Journal of Environmental Issues and Agriculture in Developing Countries
Volume 13, Number 3, December 2021
ISSN(p): 2141-2731 ISSN(e): 2795-2967
Published By
International Centre for Integrated Development Research, Nigeria
In collaboration with
Copperstone University, Luanshya, Zambia

Optimum Size Range of Nigerian Bentonite Nanoparticles for Improved Catalytic Performance in Production of Biodiesel Using Mango Seed Oil

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ABSTRACT

An experimental ball-milling study to establish a correlation between process parameters and milling efficiency of particle size reduction and morphology of nanoparticles of bentonite clay was performed in Nigeria. Different parameters were selected through continuous particle size analysis using the Master Sizer analyzer 2000. The combination of scanning electronic microscopy (SEM), X-ray diffraction (XRD), and atomic force microscopy (AFM) led to great success. An optimum particle size of approximately 33nm for which the catalytic activity is maximum, suggests that the efficiency of the process can be enhanced by optimizing the size of the nanoparticle. The increase in ball ratio and milling periods led to a decrease in nanoparticle size from 114nm to 45nm. The catalytic performance of the bentonite nanoparticles was by studying the trans-esterification reaction of mango seed oil to produce biodiesel. The comparative study revealed the base-catalyzed trans-esterification of mango seed oil in an average yield of 83% using bentonite nanoparticles gave an average at 98% under similar reaction conditions.

Keywords: *Bentonite, Nanoparticles, Ball milling, Atomic Force Microscopy, Catalytic performance, Scanning Electron Microscopy.*

INTRODUCTION

Robust, recyclable, and green catalysts are significant challenge in chemistry and material sciences. The area has been steadily expanding, and understanding its efficiency when using nanoparticles is becoming essential. More importantly, the development of green catalysts that are eco-friendly and re-usable helps minimize waste disposal, and these catalytic materials are considered indispensable [Narayan *et al.,* 2019]. As a response to the need for catalyst improvement in the biodiesel production, nano-catalysis has emerged to offer unique solutions at the interface between homogenous and heterogeneous catalysis. The main driving force behind nanocatalysts is nano-size solid nature, with the advantage of recovering and recycling [Zullani *et al.,* 2017].

Nanocatalysts are either synthesized by a top-down or bottom-up approach [Olveira *et al.*, 2014]. As the name implies, the idea behind the top-down approach is to break bulk material down mechanically into smaller and smaller particles. The top-down approach is criticized because of its inability to yield particles with uniform characteristics [Olveira *et al.,* 2014]. However, there are already improved procedures to control the size and surface composition [Olveira *et al.,* 2014].

The bottom-up approach involves in the formation of nanocatalyst by reaction or agglomeration of suitable starting molecules with or without structure-directing agents [Sando Olveira *et al.,* 2014]. The principle is used more commonly than the former approach [Sando Olveira *et al.,* 2014]; it is rather disadvantageous from an economic and environmental point of view due to harsh reaction conditions, expensive precursors, and structure-directing agents employed [Aitken *et al.,* 2006]. Nevertheless, it allows the synthesis of well-defined catalysts on nanoscale (size, shape, and surface composition).

Recently, ball milling has received huge attention as a technique for the synthesis of various nanomaterials [Ullah *et al.,* 2014, Kabezya *et al.,* 2015]. The ball milling process is performed in different high-energy ball mills such as vibrator mills, attritor mills, tumbler ball mills. The vibrator and plenary mills have been used for the processing of a small number of materials (less than 100g) within a short time. According to Ullah *et al.* (2014), the attritor mills can process higher quantities of powders (between 100g and 10kg) and take several hours for the large-scale production of nanoparticles on commercial premises. Tumbler mills are more economical than the high-energy ball mills for large-scale synthesis [Ullah *et al.,* 2014]. Vibration mills are used for the synthesis of powder; however, it is no longer attractive because of its poor yield [Ullah *et al.,* 2014].

Several research groups have already designed their own ball milling devices depending on the needs. For example, Australian Scientific Instruments (Canberra, Australia) developed the Nanotech Uniball mill. This ball mill consists of stainless steel horizontal cell with hardened steel balls [Yadar *et al.,* 2012]. In addition, rod mill, a single large ball in a vibrating frame mill and other specially designed mills have been developed following mechanical milling operations [Yadar *et al.,* 2012].

Generally, the capacity, operation speed, temperature, and contamination controls are considered while developing or selecting a ball mill for a particular operation [Yadar *et al.,* 2012]. According to Ullah *et al.* [2014], clays are versatile materials used as adsorbents, ion exchangers, decolorizing agents, catalyst support, and catalysts. Clay catalysts are materials for the low cost of the raw materials and their lack of harmful effects on the environment [Makmur Sirait *et al.,* 2012]. Although, Nigeria has abundant bentonite resources, bentonite nanoparticles are produced artificially by mechanical attrition [Sarkar *et al.,* 2016].

However, the cost of vegetable oil in Nigeria imposes one of the major drawbacks on their use as fuel currently. Accordingly, the research efforts on biofuel technology have been to reduce production costs. The approach is to develop more efficient, environmentally friendly, and economically viable novel processes [Zuliani *et al.,* 2017]. It may be desirable to use non-edible oils, particularly those grown on non-fertile or wastelands but also create jobs for rural poor. Among the non-edible oil sources, neem, cotton, and mango seeds are potential biodiesel sources [Kahraman *et al.,* 2008].

The non-edible oil crops grown in the wastelands that are not suitable for cultivation are much lower because these crops can still sustain reasonable oils that contain high free fatty acids [Kahraman *et al.,* 2008]. The use of fatty acid methyl esters (FAME), often referred to as biodiesel, instead of fossil diesel fuel is under consideration to increase the share of fuels from renewable sources and reduce greenhouse gas emissions [Kahraman *et al.,* 2008]. Different transesterification processes can be applied to synthesize biodiesel: (a) base-catalyzed transesterification, (b) acid-catalyzed transesterification, (c) enzyme-catalyzed transesterification, and (d) supercritical alcohol transesterification. The most common method is homogeneously base-catalyzed transesterification that is 4000 times faster, easier and cheaper than homogeneous acid catalysis reactions [Zulliani *et al.,* 2017].

Nowadays, more than 95% of the world's total biodiesel are from highly pure edible oil feedstock, and increased food prices and deforestation. On the other hand, non-edible oils have gained attention because of their oil content and the possibility growing in territories not suitable for agriculture with reduced cultivation costs. Residual cooking oils are possible feedstocks for biodiesel production costs are composed mainly of free fatty acids (FFAs), which strongly influence the yield and purity of the biodiesel [Zuliani *et al.,* 2017].

Although base-catalyzed transesterification is a simple process, it is sensitive to the presence of free fatty acids that lead to undesired saponification reactions of pursued products. Consequently, it requires high-cost virgin oil (high grade) as feedstock, increasing the production cost compared to the acid-catalyzed transesterification. Catalysts employed in the synthesis of biofuels are expensive or show other disadvantages such as difficult removal from the product, low stability, and low selectivity. Nanotechnology has developed nanocatalysts with intermediate characteristics between homogenous and heterogeneous systems, combining the high activity of the homogenous catalyst with the easy recovery of heterogeneous solid materials [Zuliani *et al.,* 2017].

However, homogenous catalysts cannot be recovered and reused. They must be neutralized at the end of the reaction, producing vast quantities of undesired waste chemicals that separated and limiting the implementation of continuous downstream processes. Moreover, corrosion in homogenous catalysis is especially favored [Zuliani *et al.,* 2017]. Alternatively, cost-effective and environmentally friendly approaches have become significantly important. However, the revolution of material science and technology has steeply evolved in developing materials for future technologies on a nanoscale.

The studies on the synthesis of nano-sized particles using a green chemistry approach offer an excellent platform for developing green economical, recyclable, and sustainable materials for present and future applications [Narayan *et al.,* 2019]. Nanoparticles play a notable role in catalysis applications. Especially, nanoparticles with high surface area and more active sites promote faster reactions and increase product yield [Narayan *et al.,* 2017].

Nigeria has deposits of natural bentonite. The ultimate goal of this project is to develop a suitable and environmentally friendly approach for preparing nanoparticles of bentonite clay for application as a green catalyst in the sustainable process of biodiesel production. Green production or manufacturing encompasses a broad range of approaches that:

- Design and synthesize environmentally friendly chemical compounds and processes (green chemistry).
- Develop and commercialize environmentally friendly industrial processes and products (green engineering).

Nanocatalysis (nanotechnology) is an emerging platform for the green production of biofuels.

The objectives of this project are to:

- Investigate the potential of the ball milling process for the synthesis of bentonite nanoparticles.
- Investigate the effect of ball size diameter on milling performance.
- Study the effect of ball milling time on particle size and morphology of bentonite nanoparticles.
- Determine the optimum particle size for the catalytic activity of bentonite nanoparticles.
- Carry out a comparative study of transesterification reaction of some non-edible oils, using base (NaOH) and nanoparticles of bentonite as catalysts.
- Understand the mechanism of bentonite nanoparticle catalyzed transesterification reaction.

MATERIALS AND METHOD

Nigerian bentonite, a type of calcium bentonite, was used to prepare the nanoparticles. It composes of about 80% montmorillonite content along with quartz and illite. Montmorillonite, a flaky and shaped particle with a crystal monoclinic has lateral dimensions between 1000 and 5000Å and thickness between 10 and 50Å. The mineralogy of montmorillonite is described by the combination of silica tetrahedron, aluminium and magnesium octahedron sheets [Aitken, *et al.,* 2006]. The average particle size of the bentonite was within the range of 15 – 20um. Due to the crystallized structure and mineralogical composition, bentonite shows a higher specific surface area (750m2/g).

Mechanical milling: Equipment and Process Variables

The ball milling process is performed in high-energy ball mills such as vibrator mills, planetary ball mills, and tumbler ball mills. Among them, the vibrator and planetary ball mills have been used for the processing of small amounts of materials (less than 100g) within a short period. On the other hand, the attritor mills can process higher quantities of powders (between 100g and 10kg) and take several hours for the large-scale production of nanoparticles on commercial premises [Kotake *et al.,* 2011; Anna Johanson, 2012]. Tumbler mills are more economical than the high-energy ball mills for large-scale synthesis [Ghayour *et al.,* 2016].

On the other hand, vibrator mills are used for the synthesis of very fine powders; it is no longer attractive because of their poor yield [Magdalinovic *et al.,* 2012]. Nowadays, planetary ball mills are used for research purposes [Rosenkranz *et al.,* 2011, 2012]. Bentonite nanoparticles are processed from a bottom-up technique, which includes self-assemblage and template synthesis, and a top-down technique such as mechanical attrition [Sarkar *et al.,* 2016].

The mechanical attrition and the synthesis process were assimilated to prepare nanoparticles of Nigerian bentonite. In the mechanical attrition process, the particles were ground in wet conditions using a planetary ball mill. Different parameters such as types, size of mills, types of solvent, time and speed of pulverization for grinding were selected through continuous particle size analysis. The particle size of the ball-milled bentonite clay was measured in each step with Mastersizer Analyzer2000 (Malvern Instrument Ltd, Worcestershire, UK) using laser light diffraction. The finer particles were synthesized using ultrasonification, centrifuging, and filtering techniques. A planetary ball milling machine (PM 400, Retsch, Haan, Germany) was used to ball mill 5wt% bentonite for various milling times from 0.5 to 15 hours (Fig. 1). Literature procedures were adopted according to Yadav *et al.* (2012), Sarkan *et al.* (2015).

Figure 1: Planetary ball mill (RETSCH PM 400)

Nigerian bentonite using a planetary ball mill (Fig. 1) with 80ml of zirconia bowls was pulverized. The vial in this ball mill rotates like a planet along a supporting rotating disc, causing movement around its axis. The vial and the supporting disc rotate in the opposite directions; the centrifugal force acting inside the vial causes friction between the grinding balls as they run down inside the vial chamber and soil particles. In addition, the grinding lifts and moves freely through the inside chamber and impact the inside vial wall, causing the grinding of materials. In the first stage of wet grinding, parameters such as types and sizes of grinding balls, types of solvent, and speed and duration of grinding were selected through continuous grinding and particle size analysis. Initially, steel and zirconia balls with diameters of 10.5 and 2mm were used to observe the effect of ball size and types. At first, each of the bowls was filled with 100g of balls and 7g of bentonite, and the remaining volume of the bowls was filled with water. Then the bowls were kept in the rotating vial, and content was pulverized for 30min. After completion of the grinding, the balls were separated using 4.75mm and 80um sieves, and the screened materials were sent for particle size analysis. Upon confirming the ball size and diameters, the wet grinding process was selected and the particles were ground using isopropyl alcohol (IPA) instead of water with zirconia balls having a diameter of 5 mm at a speed of 400rpm for

30min [Sarkar *et al.,* 2015]. At the final stage of grinding, the speed and the duration of grinding were confirmed in the way described [Sarkar *et al.,* 2015].

Mechanical Attrition

Szegvary (1922) invented a one high-energy ball mill that has been adopted in industries. This mill is called an attritor or attrition mill (Fig. 2a, b). Milling occurs by the stirring action of an agitator that has a vertical rotating shaft with a horizontal arm (impellers). The motion causes a differential movement between the balls and the powder; it is achieved by the horizontal impellers attached to the vertical shaft, which is rotating.

Based on the value of induced mechanical energy to the mixture, mechanical attrition is classified into low-energy and high-energy systems. In the low-energy ball mill, the ball is dropped directly from the top to the feedstock materials by controlling an optimum speed, whereas, in the high-energy ball mill, the particle size of the bentonite powder can be reduced to nanosize by changing the chemical composition of the predecessors (Koch, 1997). Attrition mills such as attritor mills, vibratory mills, high-speed blenders and shakers, planetary mills, and even large-scale ball mills are used for pulverizing the materials to prepare nanoparticles [Sarkar *et al.,* 2015]. The grinding bowls and balls are agate, silicon nitride, sintered corundum, zirconia, chrome steel, chromium-nickel (Cr-Ni) steel, tungsten carbide, and polyamide based on the hardness of the material used. The zirconia balls have greater hardness and are suitable for grinding flaky particles such as bentonite [Sarkar *et al.,* 2015].

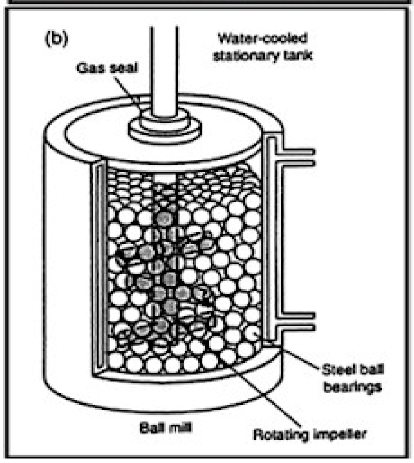

Figure 2: (a) High energy attritor ball mill (b) Arrangement of rotating arms on a shaft in the attrition ball mill.

Influencing Factors in the Milling Process

Some of the parameters that affect the constitution of the bentonite are the type of mill, milling container, milling speed, milling time, type, size, and size distribution of the grinding medium, ball-to-powder weight ratio, the extent of milling the vial and milling atmosphere. All these process variables are not independent. For example, the optimum milling time depends on the time of mill, size of the grinding medium, temperature of milling, ball-to-powder ratio and many others. Factors that play roles in the milling process are shown below:

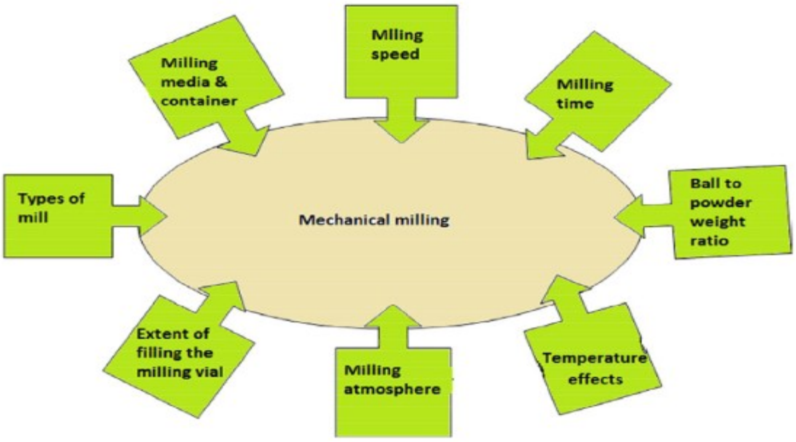

Figure 3: Factors influencing the milling process
Adopted from: Ullah, *et al.* (2014)

Characterization of nanoparticles

The particle size and the chemical composition of the dry particles were confirmed through scanning electron microscopy and energy-dispersive X-ray spectroscopy. In addition, the mineralogical change of the bentonite samples after the grinding process was observed using X-ray powder diffraction analysis. Finally, a particle size range between 40 and 100nm was confirmed for the Nigerian bentonite nanoparticle.

The morphology observation of ball-milled bentonite clay was initially performed using scanning electron microscopy (SEM Hitachi S-3400, Tokyo, Japan) and Transmission Electron Microscopy (TEM, LEO 912AB, Zeiss, Germany). Side by side comparison of atomic force microscopy (AFM) and SEM and TEM showed that AFM provided comparable results when analyzing nanoparticle sizes. AFM has the advantage that images in the sample are in three dimensions and allow the characterization of the nanoparticle height [Stephanos *et al.,* 2018]. Atomic Force Microscopy (AFM) is a microscopy technique capable of creating three-dimensional images of surfaces at high magnification. TEM is the most common for analyzing nanoparticle size and shape since it provides direct images of the sample and the most accurate estimation of the nanoparticle homogeneity.

Generally, TEM is for morphology. The X-ray diffraction (XRD) study was conducted using a Siemens D5000 diffractometer with Cu-Ka radiation. Two of the main parameters studied in the characterization of the nanoparticles (NPs) are size and shape. We can also measure size distribution, degree of aggregation, surface charge, and surface area and evaluate the surface chemistry.

This work highlights several different techniques for the characterization of nanoscale materials, demonstrates the uses and emphasizes their advantages and limitations, explains how they are effectively combined or complement each other. The acquisition of a picture of the variety of features associated with a nanomaterial requires numerous techniques, often needing to use more than one for evaluating well and even a single property [Stefanos *et al.,* 2018].

It is, therefore, desirable to know the limitations and strengths of the techniques and if in some cases, the use of only one or two of them is enough to provide reliable information when studying a specific parameter (such as the particle size), and to choose the most suitable techniques for nanoparticles characterization with the ability to assess their use in a more precise manner [Stefanos *et al.,* 2018]. The different characterization techniques used in this study are classified according to the information they can provide.

Nanoparticles characterization with AFM and Comparison of AFM with SEM/TEM

The atomic force microscope (AFM) is ideally suited for characterizing nanoparticles. It offers the capability of 3D visualization and both qualitative and quantitative information on many physical properties - size, morphology, surface texture, and roughness. Statistical information, such as, size, surface area, and volume distributions can be determined. A wide range of particle sizes can be characterized in the same scan, from 1 nanometer to 8 micrometers. In addition, the AFM can characterize nanoparticles in ambient air, controlled environments, and even liquid dispersion [Scalf and West, 2011].

AFM has several advantages over SEM/TEM for characterizing nanoparticles. Images from an AFM represent data in three dimensions so that it is possible to measure the height of the nanoparticle quantitatively. With the SEM/TEM, the images are measured on only two-dimensions [Scalf and West, 2011]. The AFM scans more slowly than an SEM. However, a complete measurement session that includes sample preparation, acquiring an image, and analyzing the image takes much less time with an AFM. Typically, it takes about ¼ of the time to get data from an AFM than with SEM/TEM. An AFM is a very cost-effective microscope for nanoscale imaging. An AFM with a comparable resolution to an SEM/TEM costs much less than the SEM/TEM. Further, the AFM requires substantially less laboratory space than an SEM/TEM, a desk or possibly vibration table for an AFM. Finally, the AFM is much simpler to operate than the SEM/TEM; the AFM does not require a specially trained operator [Scalf and West, 2011]. AFM is based on measuring the interacting forces between a fine probe and the sample. The probe is a sharp tip and coupled to the end of a cantilever of silicon nitride.

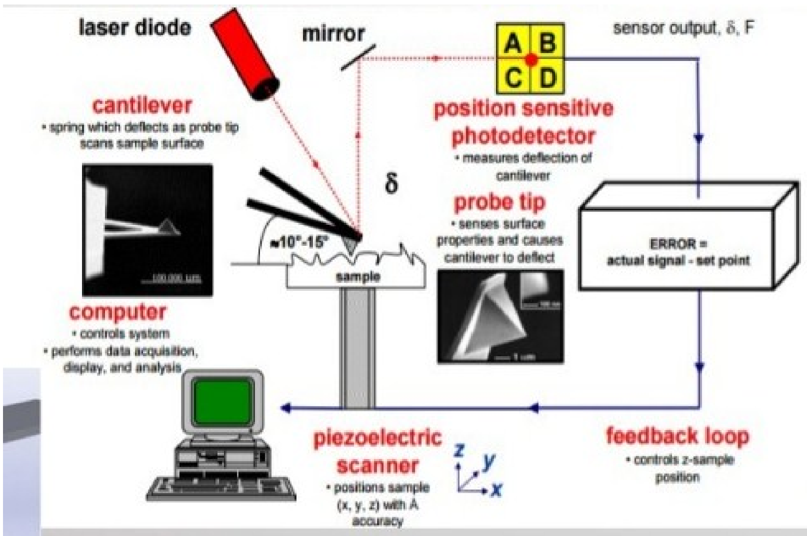

Figure 4: Atomic Force Microscopy (AFM)

Figure 5: Transmission Electron Microscopy

Evaluation of catalytic performance in Transesterification reaction

In the first experiment, the transesterification of mango seed oil using a base catalyst (NaOH) and nanoparticles of bentonite clay as a catalyst to produce biodiesel was studied comparatively. It is methanolysis reaction of esters, also called triglycerides, that contains mango seed oil in the presence of a catalyst, the NaOH in this case, at a moderate temperature that leads to the formation of glycerol and ethyl monoesters (figure 6).

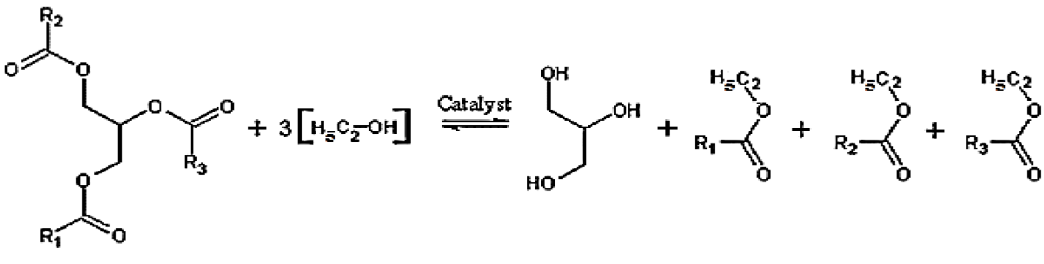

Figure 6: Transesterification reaction principle

The reaction conditions and parameters are optimally set to investigate the potential of neem oil for biodiesel production. This system uses nanoparticles of bentonite and NaOH as a catalyst at 1% of the mango seed oil mass, an ethanol/oil molar ratio of 6:1. Experiments were separately performed but under similar conditions. The set temperature of the reaction was at 70°C at atmospheric pressure with mechanical stirring for four hours of the reaction time. The calculated mass yield of the reaction according to equation (1) is as follows:

$$R = (mb/mh) \times 100 \qquad - \qquad - \qquad - \qquad \text{equation (1)}$$

In the above equation, R is the reaction yield (%), mb is the mass of biodiesel (g), and mh is the neem oil mass (g). At the end of the reaction, the ethyl ester (biodiesel) is separated from the glycerol and other by-products by static decantation using the separating funnels for 24hrs. The excess ethanol was distilled off from the biodiesel at a temperature of 90°C. The biodiesel was then purified (residual glycerine, traces of catalyst, soap and so on) by washing with hot water at 60°C followed by static decantation for 24hrs. The residual water from the washing operation was removed by drying the biodiesel by steaming it at 140°C for 20min.

In the second experiment, the effect of particle size on the catalytic activity of the bentonite nanoparticles was investigated. The catalytic performance was characterized by determining the yield of ethyl ester. Biodiesel product was determined by gas chromatography (Hewlett Packard, HP 6890) with an FID detector in the office-line mode. The GC column capillary was 10m long with a diameter of 100um. Using He gas in GC became the career gas and hexane as a solvent for biodiesel products. The oven temperature of GC was 150°C initially and 250°C as the detection temperature.

RESULTS AND DISCUSSION

The chemical composition of nanoparticles bentonite samples was analyzed by an Energy Dispersive X-ray analyzer (EDX). EDX characterization result is shown in figure 7. From the results of EDX, elements of Al, Si, Ca, Fe, and Ti are in every spectrum. Bentonite is [(Mg, Ca) $xAl_2O_3 \cdot ySiO_2 \cdot nH_2O$] as seen from the result of EDX in Figure 7 following the chemical formula of bentonite, which has a compound $CaCO_3$, SiO_2, and Al_2O_3, and the value composition is 13.73%; 69.81% and 14.27% and the element Fe is impurity caused by several factors.

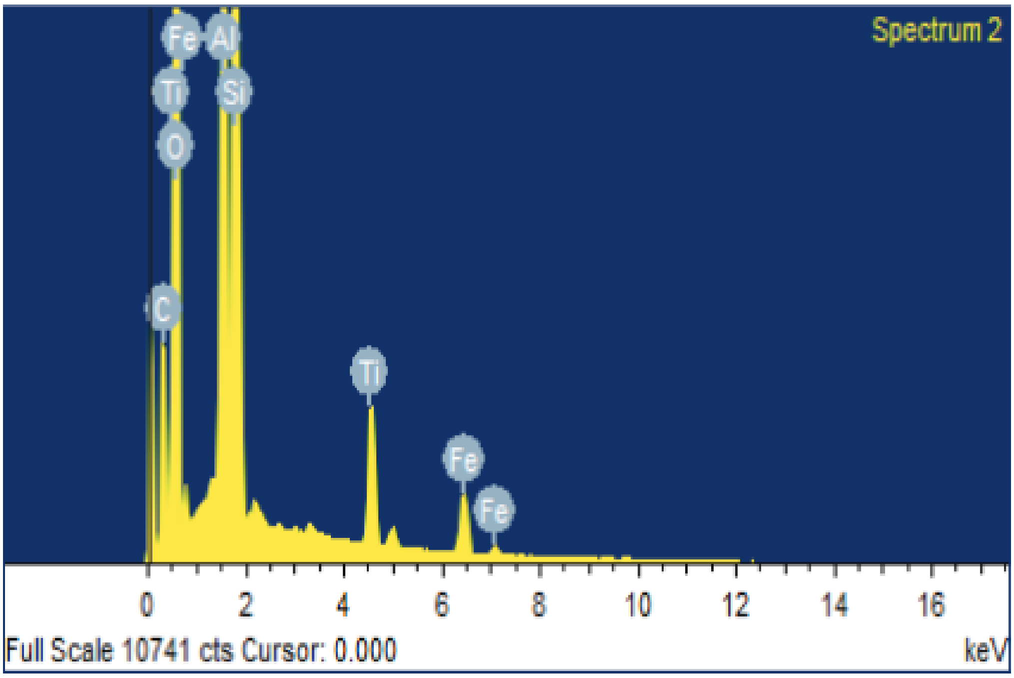

Figure 7: Spectrum EDX of bentonite nanoparticles

Based on EDX analysis, component content identified on the surface can be seen in Table 1.

Table 1: Result of EDX Analysis

Elements	Composition (%wt)
$CaCO_3$	13.73
SiO_2	69.81
Al_2O_3	14.27
Na	0.87
Fe	1.322
Total	100

Based on the result of EDX, which obtained a Ca content of 13.73 and Na content of 0.87, the nanoparticle is that of Ca – bentonite. The morphology of bentonite nanoparticles was characterized using SEM and AFM. Based on the images, agglomeration occurs on bentonite due to the interaction between bentonite and oxygen, particles showed a round shape. Figure 8 shows the morphological properties of nanoparticles of bentonite. Nanoparticles (samples) were characterized as SEM and AFM to determine the homogeneity of the grain sample shown in figure 8 and figure 9. Particles tend to form a spherical shape.

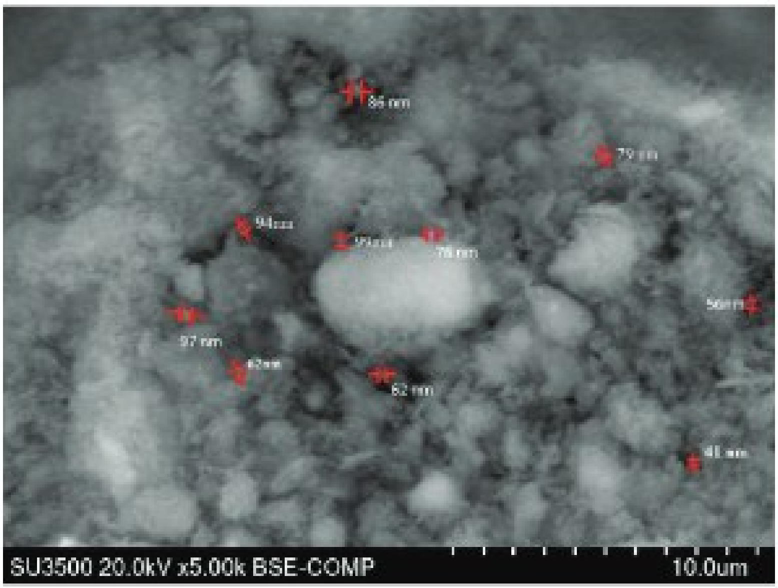

Figure 8: SEM results for Bentonite nanoparticles

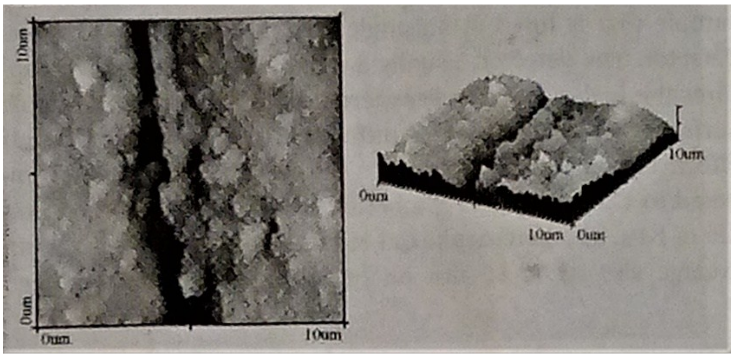

Figure 9a: AFM imaging from mm to nm of bentonite nanoparticle

AFM has a similar resolution to SEM and TEM while costing much less and occupying smaller laboratory space. However, only AFM could properly characterize nanoparticles with bimodal distribution sizes. Using the AFM, individualized particles and groups of particles can be resolved as the AFM offers visualization in three dimensions. Resolution in the vertical Z-axis is limited by the vibration environment of the instrument, wheras resolution in the horizontal X-Y axis is by the diameter of the tip utilized for scanning.

Typically, AFM instruments have vertical resolutions of less than 0.1nm and X-Y resolutions around 1nm. It is important to note that AFM scan with a physical probe is either direct contact or near contact. Therefore, particles must be anchored to the sample surface during the scan. It is because the AFM by scanning a mechanical probe across the sample surface, a structured image must have a greater affinity to the flat surface than the probe.

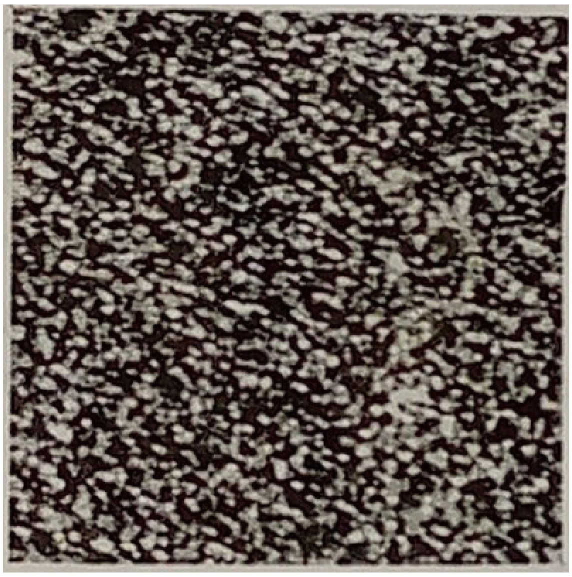

Figure 9b: 3x3 micro scan of bentonite nanoparticles

Software-based image processing of AFM data can generate quantitative information for individual particles, such as size information (length, width, and height) and other physical properties such as (morphology and surface texture) can be measured. The ability to scan from the nanometer range and the micron range is important. With AFM, particles from 1nm to 5um in height can be measured in a single scan.

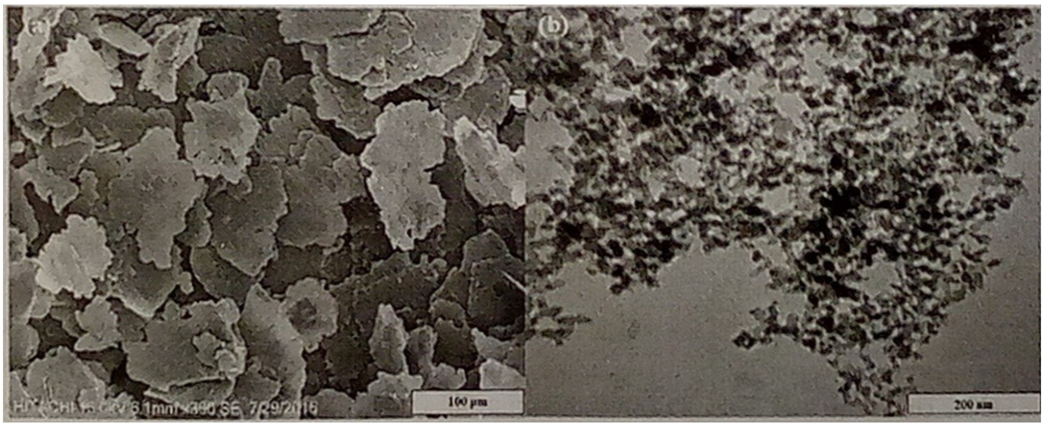

Figure 9c: Surface morphology of (a) flaky particles of bentonites and (b) nanoparticles of bentonite

Factors that affect the milling process

The ball milling process is an abrasive process to prepare nanoparticles of bentonite because the elements of the ball and the grinding bowls may intrude into the pulverized material. Therefore, suitable ball material from the elemental analysis was selected. The factors include the nature of powder, type of mill, milling speed, the size distribution of ball, dry or wet milling, the temperature of milling, and duration of milling. The effects of types and diameter of balls are in figure 10.

Steel and zirconia balls were used in the pulverizer particle size analysis showed that a particular diameter of zirconia ball results in smaller particles compared to the steel balls having the same diameter. The results encourage the use of small diameter (2mm) zirconia balls that introduce better particle size distribution than the 10mm balls. The grinding bowls and balls are generally made of agate, silicon nitride, sintered corundum, zirconia, chrome steel, chromium-nickel (Cr-Ni) steel, tungsten carbide, and polyamide depending on the hardness and are suitable for grinding the flaky particles such as bentonite [Sarkar *et al.,* 2015].

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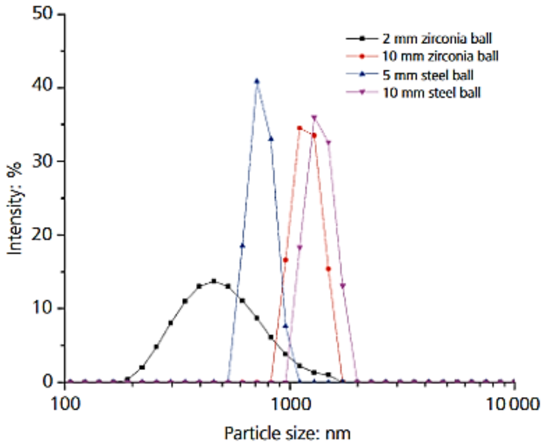

Figure 10: Effect of ball type and size on the grinding of nanoparticles at a speed of 400rpm for 30min.

The results in Figure 11 are consistent with previous experimental studies of other researchers [Sarkar *et al.,* 2015]. In the second stage, improvement of the finer particles ultrasonication and the particles having a size of more than 100nm of the dispersed solution were separated using centrifuging technique. The figure 12 indicates the SEM image of the original Nigerian bentonite and nanoparticles after grinding and centrifugation. Bottom-up and top-down approaches for size and shape controlled synthesis of nanoparticles have been proposed.

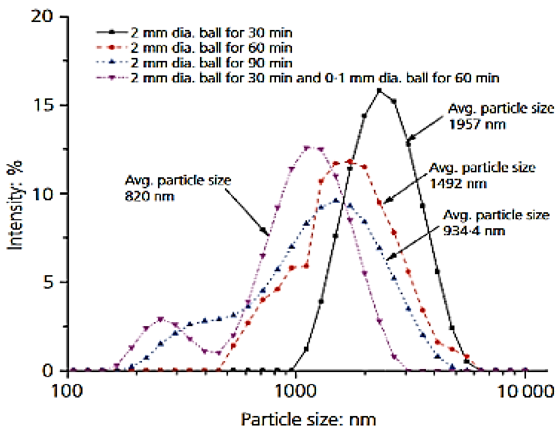

Figure 11: Effect of grinding period on the particle size of ground particles using a zirconia ball having a diameter of 2mm at a speed of 800rpm.

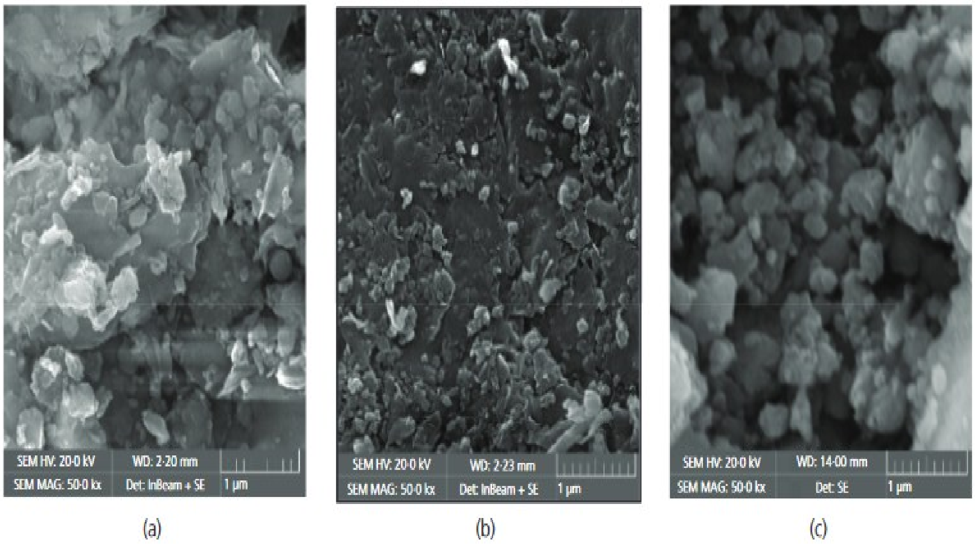

Figure 12: Microstructures of (a) bentonite, (b) ground bentonite before synthesis and (c) ground bentonite after synthesis

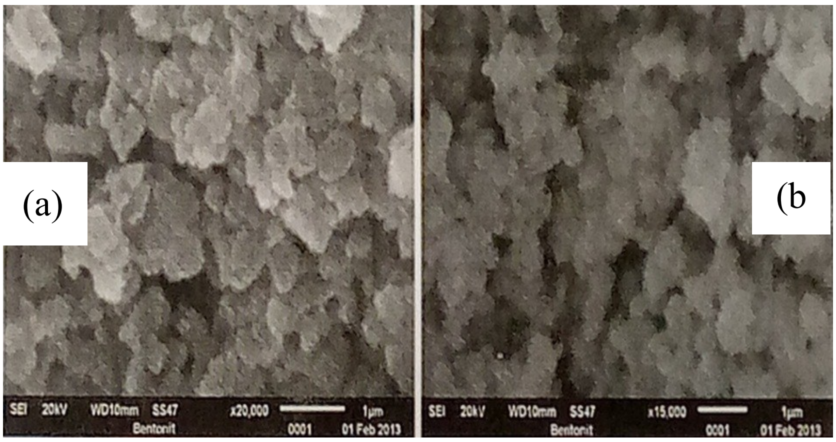

Figure 13: SEM micrographs of bentonite ball milled for (a) 2 h and (b) 8 h, showing the morphology.

In one of the experiments, the ground bentonite was milled for one (1) hour using the 2mm zirconia ball. Then, the obtained fine powder was equally (nearly 5mg) divided into four parts. The four separated fine powders were again milled (10mm balls: 300rpm) in a ball mill for different milling periods of 6, 9, 12, and

15 hours (hereafter, termed respectively as sample TP6, TP9, TP12, and TP15). The milling periods play a role in the formation of homogenous nanoparticles. The particle size analysis of all the samples shows that the average particle size of TP6, TP9, TP12, and TP15 samples are 114, 88, 65, and 45nm, respectively (Fig 14). The size of nanoparticles decreases from 114 to 45 nm at the period ball milling of the particles increases from 6 to 15h. The above results indicate that the milling time plays a dominant role in reducing the size of the produced nanoparticles.

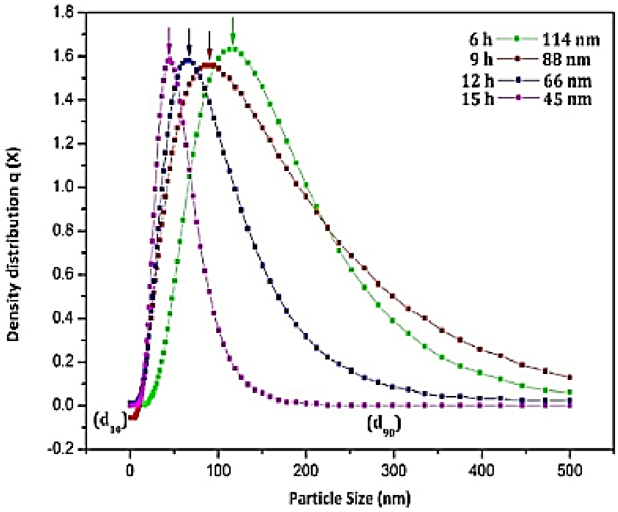

Figure 14: Particle size distribution of TP6, TP9, TP12 and TP15nanoparticles processed at different time periods.

Optimum particle size for betonite nanoparticle catalyzed transesterification reaction

Catalytic performance is governed by the size of the (nano)particles and the local surface topology, as these determine the electronic structure of the surface to which reactants bind [Norskov *et al.,* 2009]. Differences in the binding energies affect surface coverage and intrinsic barriers of the relevant elementary bond breaking and bond-making steps. Understanding structure sensitivity in detail promises to accelerate the design of better catalysts. Much progress in this field

ISSN(p): 2141-2731 ISSN(e): 2795-2967
Published By
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has been possible through careful in situ characterization and kinetic testing of structurally well-defined model systems – often in the form of surface science models, but recently also increasingly by using nanoparticles in combination with first-principles density functional theory (DFT) calculations of reaction mechanism [Liu *et al.,* 2018].

In nanoparticle catalysis, the structure sensitivity manifests itself as a strong dependence of surface atom-based turnover frequency on particle size, predominantly because of the exposure of a significant fraction of corner, edge, and step-edge atoms at the surface of these particles [Liu *et al.,* 2018]. When particle becomes clusters, well-developed facets disappear, quantum effects and local surface atom topology will start influencing catalytic reactivity [Liu *et al.,* 2018], also in figure 17. It has been demonstrated that bentonite nanoparticles with a size of 30 – 33nm are optimum for the transesterification reaction of mango seed oil.

Figure 15 shows the effect of particle size on catalytic performance in the transesterification reaction. Reducing the particle size from 57 – 33nm resulted in a significant increase in the yield of ethyl ester for a given transesterification reaction time, which indicates an increase in catalytic activity. However, reducing this particle size further to 28nm resulted in a slight decrease in catalytic activity. There is an optimum particle size of approximately 33nm for maximum catalytic activity. These are consistent with experimental studies reported in Wang *et al.,* 1997. For example, Wang *et al.* found that there exists an optimal particle size of approximately 10nm for the liquid-phase decomposition of chloroform (Wang *et al.,* 1997). It explained the result of the competing effect of the particle size on specific surface area and the charge career recombination dynamics [Zhang *et al.,* 1998; Zhang, 2004]. Decreasing the average particle size also increases the number of the surface site available for charge transfer. However, reducing the particle size also increases the rate of surface size recombination. For a sufficiently small particle size, surface recombination becomes the dominant process as the charge carriers are formed close to the surface of the particles and because the recombination process is faster than interfacial charge transfer.

Journal of Environmental Issues and Agriculture in Developing Countries
Volume 13, Number 3, December 2021
ISSN(p): 2141-2731 ISSN(e): 2795-2967
Published By
International Centre for Integrated Development Research, Nigeria
In collaboration with
Copperstone University, Luanshya, Zambia

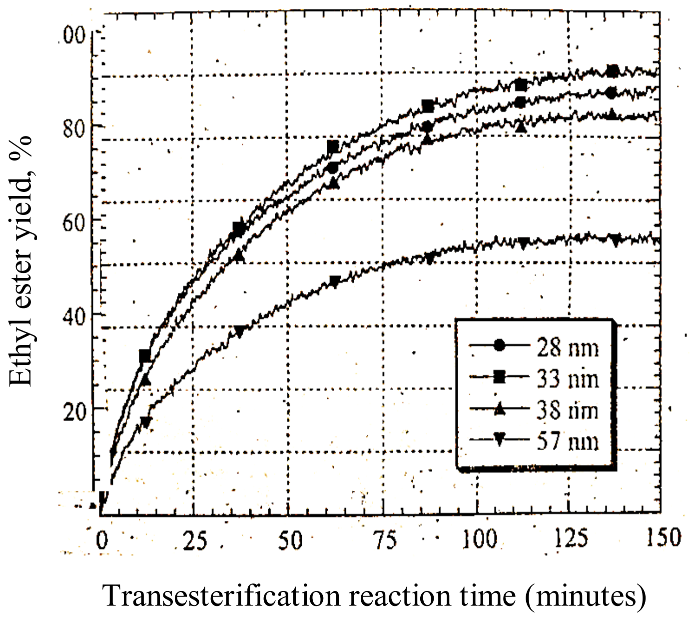
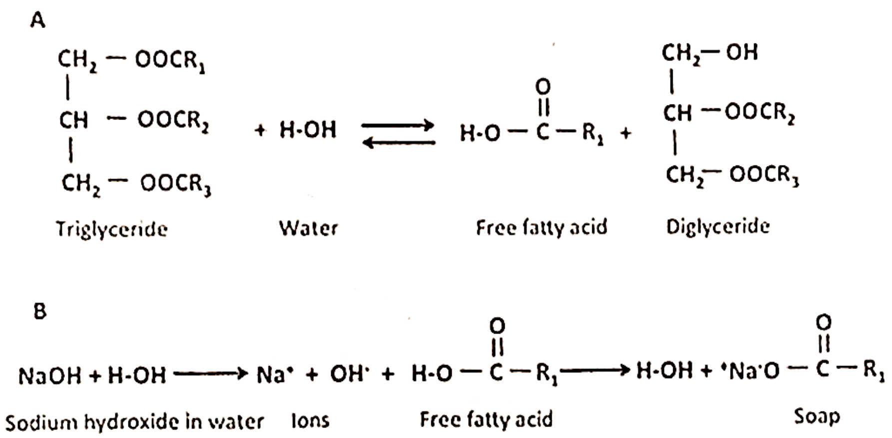


Figure 15: Effect of particle size on catalytic performance

From the result reported herein, nanoparticles of the Nigerian Bentonite exhibited great potential as an effective catalyst for the production of biodiesel from the mango seed oil, a non-edible oil. The nanoparticles not only improved the yield of biodiesel but also the problem of side reaction of soap formation of base-catalyzed transesterification:



Reaction scheme:

A side reaction of triglyceride with water B formation of free fatty acid can react with alkali ions to form soap. The base-catalyzed transesterification reaction resulted in an average yield of 83% (ethyl ester). It was relatively low-yield when compared with the ethyl ester (98%) obtained, using the bentonite nanoparticles as catalyst.

Ester of Mango seed oil:

The prepared bio-diesel, that is, the ethyl ester of mango seed oil was analyzed to determine the composition of fatty acids by GC-FID. Biodiesel is by the transesterification of saturated and monounsaturated fatty acids. The remaining polyunsaturated and some bulk saturated fatty acids are responsible for the high viscosity of the biodiesel. The high level of unsaturated fatty acid reduces fuel quality because of its oxidation [Kahaman *et al.,* 2008]. As a rule, saturated fatty acids such as 16:00 or 18:00 are more stable than unsaturated like 18:1, 18:2 and 18:3, which decreases the fuel quality [Kahraman *et al.,* 2008]. The result also shows that ethyl ester of biodiesel obtained from transesterification has more percentage of saturated acid than unsaturated fatty acids. The saturated acid in the biodiesel leads to high viscosity, high cetane number, and better biodiesel stability. The measured values of fatty acids present in the ethyl ester of biodiesel are in Table 2.

Table 2: Measured values of fatty acids in the ethyl ester of biodiesel

Type	Fatty Acids			Ethyl Ester of Mango Seed Oil
Unsaturated	1.	Oleic	18:1	37.29
	2.	Linoleic	18:2	32.15
	3.	Palmitoleic	16:1	<0.01
	4.	Lauric	12:0	<0.01
	5.	Palmitic	16:0	24.73
	6.	Stearic	18:0	4.07
	7.	Arachidic	20:0	0.42
	8.	Myristic	14:0	0.49
Saturated	9.	Margaric	17:0	<0.01

Comparative study of catalytic performance

The choice of a catalyst for transesterification mainly depends on the amount of free fatty acid (FFA) and raw materials. When the oils have high FFA and water, the acid-catalyst transesterification process is preferred. However, this process requires relatively high temperatures of 60 – 100oC, and long reaction times of 2 – 10 hours, in addition to causing undesired corrosion of the equipment. In contrast, when the FFA content in the oil is less than 1.0wt%, an alkaline-catalyst assisted process should be applied because this process required less simple equipment than that for the case of higher FFA content [Thanh *et al.,* 2012].

One of the drawbacks of the base catalyst is that it cannot be applied directly when the oils or fats contain large amounts of FFA that is greater than 1wt%. Since the FFA is neutralized by the base catalyst to produce soap and water, the activity of the catalyst also decreased. Additionally, the formation of soap inhibits the separation of glycerol from the reaction mixture and the purification of FAME with water [Thanh *et al.*, 2012]. With vegetable oil or fats containing low FFA and water, base-catalyst transesterification is most commonly used commercially on the industrial scale [Figure 16]. Promising catalysts based on the nanoparticles of Nigerian bentonite have been developed for biodiesel production. Among the tested catalysts, bentonite nanoparticles had the highest catalytic activity [Figure 16] and potential in large-scale biodiesel production from non-edible vegetable oils, such as mango seed oil.

The mechanism of transesterification catalyzed bentonite nanoparticles has not been studied systematically. Hence, a search strategy based on a combined first-principles density functional theory (DFT) and microkinetics on bentonite clusters and nanoparticles are suggested. It linked to the ball milling mechanism for the formation of nanoparticles (figure 17).

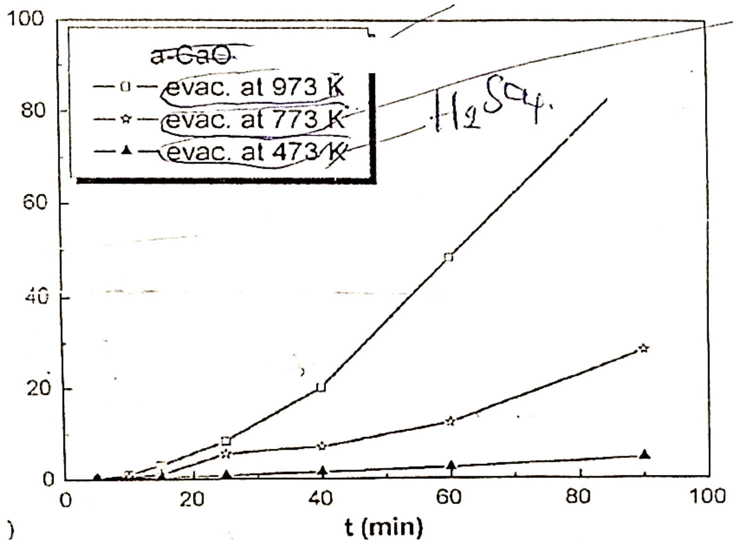


Figure 16: Effect of catalyst type on ethyl ester yield.

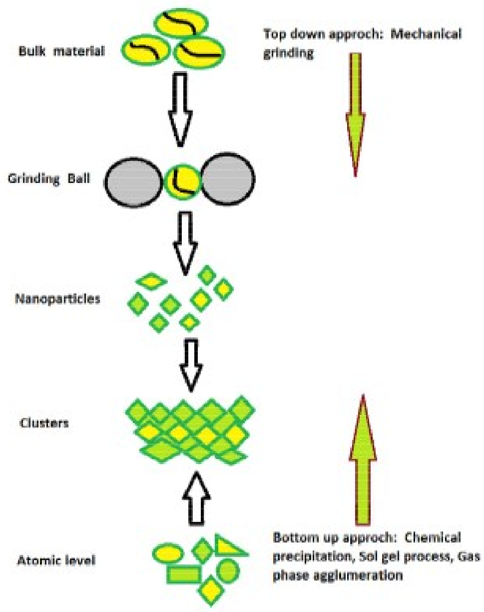


Figure 17: Schematic representation of a typical top down and bottom up approach for nanoparticle synthesis. ***Source:*** *Adopted from: Ullah et al.* (2014).

CONCLUSION

An experimental ball-milling was performed to evaluate the effect of process parameters on the particle size and morphology of Nigerian bentonite nanoparticles. Bentonite nanoparticles can be processed from a bottom-up technique, self-assemblage, and template synthesis and a top-down technique such as mechanical attrition. In this study, the processes were synchronized to prepare bentonite nanoparticles. Bottom-up and top-down approaches have helped achieve spectacular control over the synthesis of bentonite nanoparticles with various shapes, sizes, and morphology.

An investigation to determine the effect of the ball diameter sizes on the milling operations was also conducted. A zirconia ball with a diameter of 2mm for 30min and 0.1mm for 60min at a grinding speed of 800rpm to prepare nanoparticles and the synthesis process improves the particle size to a great extent by separating the larger particles. The effect of ball milling time on particle size and morphology found that the particle size reduced progressively with milling time. The influence of particle size on catalytic activity to optimize the production of potential bentonite nanoparticles for various applications such as biodiesel production by catalytic transesterification reactions was established.

The main advantages of ball milling include the large-scale production of high purity nanoparticles with improved physical properties in a cost-effective way. Ball milling with controlled parameters could be used for the synthesis of nanoparticles of bentonite which is found in abundance in Nigeria and many parts of the world. This study confirms that catalytic activity relies on nanoparticle size. The observed influence of particle size on catalytic activity will help to optimize the production of potential bentonite particles for different industrial applications, such as biodiesel production.

ACKNOWLEDGEMENT

The multidisciplinary aspects of nanoscience and nanotechnology do not permit every research team or group to have access to a broad range of characterization facilities.

The author is grateful to the following institutions for most of the analytical services and facilities reported in this work.

- Material science and characterization Laboratory, Institute of Advanced Technology, Universiti Putra, Malaysia. This link was made possible by Dr. Audu Buba who did his doctoral studies in Malaysia.
- The American University of Nigeria for Atomic Force Microscopy (AFM).
- Interdisciplinary Excellence Centre, Department of Applied and Environmental Chemistry, University of Szeged, Rerrich Bela ter 1, H-6720, Hungary.

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