiation and Isotopes 65 (2007) 1108-1114.
- [46] L. Zhang, F. Lv, W. Zhang, R. Li, H. Zhong, Y. Zhao, Y. Zhang, X. Wang, Journal of Hazardous Materials 171 (2009) 294-300.
- [47] F. Qiu, Y. Li, D. Yang, X. Li, P. Sun, Applied Energy 88 (2011) 2050-2055.
- [48] B. Krupay, Y. Amenomiya, Journal of Catalysis 67 (1981) 362-370.
- [49] Y. Li, B. Ye, J. Shen, Z. Tian, L. Wang, L. Zhu, T. Ma, D. Yang, F. Qiu, Bioresource Technology 137 (2013) 220-225.
- [50] P. Pushpalettha, M. Lalithambika, Applied Clay Science 51 (2011) 424-430.
- [51] G. Knothe, Journal of the American Oil Chemists' Society 83 (2006) 823-833.
- [52] S. Benjapornkulaphong, C. Ngamcharussrivichai, K. Bunyakiat, Chemical Engineering Journal 145 (2009) 468-474.
- [53] N. Boz, N. Degirmenbasi, D.M. Kalyon, Applied Catalysis B: Environmental 89 (2009) 590-596.
- [54] M. Cerro-Alarcon, A. Corma, S. Iborra, J.P. Gómez, Applied Catalysis A: General 346 (2008) 52-57.
- [55] L. Meher, V.S. Dharmagadda, S. Naik, Bioresource Technology 97 (2006) 1392-1397.
- [56] M.G. Kulkarni, R. Gopinath, L.C. Meher, A.K. Dalai, Green Chemistry 8 (2006) 1056-1062.
- [57] J. Marchetti, V. Miguel, A. Errazu, Fuel 86 (2007) 906-910.
- [58] D.Y. Leung, X. Wu, M. Leung, Applied Energy 87 (2010) 1083-1095.
- [59] N. Laosiripojana, W. Kiatkittipong, W. Sutthisripok, S. Assabumrungrat, Bioresource Technology 101 (2010) 8416-8423.
- [60] L.C. Meher, V.S.S. Dharmagadda, S.N. Naik, Bioresource Technology 97 (2006) 1392-1397.
- [61] J.M. Encinar, J.F. González, E. Sabio, M.J. Ramiro, Industrial & Engineering Chemistry Research 38 (1999) 2927-2931.
- [62] A.P. Vyas, N. Subrahmanyam, P.A. Patel, Fuel 88 (2009) 625-628.
- [63] W. Xie, L. Zhao, Energy Conversion and Management 76 (2013) 55-62.
- [64] T. Eevera, K. Rajendran, S. Saradha, Renewable Energy 34 (2009) 762-765.
- [65] Z. Wen, X. Yu, S.-T. Tu, J. Yan, E. Dahlquist, Bioresource Technology 101 (2010) 9570-9576.