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Transesterification of Cotton Seed Oil to Biodiesel using Nanoparticles of Bentonite Clay Catalysed Reaction

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ABSTRACT

This work focuses on optimizing various process parameters involved in transesterification of cotton seed oil to biodiesel by bentonite clay catalyzed reaction. The various process paramaters studied include temperature, oil to alcohol ratio, reaction time and amount of catalyst to improve the yield of biodiesel. The various properties of biodiesel produced such as calorific value, Cetane index, flash point and pour point were determined. The aim of applying nano-catalysis in the present project is to produce catalysts with improved selectivity, extremely high activity, low energy consumption, and long lifetime. This can be achieved only by precisely controlling the size, shape, spatial distribution, surface composition and electronic structure, and thermal and chemical stability of the individual nano-components. Cotton seed oil is extracted from the seeds of cotton plants (Gossypium herbaceum, G. barbadense and G. hirsutum) and other related species of Gossypium. Current production technology for the extraction of cotton seed oil generally relies on crushing with solvent extraction. The clay used in this work is calcium bentonite clay from North-eastern Nigeria. The biodiesel produced is characterized using FT-IR spectral analysis and GC-MS analysis to ascertain the various functional groups and compounds present. The major finding is that genotype differences in characteristics of cotton seed oil exist under field conditions. Highest oil content and amount of tocopherol is obtained from Funtua, while the highest oleic and linoleic acid content is found in Zaria and Funtua cotton species respectively. It is desirable to use non-edible oils, particularly those which can be grown on non-fertile or waste lands unfit for growing food crops. This will help in not only utilization of waste land but also create jobs for the rural poor.

Keywords: *cotton seed oil, nanoparticles, bentonite clay, biodiesel, transesterification.*

INTRODUCTION

Cotton is one of the most important commercial crops of Nigeria and is the single largest natural source of fibre. It plays a dominant role in industrial economy as the backbone of textile industry. Cotton is not classified as a food crop. Nigeria has a

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strong potential for implementation of biodiesel production programme, using non-edible oils as feedstock. The non-edible oil crops are grown in the waste lands that are not suitable for cultivation. The cost of cultivation is much lower because these crops can still sustain reasonable oils and high free fatty acids. The use of Fatty Acid Methyl Esters (FAME), often referred to as biodiesel, instead of fossil diesel fuel has a great potential to increase the share of fuels from renewable sources and to reduce greenhouse gas emissions.

Due to the increasing price of petroleum together with environmental concerns caused by the combustion of fossil fuels, the search for alternative fuels has gained much attention (Canakci and Van Gerpen 2001; Antolin, Tinaut, Briceno, Castano, Perez, and Ramirez 2002; Alterntive fuels Data Centre, 2018). Waste cooking oils, and non-edible oils, which are available cheaply, are attractive starting materials for biodiesel production (Chang, 1997; Ketlogetswe and Gandure, 2011). The main advantage of this fuel is that its properties and performance are similar to conventional diesel fuels (Ma and Hanna, 1999; Kumar Pradeep 2012). Diesel fuel is very important for the economy of a country as it has a wide range of usage. Direct use of vegetable oils or animal fats as fuel can cause numerous engine problems like poor fuel atomization, incomplete combustion, engine fouling and lubrication oil contamination, which is due to higher viscosity (Fan, 2008). Hence the viscosity of vegetable oils can be reduced by several methods which include blending of oils, micro emulsification, cracking/pyrolysis and transesterification (Sarada, Shailaja and Sita Rama Raju, 2010) cited in Nair, Deepthi and Siva kalyani, 2013). Among these, transesterification is widely used for industrial biodiesel production (Xiao, Mathew and Obbard, 2009).

Blending Biodiesel is mixing conventional petroleum diesel with biodiesel to give a biodiesel blend which can be added in any proportion to the petro-diesel (Shahid and Jamal, 2011). Biodiesel can be used in its pure form (B100), but may require certain engine modifications to avoid maintenance and performance problems. Biofuel, which is similar to biodiesel is commonly used in the United States more than Europe (Teffer, 2018). It is produced from oils or fats using transesterification, which is the chemical process between triglycerides and short-chain alcohol in the presence of basic or acidic catalyst to produce mono-alkylester (Antolin, Tinaut, Briceno, Castano, Perez and Ramirez, 2002) and is a liquid similar in composition to fossil/mineral diesel (Khan 2012). Chemically, it consists mostly of fatty acid methyl (or ethyl) esters (FAMEs). The direct use of oils and fats as diesel is in fact hindered by the high kinematic viscosity of the feedstock and by the carbon deposition. Hence, oils and fats must be processed to be compatible with existing engines (Nayaka, 2011).

There are different transesterification processes that can be applied to synthesize biodiesel: (a) base-catalyzed transesterification, (b) acid-catalyzed transesterification,

(c) enyzyme-catalyzed transesterification, and (d) supercritical alcohol transesterification. The most common method is homogeneously base-catalyzed transesterification, which is much faster than any of the others (e.g. 4000 times faster than homogenous acid catalysis reaction), in addition to be easier and cheaper (Ramaswamy, ?Huang and ?Ramarao, 2013). Nowadays more than 95% of the world total biodiesel is produced from highly pure edible oil feedstock, entailing the increasing of food prices and deforestation. On the other hand, non-edible oils have gained attention because of their elevated oil content and the possibility to be grown in territories suitable for agriculture with reduced cultivation costs.

Residual cooking oils are also considered as possible feedstock for biodiesel production due to the low costs, but they are composed mainly of Free Fatty Acids (FFAs), which strongly influence the yield and purity of the biodiesel. Although base-catalyzed transesterification is a simple process, it is very sensitive to the presence of free fatty acids which leads to undesired saponification reactions of pursued products. Consequently, it requires high cost virgin oil (high grade) as feedstock, highly increasing the production cost as compared to the acid-catalyzed transesterification.

Catalysts normally employed in the synthesis of biofuels are expensive or show other disadvantages such as difficulty of removal from the product, low stability and low selectivity. Nanotechnology has developed nano-catalysts with intermediate characteristics between homogenous and heterogenous systems, combining the high activity of homogenous catalysts, with the easy recovery of heterogeneous solid materials. Some methodologies successfully use homogenous catalysts to speed reaction rates up, increasing conversion and selectivity, minimizing side reactions and by-products. However, homogeneous catalysts cannot be recovered and reused. They must be neutralized at the end of the reaction, producing vast quantities of undesired waste chemicals that have to be separated, and limiting implementation of continuous downstream processes. Moreover, corrosion is especially favoured in homogeneous catalysis. Alternatively, heterogeneous catalysis offers, in addition to the aforementioned advantages inherent to a catalytic reaction, the possibility of recycling the solid catalyst.

Nevertheless, mass transfer effects are mostly negligible in homogeneous catalysis, where reactants, products, and catalysts are in the same phase. On the contrary, typical; liquid-solid heterogeneous catalyzed reactions for biomass conversion are limited by mass transfer or diffusion processes between solid phase of catalysts and liquid phase of reactants, leading to long reaction rates and low efficiency. Therefore, heterogeneous catalysis research has focused on developing solid catalysts in nanometer-size scale (nanocatalysts), where mass transfer resistance is minimized by the intrinsic large surface to volume ratios. Feed stocks for diesel include: animal fats, vegetable oils, soy, rapeseed, Jatropha, Mahua, Mustard, flax, sunflower, palm oil, hem, field pennycress, Pongamia Pinnata and algae (Brunet Solé, 2012). Research into the use of Fatty Acid Methyl Esters (FAMEs) (alkylester) as an alternative fuel diesel engine has continued to gain ground especially in the developed economy. It is projected, considering attributes like biodegradability and low combustion emissions, that alkylester will eventually replace regular petroleum diesel fuel. However, cost of vegetable oil, especially in Nigeria, imposes one of the major draw backs on their use as fuel currently. Accordingly, the research efforts on biofuels technology have been intensified in order to reduce production costs. The main approach has been to develop more efficient, environmentally friendly and economically viable novel processes. The shift from food crop feed stocks to non-edible oil provides an opportunity to enhance sustainable energy farming in the area of seeds considered to be a viable source of biofuel feedstock.

More research and investment will focus on crops such as cotton suitable for growing in arid, subtropical and tropical conditions. This will culminate in responsible commercialization of biofuels, driven by the need for increased energy security. The selection of land on which to grow the feed-stocks is a critical component of the ability of biofuels to deliver sustainable solutions. A key consideration is the minimization of biofuel competition for prime cropland. Significant opportunities are offered to a range of players from farmers to project developers and investors.

MATERIALS AND METHOD

Cotton seed oil Extraction: Cotton seed Oil is extracted from the seeds of various species of cotton plants, grown in Northern Nigeria- Kano, Funtua and Zaria. Generally, there is 18% oil content in cotton seed. It is pale yellow in color. The Gossypium herbaceum and Gossypium hirsutum species are more generally used to extract oil. But it should be mentioned that most of the cotton production in Nigeria is used in the textile industry.

In order to determine oil content, cotton seeds were crushed in blender and dried at 103±2 °C till the constant weight. Crude oils of seeds were extracted with the soxhlet method for 6 hours. Recovered crude oils were taken to a rotary evoparator at 35°C (Anderson 2004). Obtained oil samples were filtered and stored at 4°C in dark glass bottles prior to analyses. Seed oil content in which oil was extracted three times with hexane according to the method outlined by O'Brien (Last, Krüger and Dürnholz (Nd); Hanna, Isom and Campbell 2005). Oil can be extracted from cotton seed either by direct crushing or by scientific processing. Majority of cotton seed in developing countries is processed by direct crushing of ginned white cotton seeds in expellers. The process is inefficient as a large amount of oil remains in the cake, but due to its simplicity, low machinery cost and ready market for undecorticated (UD) cake for cattle feed, it is very popular. In scientific processing of cotton seed, first linters and hulls are removed from the seeds by delinting and dehulling/decortication operations respectively and oil is then extracted from the kernels either by first using expellers and then solvent (hexane) or entirely by solvent extraction.

Fatty acid pattern: before the determination of the fatty acid composition, the oil was fractioned into triglycerides (TG's) as major fraction, and the minor partial glycerides, namely, diglyceries (DG) and mono-glycerides (MG) as well as free fatty acids (FFA). Fractionation was conducted with the help of TLC using hexane/diethyl ether/formic acid mixture (70/30/1 v/v/v) as a developing solvent. The located zones of TG (R_f = 0.76), DG (R_f = 0.15), MG (R_f = 0.01), and FFA (R_f = 0.4) were scraped off the plate and extracted with n-hexane. The hexane solution was dried over anhydrous sodium sulphate and the solvent was distilled of under N_2. Each fraction was converted into ME (**methyl ester**) using 5% HCL in methanol (Chrestie, 1973) and the mixture was refluxed at 70-80°C for one to two hours till complete transesterification. The reaction was monitored with the help of TLC to ensure the conversion of all glyceride fractions and FFA into ME (**methyl ester**). Silica gel G plates and n-hexane: diethyl ether: acetic acid (80: 20: 1, v/v/v), as a developing solvent, were used.

The ME (**methyl ester**) solution was washed with distilled water until acid free, dried over anhydrous sodium sulphate and the solvent was distilled off under N2. The ME (**methyl ester**) was kept in 5 ml dark vials and stored until use at 4°C. Hewlett Packard-HP 5980-A gas chromatograph was employed for the analysis of ME (**methyl ester**) under the following operating conditions: column, DB-23 (0.32mm x 30m); temperature programming, 150 - 230°C, 3°C/min; injector temperature, 230°C; detector, FID at 240°C; carrier gas, Helium at flow rate of 1.3ml/min and split ratio, 100:1. Peak areas were determined by an electronic integrator and percentages compositions of fatty acids were automatically calculated. Calibration was made using the standard fatty acid methyl esters.

Statistical Analysis: All experimental data are expressed as mean ± S.D. Significant differences among the groups were determined by one-way anaylsis of variance (ANOVA) using the SPSS statistical analysis programme. Statistical significance was considered at $p < 0.05$.

The Preparation of Catalyst: The bentonite clay is typically extracted from open-air mines with deposits of varying depths, from few centimeters to several meters containing many impurity types in North-eastern Nigeria. The distribution of clay particle sizes was measured before and after purification using a Laser Particle Size Analyzer.

Purification of Clay Samples: Bentonite Clays contain the essential montmorillonite clay mineral as well as substantial inert impurities. The activity level attainable depends upon the concentration of the montmorillonite. High activity clay cannot be obtained by bentonite containing a low percentage of montmorillonite. Removal of inert impurities from bentonite to effect concentration of montmorillonite is a method for improving the activity of bentonite clays. A simple technique which can be employed to concentrate certain montmorillonites is dispersion and centrifugation. This process is schematically presented in Figure 1. Sodium bentonites are readily dispersed and respond well to centrifugal separation. This process is inadequate for the more important calcium-magnesium bentonites from which the majority of activated clays are prepared. These bentonites require special chemical treatments to render them satisfactory for centrifugal concentration. One commercial process employs the addition of ammonium carbonate to the aqueous slurry of bentonite prior to concentration. Figure 2 illustrates this process for obtaining concentrated calcium-magnesium montmorillonite.

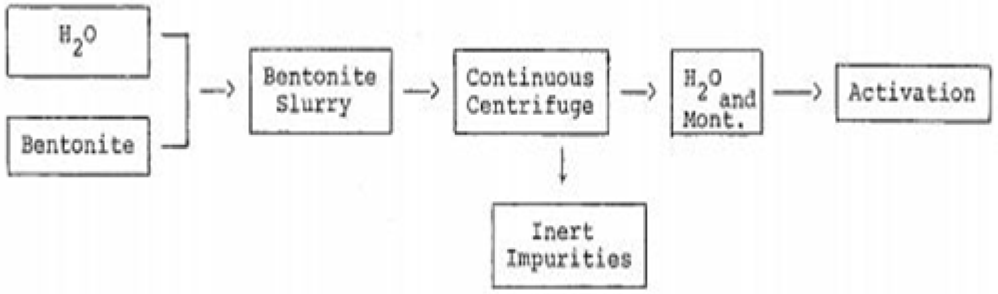


Figure 1: Schematic presentation of a simple technique which can be employed to concentrate certain montmorillonites is dispersion and centrifugation

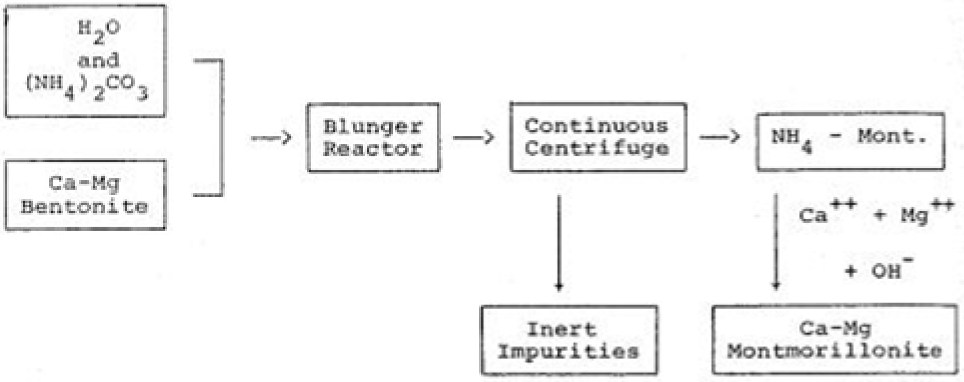


Figure 2: Process for obtaining concentrated calcium-magnesium montmorillonite

Characterization of Bentonite Clay Catalysts: The chemical composition of the samples were determined using a sequential spectrometer of X-ray fluorescence per wavelength XRF – 1800 Shimadzu; the powdered samples were pressed to disc shape under a pressure of 10 ton, using boric acid as support (base). The morphology of the samples were observed with a scanning electron microscope (SEM) SSX-550 Shimadzu, with 10 kV voltage under vacuum; preparation was performed applying a little amount of powder on a carbon tape and all samples were metalized with gold. The scanning electron micrograph of parent calcium bentonite (a) and (b) showing impurities.

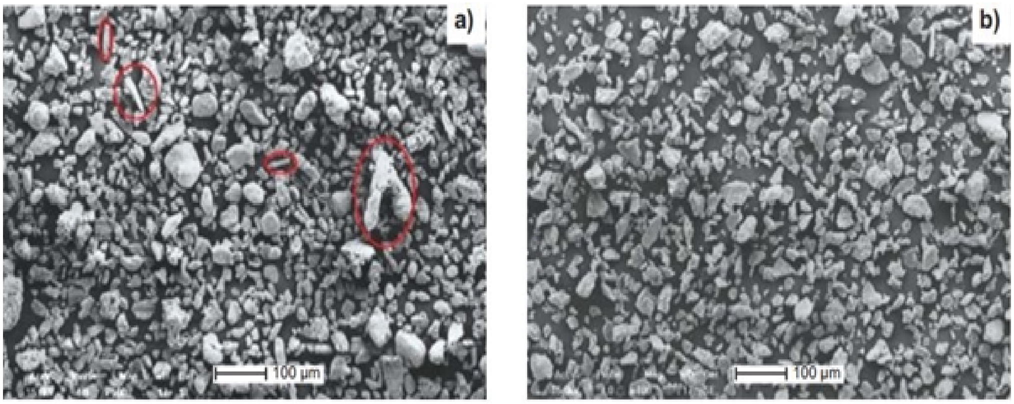


Figure 3: SEM micrographs of samples (parent) (a) and (b) indicating the possible impurities as quartz, present in the sample.

X-ray diffraction measurements were conducted in a X-ray diffractometer Shimadzu XRD-6000, Cu-$K_{á}$ radiation (ë = 1.542 Å), 30 kV voltage, 15 mA electric current, scanning from 2 to 50° in 2è and scan speed of 0.25° per step, with a counting time of 1sec per step. The data were collected using a 0.5mm divergence slit along with a 0.5 and 0.3mm receiving slits. Powder samples were placed on an aluminum sample holder, pressed to obtain a regular surface and inserted in the diffractometer goniometer support. A silicon standard was used to calibrate the equipment. The qualitative interpretation was performed by comparison with existing standard was used with PDF2 database (the International Centre for Diffraction Data, ICDD: www.icdd.com, 1996) using specific software. Quantitative analysis was performed by means of Rietveld refinement method by means of the DBWS Tools 2.4 for Windows.

Biodiesel Production: Transesterification is the chemical process between triglycerides and short-chain alcohol in the presence of basic or acidic catalyst to produce mono-alkylester (Antolin *et al,* 2002). The long- and branched-chain triglyceride molecules are transformed to mono-alkylesters and glycerol. Commonly used short-chain alcohols are methanol, ethanol, propanol, and butanol (Last, Krüger and Dürnholz, Nd). Methanol is commercially used due to its availability and cost effectiveness (Ketlogetswe and Gandure, 2011). The subsequent useful product is Fatty Acid Methyl Ester (FAME) commonly known as biodiesel.

A laboratory-scale biodiesel production set-up was designed and fabricated in the laboratory as shown in the Figure 4. It consists of a motorized stirrer, straight coil electric heater and stainless steel containers. The system was designed to produce 5litres of biodiesel. Temperature of the mixture of triglyceride, methanol and catalyst were maintained at about 55°C. Triglyceride is readily trans-esterified in the presence of clay catalyst at atmospheric pressure and at 55 to 66°C with an excess of methanol. The mixture at the end of reaction is allowed to settle. The lower Glycerol layer is drawn off, while the upper methyl ester layer is washed to remove entrained Glycerol and then processed further.

During the preliminary investigation, 200g of methanol and 5g of clay catalyst were firstly mixed and refluxed at 80°C for 1hr as the catalyst activation step. The ratio of methanol: cotton oil is kept constant at 2:5 without any changes in this research. Secondly, the 250g of cotton oil had been added to transesterify for 8 hours. The weight ratio among methanol: catalyst: cotton oil was 10.1: 25. During the reaction, every 2 hours, the mixture in the reaction was successively taken and characterized. The schematic diagram of experimental set up is illustrated in Figure 4. All sampling solutions were filtered to remove catalyst particle and impurities prior to biodiesel analysis. Then they became clear and ready for further determination of biodiesel properties after glycerol/biodiesel separation. The clay-based catalyst was reused after separation by filtration.

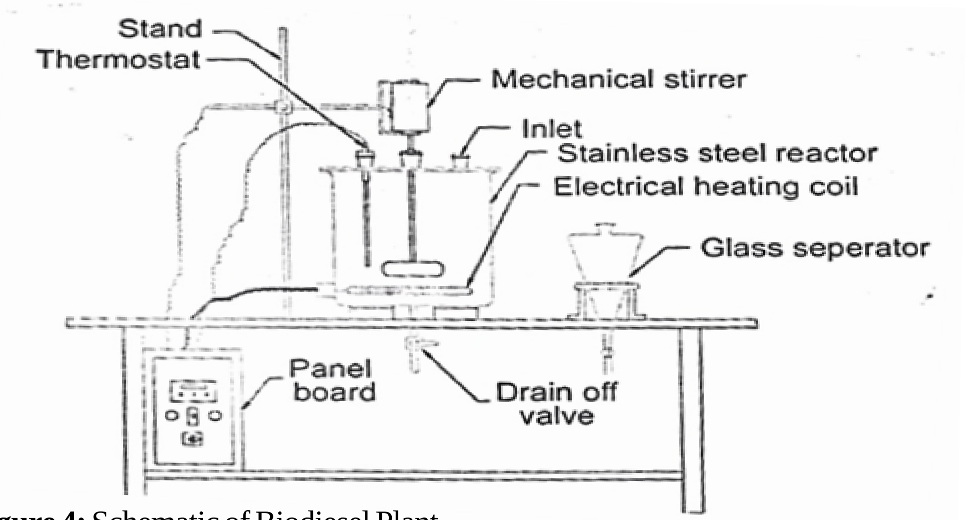
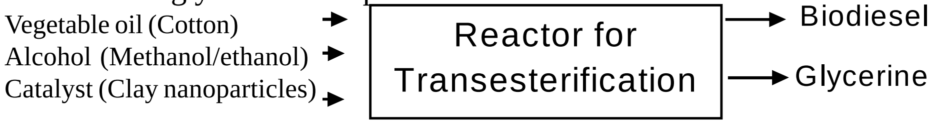


Figure 4: Schematic of Biodiesel Plant

In the process of making biodiesel through trans-esterification, it was noted that biodiesel and glycerol are the products.



The products are liquid, but they are also immiscible (do not dissolve in each other) and have differences in specific gravity. The specific gravity of the products is shown in Table 1.

Table 1: Specific gravity of products and unused reactants in biodiesel transesterification

Material	**Specific gravity (g/cm^3)**
Glycerol (Pure)	1.26
Glycerol (Crude)	1.05
Biodiesel	0.88
Methanol	0.79

Source: Antolin *et al* (2002).

In batch processing, gravity separation is used, and the products remain in the reactor; the reactor then becomes a settler or decanter. Once the reaction is finished, the product mixture then sits without agitation. After 4-8 hours, the glycerol layer settles at the bottom (because it has higher gravity) and the biodiesel settles at the top. However, if a continuous flow facility is utilized, the products separate too slowly in a settler, so a centrifuge is used. A centrifuge will spin the liquids at a very high speed, which helps to promote density separation. There are a few different types of industrial centrifuges that can be used for biodiesel separation (Antolin *et al* 2002).

Determination of biodiesel properties: For the fuel properties, some major methods were used to characterize important properties of biodiesel. They consisted of Saybolt kinematic viscosity (ASTM D2161-87) at 37.8°C and 100°C, flash point (ASTM D93-90), cloud point (ASTM D2500-91), pour point (ASTM D97-87) and Conradson carbon residue (ASTM D189-88). Saybolt viscometer was supplied by Koehler Instrument Co., Modeled K 21420. The closed-up apparatus for flash point determination is model K 16270 from Koehler Instrument Co. as well.

Cetane Number (CN): The CN is one of the common indicators of diesel fuel quality. It measures readiness of the fuel to auto ignite when injected into the engine. ASTM standard test method D 613 states that, for fuels with Cetane Numbers in the range 44 to 56, the repeatability should be within 0.7 to 0.9 Cetane Number Units. The GC-

MS analysis of liquid products was performed on a Hewlett Packard HP 5890 Series II GC gas Chromatograph interfaced to Hewlett Packard 5972 series mass selective detector using a Zebron ZB-5MS capillary column (30m x 0.25mm ID x 0.25µm film thickness) with the following temperature program: the initial temperature of 40°C was held for 10mins, increased with 4°C.min^{-1} at 280°C and maintained at this final temperature for 10min. total runtime was 80min. the helium was the carrier gas.

Temperature of the injector was 250°C. the volume of injected sample was 0.1µL. MS mode was carried out in full scan, with the scan range of 10-700 amu and the scan speed up to 1800 amu*s^{-1}. The ionization intensity of 70 eV was used. The acquisition of chromatographic data was performed by means of the HPchem software. All mass spectra obtained by GC-MS were interpreted based on an automatic library search (DATABASE/wiley6.1). The liquid products were analyzed also by a Fourier-transform infrared spectrometry (FTIR) using a JASCO-FTIR 610 spectrometer, in the 4000-400 cm^{-1} wavenumber range, using the liquid film technique. The FTIR analysis of solid samples was performed using the KBr pellet technique. The liquid products were analyzed also by ultraviolet-visible spectroscopy (UV-Vis) using a UNICAM UV-4 spectrometer equipped with photomultiplier detector. All UV-Vis spectra were recorded in the range of 190-400nm bandwidth, cell path length of 1cm and hexane as reference. The FTIR and UV-Vis spectra of all the studied samples were registered at room temperature.

Study of Transesterification Process Parameters: The transesterification process of conversion of cotton seed oil to biodiesel was performed by varying the various factors affecting the reaction like temperature of transesterification, amount of catalyst used, alcohol to oil molar ratio and reaction time. The study range of variables affecting the biodiesel yield is given in **Table 2**.

Table 2: Range of Biodiesel production parameters

Factors	**Minimum value**	**Maximum value**
Temperature of trans-esterification (°C)	50	70
Amount of bentonite clay nanoparticles, g/L	0.5	1.5
Alcohol to oil molar ratio	6:1	10:1
Reaction time (min)	60	120

Source: Chang (1997); Shahid and Jamal (2011).

Emission Characteristics determined according to literature procedure (Chang, 1997; Shahid and Jamal 2011).

RESULTS AND DISCUSSSION

Catalysts Characterization: The calcium bentonite clay used in this work was obtained from north-eastern Nigeria. Details of the characteristics of the calcium bentonite clay have been reported elsewhere (Diman and Wijeyesekera, 2008). The technique of scanning electron microscopy (SEM) is used to evaluate the morphology of the clay particles, i.e., the geometry (shape), size, and size distribution (Abdullahi and Audu, 2017). The modifications during the process of purification correlate with increased content of monmorillonite and nanoparticles. The techniques of purification of parent calcium bentonite clay indicate the possibility of building a pilot plant for the production of kilograms of high quality bentonite.

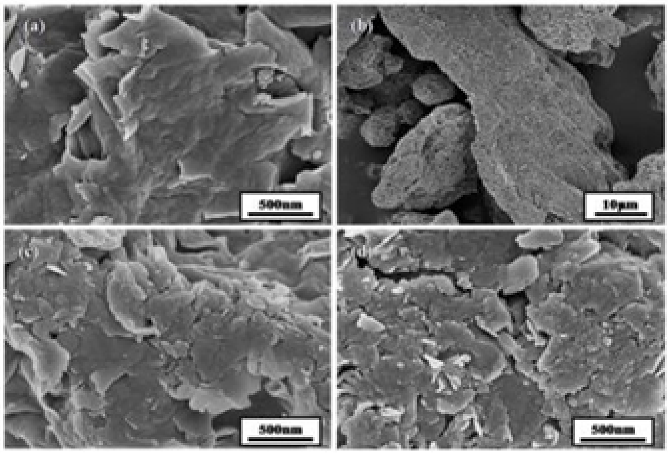


Fig. 5: SEM images of different products obtained after purification and the modified purified bentonite. (a):RB; (b): centrifugal sediment; (c):PB; (d) MB.

Table 3: Chemical analysis from X-ray fluorescence (in wt%) of calcium bentonite from north-eastern Nigeria.

Component	Adamawa	Borno	Gombe
SiO_2	55.5559	60.9223	62.8574
AI_2O_3	22.0061	22.0078	22.618
Fe_2O_3	6.7387	9.4662	8.2045
Mgo	3.1727	3.3696	3.4978
Cao	0.1505	1.7214	0.0238
Na_2O	0.0578	0.0726	0.1212
K_2O	0.0202	-	0.0495
TiO_2	0.3741	1.1433	0.2057
CuO	0.0163	0.1818	0.1069
CO_2	11.6495	-	-
SO_3	-	0.0429	0.0558

Source: Experimentation, 2017

Table 3 presents the variation of chemical composition of these samples. Silica (SiO_2) is related to quartz mineral impurities, and it is also one of the constituents of clay mineral montmorillonite. AI_2O_3 is mainly associated with montmorillonite and kaolinite, because impurities like quartz do not have aluminum in its composition.

Bentonite Clay Nanoparticles Size Distribution: The results of the XRD analysis reveal that most of the impurities, which included quartz, cristobalite, calcite, gibbsite and feldspar, were removed from the clay by the purification process. Finally, the thickness of the layers in the crystal structure of montmorillonite and the patterns generated by XRD indicate that the clay was comprised of crystal layers on top of each other following purification (Fig. 6). The size distribution of various samples clay nanoparticles is shown in Figure 6. The size of the diameter for nano-particles was determined. The volume percentage distribution shows size with mean particle diameters of less than 1, 50 and 500nm for NPs clay.

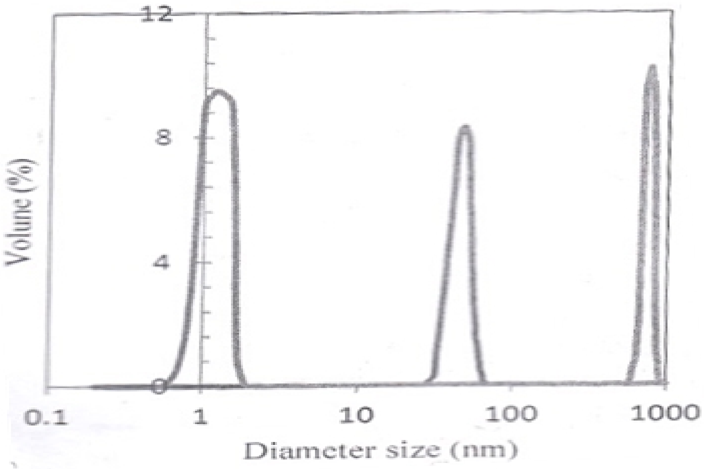


Figure 6: XRD pattern, local pure sample and particles size distribution.

Nanoparticles varying in size from 1 to 500nm and a concentration of 0.1 and 1 wt% are shown to be effective in transesterification. As mentioned above, the disadvantages of homogeneous base-catalyst transesterification are high energy-consumption, costly separation of the catalysts from the reaction mixture and the purification of crude biodiesel fuel (BDF). Therefore, to reduce the cost of the purification process, nanoparticles of bentonite clay, have been used because these catalysts can be easily separated from the reaction mixture, and can be reused.

Cotton seed Oil Composition and Properties: The fatty acid of Cotton seed Oil generally contains 70% unsaturated fatty acids. The oil contains:

- Palmitic acid: 22-26%
- Linoleic acid: 49-58%
- Oleic acid: 15-20%
- Arachidic/behenic and lignoceric acid: 10%

Cotton seed oil is described as a “naturally hydrogenated” substance by scientists. This is due to the fact that the saturated fatty acids in it are natural palmitic, mysristic and stearic acids. The fatty acids composition for cotton seed oils are shown in Table 4. The linoleic, palmitic, oleic and stearic acids were the principal fatty acids for all genotypes analyzed. The values of myristic, palmitoleic, linolenic, arachidic did not exceed 1%. It was found that the content of oleic acid varied between 14.06-17.00% in cotton seed oil according to genotypes. Highest oleic and linoleic contents were found in oils obtained from genotypes of Zaria (17.00%) and Funtua (55.82%), respectively. Sharma et al (2009) have reported highest oleic and linoleic acid contents of 24.81% and 52.78% in cotton genotypes, respectively. Highest palmitic and stearic acid contents were detected in oils of Zaria (25.63%) and Kano (3.13%), respectively. The concentration of palmitic acid (16:0), a saturated fatty acid, is higher in cotton seed oil (~24%) than in many other vegetable oils (Sarada, Shailaja, Sita Rama Raju and Radha, 2010). The results obtained are in accordance with O’Brien (2003) and Baydar and Turgut 1999; Roche, Essahat, Bouniols, Asri, Mouloungui, Mondiès and Alghoum (2004) whose reports indicate that fatty acid compositions of seeds vary according to genotype and environmental factors.

As with other vegetable oils, quality of cotton seed oil usually comes from fatty acid composition and unsaponifiable matters mentioned. Their amount and oil yield varies depending on genotype, ecological conditions of region process and storage conditions (Baydar and Turgut 1999).

Table 4: Fatty acids profiles of cotton seed oil of cotton varieties (%)

Fatty acids	**Kano**	**Funtua**	**Zaria**	**Mean**	**Range**
Myristic (C14:0)	0.79	0.78	0.80	0.79	0.78-0.80
Palmitic (C16:0)	25.52	24.85	25.63	25.33	24.85-25.63
Palmitoleic (C16:1)	0.55	0.54	0.57	0.55	0.54-0.57
Stearic (C18:0)	3.13	3.01	3.12	3.08	3.01-3.13
Oleic (C18:1)	15.11	14.06	17.00	15.39	14.06-17.00
Linoleic (C18:2)	54.01	55.82	52.00	53.94	52.00-55.82
Linoleic (C18:3)	0.14	0.14	0.12	0.13	0.12-0.14
Arachidic (C20:0)	0.29	0.30	0.31	0.30	0.29-0.31

Source: Experimentation, 2017

Table 5: Fatty acid constituents present in cotton seed oil (Gossypium hirsutum).

Fatty acid	**% Composition**
Myristic (C14:0)	0.8
Palmitic (C16:0)	24.4
Palmitoleic (C16:1)	0.4
Stearic (C18:0)	2.2
Oleic (C18:1)	17.2
Linoleic (C18:2)	55.0
Linoleic (C18:3)	0.3

Source: Experimentation, 2017

Table 6: Optimization of biodiesel synthesis from cotton seed oil

Run	Temperature (°C)	Amount of Bentonite Clay nanoparticles (g/L)	Alcohol to oil ratio	Reaction time (min)	Yield (%)
1	70	0.5	6	120	88.0
2	50	0.5	10	120	91.0
3	50	1.5	10	60	71.5
4	70	1.5	10	120	90.0
5	70	0.5	10	60	95.0
6	70	1.5	6	60	94.0
7	50	0.5	6	60	95.0
8	50	1.5	6	120	95.0

Source: Experimentation, 2017

Table 7: Physical and chemical properties of cotton seed oil

Property	**Characteristic/Value**
Percent Composition	Fatty Acids: Linoleic (46.7-58.2%), Palmitic (21.4-26.4%), Oleic (14.7-21.7%), Stearic (2.1-3.3%), Mysristic (0.6-1.0%), Palmitoleic (0.0-1.2%), other fatty acids; unsaponifiable tocopherol <1%.
Physical state at 25°C/1 Atm.	Liquid
Color	Pale yellow
Odor	Practically odorless
Density/Specific Gravity	0.915-0.921 at 25°C
Smoke-point	232°C (450°F)
Viscosity	n= 80 mPas at 20°C

Source: Experimentation, 2017

Figure 7: Cotton seed Oil Image

Figure 8: Cotton seed Oil Image

Table 8: The range of fatty acid content of four cotton species

Name of the species	Extent of Variability				Reference
	Palmitic acid %	**Stearic acid %**	**Oleic acid %**	**Linoleic acid %**	
G. arboreum	23.1-25.9	2.3-3.4	20.8-6.3	41.1-50.6	Pande (1998)
G. herbaceum	20.5-23.4	3.2-4.4	17.5-20.8	51.3-55.1	Pande (1998)
G. hirsutum	23.1-28.0	2.4-3.4	14.7-20.9	47.6-55.4	Pande (1998)
G. barbadense	24.4-25.5	2.6-3.0	18.7-19.7	50.0-51.7	Pande (1998)
G. arboreum	8.90-21.2	1.1-2.9	16.5-30.7	30.3-59.3	Dani *et al.* (1997)
G. hisutum	8.83-24.4	1.2-4.5	10.3-30.2	20.6-58.0	Dani *et al.* (1997)

Extent of variability observed in fatty acid profiles in above mentioned studies for all the cultivated cotton species could well be utilized in developing lines with high polyunsaturated and monounsaturated fatty acids contents through appropriate breeding techniques.

Biodiesel Properties and Specifications: To insure quality biodiesel, there are standards for testing the fuel properly to see that it meets specifications for use. ASTM (An international Standards and Testing Group) has a method to legally define biodiesel for use in diesel engines, labelled ASTM D6751, "Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillates." Also biodiesel should meet the European specifications of EN 14214, other than the parameters of Cetane Number, Iodine Value and some of the seasonal requirement. The biodiesel synthesized using transesterification process using cotton seed oil was analyzed by estimating the various physical properties. The various properties of biodiesel synthesized like acid value, viscosity, flash point, density, calorific value, pour point and cloud point estimated are shown in Table 9. The results obtained were compared with ASTM D6751 and EN14214 standards and were observed to be in the range meant for quality biodiesel as shown in Table 9.

Table 9: Estimated values of physical properties of biodiesel.

S/N	Property	Biodiesel synthesized from cotton seed oil	ASTM D6751	EN14214
1	Acid Number, mg KOH/g	0.313-0.38 mg KOH/I	Max 0.8/KOH/g	Max 0.5 KOH/g
2	Kinematic viscosity, 40°C	2.496 mm^2/s	1.9-6mm^2/s	3-5mm^2/s
3	Flash Point, °C	156°C	Min 130°C	Min 120°C
4	Density at 15° C	0.8855 g/cc	-	0.860-0.900 g/cc
5	Calorific value	33.78 MJ/kg	-	~35 MJ/kg (EN14213)
6	Pour Point	2°C	15 to 10	0°C Max (EN14213)
7	Cloud Point	9°C	-3°C to 15°C	-
8	Cetane Number	52	>49	>47

Source: Experimentation, 2017

Table 10: Conversion of glycerides to biodiesel showing intermediates.

Properties		Test method^a	Limit
Ester content/(mol mol^{-1})	98%	EN 14103	min 96.5%
Mono-glycerides content/(mol mol^{-1})	0.06%	EN 14105	max 0.80%
Di-glycerides content/(mol mol^{-1})	0.03%	EN 14105	max 0.20%
Tri-glycerides content/(mol mol^{-1})	<0.02%	EN 14105	max 0.20%
Free glycerol content/(mol mol^{-1})	<0.02%	EN 14105	max 0.02%
Total glycerol content/(mol mol^{-1})	0.05%	EN 14105	max 0.25%

Source: Experimentation, 2017

As with all materials, production and quality of biodiesel is important. Most importantly, the transesterification reaction should reach completion for highest production and quality. Due to the nature of transesterification of triglycerides, a small amount of tri-, di-, and mono-glycerides remain. Table 10 shows the changes in these compounds as the glycerides react to form biodiesel. Some terminology to be aware of: 1) bound glycerol is glycerol that has not been completely separated from the glyceride and is the sum of tri-, di-, and mono-glycerides and 2) total glycerol combines the bound glycerol with the free glycerol. The estimation of various properties of biodiesel is done to ascertain its quality. The Fourier transform infrared spectroscopy (FT-IR) is used to characterize the biodiesel and glycerol obtained by transesterification of cotton seed oil. The absence of the OH peak and the presence of ester peak at 1750 cm^{-1} and C_H peak near 2800-3000 cm^{-1} shows the presence of chain fatty ester.

Most of the carbons are all single bonded carbons C__C, and sp^3 hybridized and hence C__H bond stretching is observed at 2800-3000 cm^{-1}. The C_H bending will show good absorbance around 1350-1480 cm^{-1} as observed in Fig. 10. The C__O bond in the range of 1000-1300 cm^{-1} is present in the ester group, and can be seen as more than one peak. Since there are C__C bonds also present due to linolenic acid and other unsaturated acid methyl ester as observed from peak at 1653 cm^{-1}

characteristic of C__C stretching. The C__H stretching is observed at wave number 675-1000 cm^{-1}. Product identification gave methyl esters such as methyl oleate from acid components.

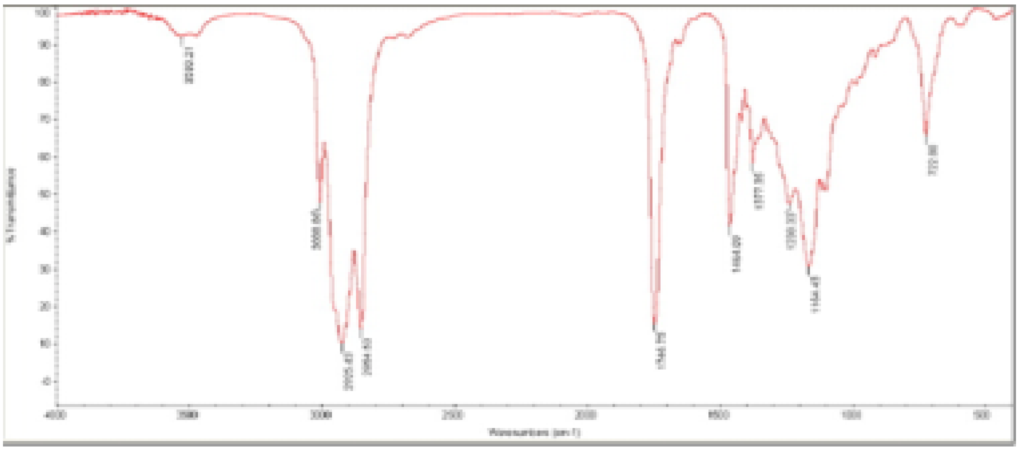


Figure 9. *FT-IR spectrum of biodiesel synthesized by trans-esterification of cotton seed oil.*

Glycerol content in biodiesel must be as low as possible, as ASTM standards state. The Biodiesel will not technically be "biodiesel" unless ASTM standards are met, which means being below the total glycerol specifications. High glycerol content can cause issues with high viscosity and may contribute to deposit formation and filter plugging. Crude glycerol is often a dark brown color and must be refined and purified before use elsewhere. In biodiesel preparation, brown layers will form, and, possibly, white flakes or sediments, formed from saturated mono-glycerides, that will fall to the bottom of the tank the biodiesel is being stored in (Gerpen, 2013).

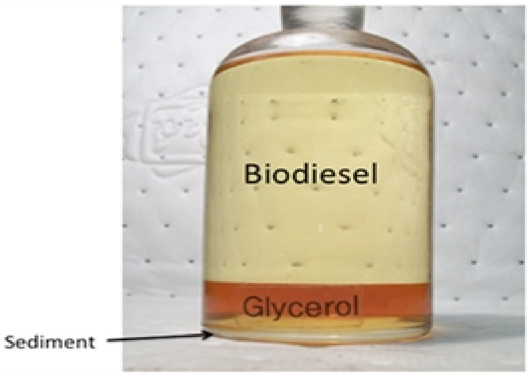
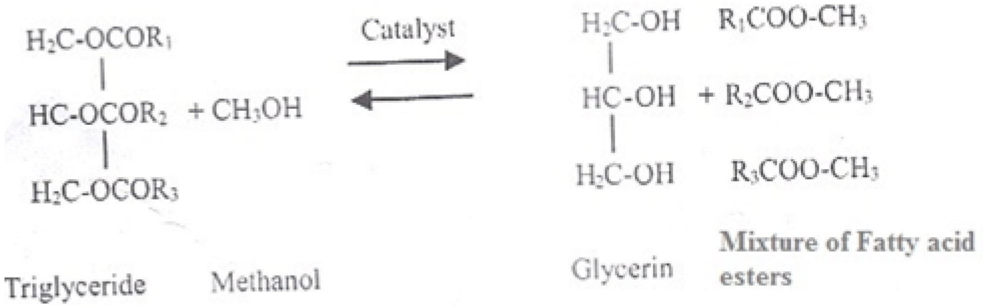


Figure 10: *B*iodiesel with crude glycerol and saturated mono-glyceride settled at bottom

Source: Gerpen, J. V. (2013, February 16). Biodiesel Production Principles and Processes. Farm Energy

Nano-catalysts for biodiesel production: In the biodiesel production method, transesterification is the chemical reaction between triglycerides and alcohol in the presence of nanoparticles of bentonite clay for producing monoesters. The triglyceride molecules are transformed to monoester and glycerol. The transesterification method incorporates a sequence of three reversible reactions. The conversions of triglycerides to di-glycerides, di-glycerides to mono-glycerides and glycerides into glycerol yield one ester molecule in each stage. The general transesterification reaction can be represented by reaction scheme below (Gerpen, 2013).



Reaction scheme of transesterification of triglycerides with methanol: The transesterification reaction of oil and alcohol with a homogeneous catalyst is the general method for the preparation of biodiesel. However, the homogeneous catalysts have many shortcomings, such as requiring large amounts of water, difficulties in product isolation, and environmental pollution caused by the liquid wastes. The use of “a green” method based on heterogeneous catalysts is a new trend in the preparation of biodiesel. Among the different possible options to produce biofuels, the alcoholysis of oils has been frequently utilized, especially for the synthesis of biodiesel. Most advanced nano-catalysts for the production of biodiesel are base nano-catalysts, acid nano-catalysts, and bi-functional nano-catalysts. Base nano-catalysts accelerate the reaction in mild reaction conditions, but need pure oils. In contrast, acid catalysis can catalyze the alcoholysis of low-grade feedstock, but is time consuming process. Bi-functional catalysts have been proposed as solutions for biodiesel production from low-grade oils in a one-step reaction, catalyzing at the same time the transesterification and esterification reaction of oils and fats. From the results reported above, nanoparticles of bentonite clays exhibited great potential as effective catalysts for the production of biodiesel from Nigeria cotton seed oil. The nanoparticles not only improved the yield of biodiesel but also solved the problem of side reaction of soap formation of base-catalyzed transesterification:

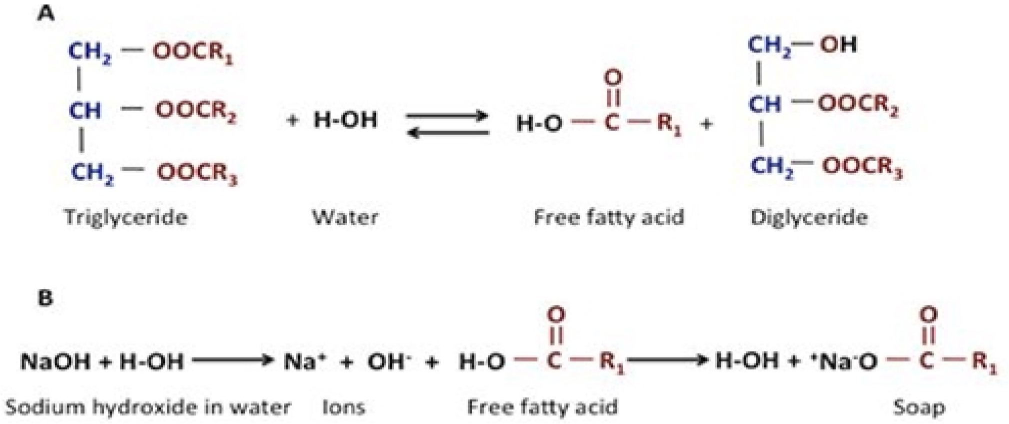
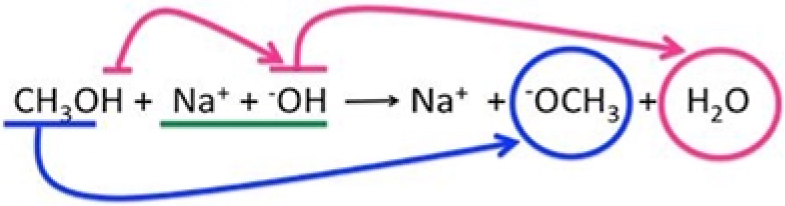


Fig 11: A: Side reaction of triglyceride with water. **B:** Formation of free fatty acid can react with alkali ions to form soap

Source: Clifford C. B. (Nd). EGEE 439: Alternative Fuels from Biomass Sources. ***https://www.e-education.psu.edu/egee439/node/684*****.**

Reaction scheme 2: A side reaction of triglyceride with water. B. Formation of free fatty acid can react with alkali ions to form soap, during base catalyzed reaction.

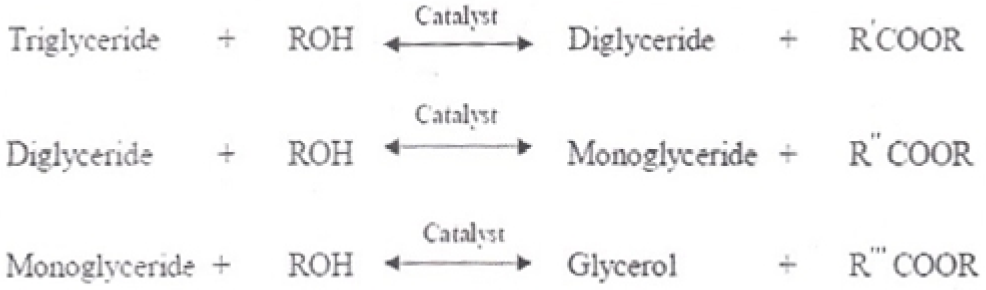
- ***Methanol and base (NaOH in this case) is combined. NaOH separates into ions in methanol. The ^-OH reacts with the H of methanol to make H_2O, leaving the $^-OCH_3$ to react with the fatty acid.***



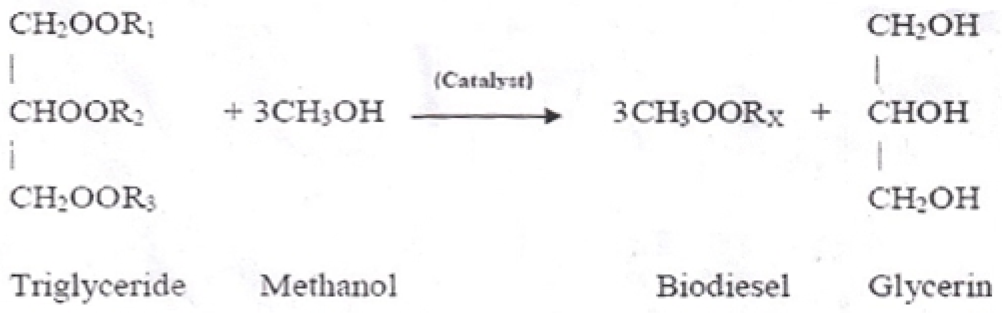
- ***Both should be as dry as possible***
- ***Water production increases the side reaction of soap formation, which is unwanted.***

Figure 12: Formation of methoxide
Source: Clifford C. B. (Nd). EGEE 439: Alternative Fuels from Biomass Sources.

Comparison between trans-esterification by base catalysts and clay-based catalysts showed that the clay-based catalysts trans-esterification can be represented as follows:



The first step is the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides and of monoglycerides to glycerol. The overall chemical reaction of the transesterification process is:



As seen above, the transesterification is an equilibrium reaction in which excess alcohol is required to drive the reaction close to completion. The reaction takes place with maximum yield obtained at temperature ranging from 45-60°C.

Application of biodiesel and Emission Characteristics of biodiesel

Based on literature review and experimental data, it has been reported that in most cases, biodiesel is compatible with diesel engines from 1994 onwards, which use 'Viton' (by Dupont) synthetic rubber in their mechanical fuel injection systems. Note however, that no vehicles are certified for using pure biodiesel before 2014, as there was no emission control protocol available for biodiesel before this date (Chang 1997; Shahid and Jamal 2011; O'Brien *et al* 2005).

Biodiesel mixing with diesel improves most of the fuel properties and can be used as an alternative fuel for diesel engines. They have lower emissions and high flash point (usually >300F), hence they are safer. They are biodegradable and essentially non-toxic. Mass emissions of carbon monoxide and particulates found lower with

Biodiesel blends, but NOX increased (Chang, 1997; O'Brien, 2002; Jain, Kumar and Chaube, 2011). Other advantages of biodiesel include that its physical and chemical properties are very similar to petroleum based diesel fuel in terms of operation. Therefore, it can be used in diesel engines without expensive alterations to engine or fuel system. It is also biodegradable and free from sulphur and aromatics, making it safer to handle and transport. Biodiesel runs in any conventional, unmodified diesel engine. Addition of even 2% biodiesel helps in significant improvement of lubricity of diesel. The best advantage is the fact that it is a renewable fuel source, while petroleum is limited. This alone will be the reason for its ever increasing popularity.

Biodiesel used as blends in different portions to petroleum diesel showed significant improvement in terms of GHG emission. It was observed that on combustion of biodiesel – petroleum diesel blends, the level of carbon monoxide (CO), carbon dioxide (CO_2), smoke, particulate matter (PM) were reduced significantly; whereas the amount of oxides of Nitrogen (NOX) was increased. Since biodiesel is oxygenated, engines have more complete combustion than with ordinary diesel (O'Brien, Jones, King, Wakelyn and Wan, 2005; Kumar 2012; Chattopadhyay and Sen, 2013).

Since biodiesel is an effective solvent and cleans residues deposited by mineral diesel, engine filters may need to be replaced more often, as the biofuel dissolves old deposits in the fuel tank and pipes. It also effectively cleans the engine combustion chamber of carbon deposits, helping to maintain efficiency. In many European countries, a 5% biodiesel blend is widely used and is available at thousands of gas stations (Ma and Hanna 1999; Kumar 2012; Malhotra 2005 cited in Khan, Baseer and Shakoor 2016).

CONCLUSION

The results of this study reveal that cotton seed oil has the potential for use as a renewable and industrial feedstock for biodiesel production. This research project focused on developing an environmentally friendly and economically viable process for the production of biodiesel. The transesterification of cotton seed oil using nanoparticles of bentonite clays as catalyst to produce biodiesel was studied. The interaction effects of various factors such as temperature, amount of catalysts used, alcohol to oil ratio and reaction time on yield of biodiesel were investigated. The maximum yield of 98% biodiesel was obtained. The reported results reveal that the high specific surface area of nanostructure materials in comparison with bulk catalysts is favourable for contact between catalyst and substrates, which effectively improve the yield of products.

The nanoparticles of bentonite clays used in this work have the advantage of being recoverable and recyclable. Currently, most of the biodiesel production processes are based on the transesterification of vegetable oils using heterogeneous nano-catalysts, which are known for their high activity and low cost, making them suitable for large-scale industrial operation. In fact, this class of catalysts offers economical, ecological and technical advantages, which are critical parameters for improvement of the efficiency and sustainability of biodiesel manufacture. As a whole using milder operating conditions could lead to a reduction in energy consumption requirements of the process which could be feasible with using nano-catalysts. Nanoparticles have a large surface-to-volume ratio compared to bulk materials. They are attractive candidates for use as catalysts. The bentonite clays are locally available in Nigeria. The non-edible cotton seed oil has been found to be a potential raw material for the production of biodiesel.

The methyl ester of cotton seed oil has properties that meet the international standard (ASTM D6751 and EN14214) for biodiesel. From the findings of the present study, it seems rational to recommend the implementation of biofuels programme in Nigeria. The biodiesel production is yet to commence on a commercial scale in the country. Although there seems to be strong potential for the production of biodiesel, the implementation of programmes for collection of seeds and investments for the economic production of fuel grade biodiesel would need government support. Nigeria has large degradable land where non-edible oil seeds could be grown for conversion into biodiesel. This can help in creation of millions of jobs particularly in the rural area, besides providing energy security through the production of home grown cotton seed genotypes for use in production of cotton seed oil biodiesel. There is a need for Cotton Ginners Association of Nigeria (CGAN) to promote investment in the production of home grown cotton in Northern Nigeria and beyond.

REFERENCES

Abdullahi, S. L. and **Audu, A. A.** (2017). Comparative Analysis on Chemical Composition of Bentonite Clays Obtained from Ashaka and Tango Deposits in Gombe State, Nigeria. *ChemSearch Journal* 8(2): 35 – 40.

Alterntive Fuels Data Centre (2018). Energy efficiency and Renewable Energy: Biodiesel blends-Review. U. S, Department of Energy. Available online at (https://www.afdc.energy.gov/fuels/biodiesel_blends.html). Accessed on 18/04/2018.

Antolin G., Tinaut F. V., Briceno Y., Castano V., Perez C. and **Ramirez A. I.** (2002). Optimization of biodiesel production by sunflower oil transesterification. *Bioresource Technology,* 83, 111-114.

Baydar H. and **Turgut I.** (1999). Variations of fatty acid composition according to some morphological and physiological properties and ecological regions in oilseed plants [Yaçli tohumlu bitkilerde yaç asitleri kompozisyonunun bazi morfolojik ve fizyolojik özelliklere ve ekolojik bölgelere göre deçi°imi]. *Turkish Journal of Agriculture and Forestry* 23:81-86

Brunet Solé, Robert (2012). Optimal design of sustainable chemical processes via a combined simulation-optimization approach. Doctoral Thesis submitted to Department of Chemical Engineering, UNIVERSITAT ROVIRA I VIRGILI, Tarragona. Available at: *http://hdl.handle.net/20.500.11797/TDX1182*.

Canakci M. and **Van Gerpen J.,** Biodiesel production from oils and fats with high free fatty acids, *Transac. ASAE,* 2001; 44:1429-1436.

Chang, D. Y. (1997). Determination of particulate and unburned hydrocarbon emissions from diesel engines fueled with biodiesel. A dissertation submitted to the Graduate Faculty, Iowa State University Ames, Iowa in partial fulfillment of the requirement for the degree of Doctor of Philosophy. SAE Paper No. 982527.

Chattopadhyay, S. and **Sen, R.** (2013). Fuel properties, Engine performance and environmental benefits of biodiesel produced by a green process. *Applied Energy. 105. 319–326. 10.1016/j.apenergy.2013.01.003.*

Clifford C. B. (Nd). EGEE 439: Alternative Fuels from Biomass Sources. *https://www.e-education.psu.edu/egee439/node/684.*

Dani C., Smith A. G., Dessolin S., Leroy P., Staccini L., Villageois P., Darimont C. and **Ailhaud G**. (1997). Differentiation of embryonic stem cells into adipocytes in vitro. *Journal of Cell Science,* 110: 1279-1285

Diman, S. F. and **Wijeyesekera, D. C.** (2008) 'Swelling Characteristics of Bentonite Clay Mats' Proceedings of the AC & T, pp 179 -185.

Fan, X. (2008), Optimization of biodiesel production from crude cottonseed Oil and waste vegetable oil: conventional and ultrasonic Irradiation methods. A Thesis Presented to the Graduate School of Clemson University. https://tigerprints.clemson.edu/all_dissertations/310

Fukuda H., Kondo A. and **Noda H.** (2001). Biodiesel fuel production by transesterification of oils. *J Biosci Bioeng*; 92:405–16

Gerpen, J. V. (2013, February 16). Biodiesel Production Principles and Processes. Farm Energy. https://articles.extension.org/pages/27137/biodiesel-production-principles-and-processes

Hanna M.A., Isom I. and **Campbell J.,** Biodiesel: Current perspectives and future. *J. Scientific Ind. Res.,* 2005; 64: 854-857.

Jain S. K., Kumar S. and **Chaube A.** (2011). Technical Sustainable of biodiesel and its blends with Diesel in C. I. Engines: A Review. *International Journal of Chemical Engineering and Applications,* Vol. 2, No. 2. Available online at: *http://ijcea.org/papers/84-A565.pdf*

Ketlogetswe, C. and **Gandure, J.** (2011). Blending cooking oil biodiesel with petroleum diesel. *A comparative performance test on a variable IC Engine, T23:59,000Z.*

Khan M. A., Baseer M. and **Shakoor A.** (2016). Bio-diesel as an Alternative Fuel (Description, Benefits and Production Process). Proceedings of the 2016 International Conference on Industrial Engineering and Operations Management Detroit, Michigan, USA, September 23-25.

Khan, F. A. (2012). Biotechnology Fundamentals. Boca Raton: CRC Press

Kulkarni M. G. and **Dalai A. K**. (2006). Waste cooking oil — an economical source for biodiesel: a review. *Ind Eng Chem Res*; 45:2901–13.

Kumar Pradeep (2012). Vehicle emissions from biodiesel and its blends - a review. *International Journal of Research in Biochemical Process Engineering - IJRBPE* Volume 1, No. 1

Last R. J., Krüger M. and **Dürnholz M.** (Nd). Emissions and Performance Characteristics of a 4-Stroke, Direct Injected Diesel Engine Fueled with Blend of Biodiesel and Low Sulfur Diesel Fuel. SAE paper no. 950054.

Ma, F. and **Hanna, M. A.** (1999). Biodiesel production: A review *Biores. Tech.,*; 70: 1-15.

Nair J. N, Deepthi J. and **Siva kalyani, K.** (2013). Study of Biodiesel Blends and Emission Characteristics of Biodiesel. *International Journal of Innovative Research in Science, Engineering and Technology*, 2 (8), 3710-3715.

Nayaka, P. (2011). A review on cottonseed oil as biodiesel (*http://www.slideshare.net/nayaka-ds/a-review-of-cotton-seed-as-biodiesel*).

O'Brien D. R., Jones L. A., King C. C., Wakelyn P. J. and **Wan P. J.** (2005) Bailey's Industrial Oil and Fat products, Sixth Edition, Six Volume Set. Edited by Fereidoon Shahidi. Copyright # John Wiley $ Sons, Inc.

O'Brien, R. D (2002) "Cottonseed oil" in: Vegetable Oils in Food Technology Composition, Properties and Uses Edited by FRANK D. GUNSTONE.

Pande H. (1998). Non-wood fibre and Global fibre supply. Unasylva, 49(193), 40-50

Ramaswamy S., ý Huang H. and **ý Ramarao B. V.** (Eds) (2013) Separation and Purification Technologies in Biorefineries. ýScience. *https://books.google.com.ng/books?id=Bz6EaVlsEfkC&pg=PT490&lpg=PT490&dq*

Roche J., Essahat A., Bouniols A., Asri M. El, Mouloungui Z., Mondiès M. and **Alghoum M.** (2004). Diversified Composition of Sunflower (Helianthus annuus L.) Seeds within Cultural Practices and Genotypes (Hybrids and Populations). HELIA, 27, Nr. 40, 73-98.

Sarada S. N., Shailaja M., Sita Rama Raju A. V. and **Radha K. K.** (2010). Optimization of injection pressure for a compression ignition engine with cottonseed oil as an alternative fuel *International Journal of Engineering, Science and Technology*, 2 (6), 142-149.

Shahid E. M. and **Jamal Y. (**2011). Performance Evaluation of a Diesel Engine Using Biodiesel. *Pak, J. Engg. & Appl. Sci.* Vol. 9 (p. 68-75).

Teffer, Peter (2018). EU to phase out most harmful biofuels. *https://euobserver.com/environment/142101*

www.biodiesel.org/docs/ffs-basics/emissions-fact-sheet.pdf. Biodiesel Emissions.

Xiao M., Mathew S. and **Obbard J. P.** (2009). Biodiesel fuel production via transesterification of oils using lipase biocatalyst. *Global Change Biology Bioenergy*, 1 (2), 115–125, *doi: 10.1111/j.1757-1707.2009.01009.x*