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African Pear Seed Oil Methanolysis Catalyzed by Thermally Activated Clay

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Abstract
The heterogeneously catalysed transesterification reaction for the production of biodiesel from African pear seed oil (APO) was investigated. The oil was extracted from the seeds using n-hexane by solvent extraction and characterized to determine its physio-chemical properties. Heterogeneous catalyst synthesized by thermally activating clay in a muffle furnace at a temperature of 800°C for 1hr was used to examine the effect of time, temperature, methanol/oil molar ratio, catalyst concentration and agitation speed on the biodiesel yield. The activated catalyst was characterized to determine its elemental compositions and physio-chemical properties. The results obtained showed that the thermally activated clay catalyst, TACperformed as montmorillonite clay with characteristic property of Bronsted and Lewis acid. The TAC was able to convert APO to standard biodieselwith the variation of catalyst concentration, temperature methanol, speed and reaction time having significant effect in the production. About 78-80% biodiesel production was obtained with 10:1 methanol/oil molar ratio, 3wt% TAC catalyst concentration, time 3hrs, speed 300rpm and at 60°C temperature. Hence the production of biodiesel from non edible oil APO with cheap and available heterogeneous catalyst (TAC) is achievable.

Keywords: Clay, African pear seed oil, thermally activated clay, Heterogeneous catalyst.

1.0 Introduction

Depletion of world petroleum reserves and increasing environmental concerns has stimulated the search for renewable fuels such as biodiesel in recent years. Biodiesel is the most promising alternative diesel fuel which has attracted attention worldwide (Fan et al. 2011). This is primarily due to its outstanding benefits over the conventional petro diesel. It is renewable, biodegradable, non-toxic, with high flash point and good reduction in greenhouse emissions (Demirbes 2009; Kaya et al. 2009; Ghesti et al. 2009; Aderemi & Hameed 2010). Vegetable oils can be used in diesel engines as an alternative fuel owing to its comparable and competent physicalproperties as that of diesel. On the other hand when raw vegetable oil is directly used indiesel engine, the high viscosity and volatility nature of vegetable oil caused problems suchas chocking of injector, deposits on engine cylinder and sticking of piston (Dwivedi & Sharma 2011).These effects are reduced when vegetable oils are transesterified to biodiesel. The cost of raw material typically accounts for about 70–80 % of the total cost of biodiesel production. Therefore, there is a need to develop technologies for producing biodiesel from non-edibleresources using natural catalysts (Gole & Gogate 2012a; Maddikeri et al.2012; Gaikwad & Gogate 2015).

Biodiesel produced from non-edible feedstock can positively supplement the rapidlyincreasing energy requirements of the world; especially the countries which have limited fossil fuel resources. There are various sources of non-edible renewable vegetable oil options available to augment the supply of fuel source to the huge requirements of diesel. Biodiesel is produced from non-edible seeds such as castor (Paula et al. 2011), tamanu (Anthony et al. 2014), rubber seed (Melvin Jose et al. 2011), jatropha curcas (Sunil et al. 2012), neem (Anyanwu et al. 2013), pongamia pinnata (Veeraprasad & Srinivas 2012), mahua (Manjunath et al. 2015), cottonseed (Georgogianni et al. 2008) etc. Biodiesel produced from non-edible renewable resources can be a possible solution to the crisis of environmental pollution and fossil fuel depletion (Jinlin et al. 2011; Mythili et al. 2014; Sahro et al. 2008). Most cheap and natural catalysts used for transesterification of non-edible oil are heterogeneous catalysts because they are not sensitive to

small amounts of FFA and moisture (Veljkovic et al. 2009; Boey et al. 2011). Comparing homogenous catalysts with heterogeneous catalysts, the later have the advantages of easy and cheap separation and regeneration (Birla et al. 2012; Gaikwad & Gogate 2015). Attention is shifting to use of cheap and available catalysts such as clay for transesterification of vegetable oils.

Clay is a type of soil which is naturally available in most of the states in Nigeria. Clays are essentially alumina silicates which have resulted from weathering of rocks and aluminum silicates (Igbokwe & Ogbuagu 2003). Clays have adsorptive and catalytic capacities. They can be used as catalysts for transesterification reaction. Some researchers worldwide have investigated clay catalysts for esterification but very few for biodiesel production (Manuit & Statit 2007). Prakash et al. (2005) reported transesterifcation of dicarboxylic acid with various alcohols by Mn^{+}-montmorillonite clay catalysts. AlsoVijayakumar et al. (2005)had used Indian bentonite as esterification catalyst for ester synthesis. Dubios et al. (2006) had prepared biodegradable polyester by transesterification catalysts to improve clay exfoliation. Liu et al. (2004) produced ethyl/methyl β -ketoester bymontmorillonite K-10 as an efficient reusable catalyst. Manut and Satit (2007) studied biodiesel synthesis from transesterification by clay-based catalyst. They discovered that biodiesels from clay–based catalysts have some encouraging properties to supersede low speed diesel fuel and to lower the cost of production in some extent.Calgaroto et al. (2013)studied production of biodiesel from soybean and Jatropha Curcas oils with KSF and amberlyst 15 catalysts in the presence of co-solvents.

Therefore, the present study focused on exploring the potential of non-edible seed oil like African pear (Dacryodes edulis) feedstock for the production of biodiesel through thermally activated kaolinite clay catalysed trans esterification reaction.

2 Material and Methods

2.1 Materials

African pear was bought from Odegba in New Market, Enugu, Enugu State, Nigeria. The seeds were dried in sunlight, deshelled and the kernel crushed using a grinder prior to oil extraction. N-hexane was used for oil extraction while methanol was used for transesterification and both are of analytical grade. All other solvents and chemicals used were ofanalytical grade, and they were procured from commercial sources and used as such without further treatment.

2.2 Oil extraction

The method employed by Sanjay et al.(2012) was used in extraction of oil from the seed. The extraction of oil from the seed was carried out by solvent extraction. 100g of crushed kernel of a particle size of 900 µm was mixed with n-hexane in a solvent/solute ratio of 1.5ml/g. The mixture was then magnetically stirred at a constant speed of 200rpm at temperature range of 50ºC for time 45minutes.The yield of the crude oil extracted was calculated using Equation (1).

$$Y = \frac{W_o}{W} * 100 \qquad (1)$$

Where, Y is the oil yield (%),
W_o is the weight of pure oil extracted (g) and
W is the weight of the sample of seed used in the experiment
The oil was characterized using ASTM methods to determine the physiochemical properties.

2.3 Synthesis of catalyst

The catalyst employed in this study is clay catalyst. The clay was immersed in hydrogen peroxide solution (30%) in the ratio of 1:2 wt/wt at 30°C for 24h to remove organic impurities. The mixture was gently heated in a boiling water bath to remove excess H_2O_2 and subsequently separated from the clay. The purified clay was then suspended in distilled water in the ratio of 1:4 wt/wt and allowed to settle. The water was removed and the purified clay was dried in an oven at a temperature of 110°C until its moisture content reached 10%. The clay was then crushed and sieved with 80/100mesh. The dried clay catalyst was modified by subjecting it to heat treatment in a muffle furnace at a temperature of 800°C for 1hr to improve its catalytic activity.

2.4 Characterization of the clay sample

The raw and thermally activated clay samples were characterized by X-ray fluorescence (ARL 9400XP + Wavelength-dispersed XRF spectrometer) to determine metallic compositions, Fourier Transform Infra-red Spectrometer (BUCK model 500 M) to determine the functional group; Scanning Electron Microscope (Carl Zeiss Sigma Field Emission) to determine the morphology of the clay samples and X-ray Diffractometer (model XRD-7000 with Cu Ka X-ray) to determine the group of the clay. The Brunauer-Emmett-Teller (BET) method was used to calculate the surface area, average pore diameter and total pore volume of the clay. Surface area, pore volume and average pore diameter were determined from N_2 adsorption isotherms using a micrometrics ASAP 2020 surface analyzer.

2.5 Transesterification process

Transesterification reactions were carried out in a batch reactor. The APO was precisely and quantitatively transferred into a three-necked roundbottom flask fitted with a reflux condenser and mechanical stirrer in a water bath. Then a specific amount of thermally activated clay, TAC catalyst (3% of the weight of APO) dissolved in the required amount of methanol was added. The solution was then mixed with APO/methanol in 1:6 molar ratios. The mixture was stirred vigorously with an agitation speed of 250 rpm at a temperature of 55°C for 3 hours. Aftercompletion of the transesterification, the catalyst was recovered by filtration through Whatman filter paper (size 42). The resultant mixture was allowed to separate; the upper layer was subjected to rotary evaporation to recover excess methanol and the product obtained was dried over sodium sulphate.

3 Results and Discussion

3.1 Extraction of oil

The percentage oil yield of the African pear oil, APO obtained was 53.1% and it falls within the range reported by Umoti and Okyi (1987). Umoti and Okyi (1987) gave the range of oil yield of African pear oil extracted by solvent extraction as 40 – 65% and 25 – 49 % as the range of yield obtained by press extraction was given as 25 – 49 %. Isaac and Ekpa(2009) obtained that the oil content of African pear (*D. edulis*) varies from species to species. The high oil content of *Dacryodes* will reduce dependency on edible oils as feedstock for biodiesel production, therefore promotes food security and food availability.

3.2 Characterization of the extracted oil

Table 1 shows the physiochemical properties of the rawoil of *Dacryodes edulis*(African pear seed) seed. The oil has moderate acid number and free fatty acid values of 5.49mgKOH/g (African pear seed oil, APO)and 2.75% (APO) respectively. These values suggested the pre-treatment step on the raw-oil before the transesterification step using homogeneous catalyst but the process could be circumvented using heterogeneous catalysts. The physicochemical properties of the raw oil compare favourably with those of some other non–edible oils such as Pongamia pinnata (Agarwal & Garima 2011), Jatropha Curcas (Adebayo et al. 2011), Madhuca Indica (Azam et al. 2005) that has been used for feedstock for biodiesel production.

The density and high viscosity of the oil will make their atomization difficult in internal combustion engine hence they cannot be used directly as bio-fuel. The low pour point shows that the oil will hardly solidify at room temperature hence can be stored for a long time. The oxidation stability of the oil was high and is good for production of biodiesel. The high oxidation stability of the oils could be as a result of method used in extracting the oils. Solvent refining results in the production of base oils, which retain some sulphur compounds that are natural antioxidants. These base oils retain a natural ability to prevent oxidation, while hydro treated base oils must be further fortified with antioxidants in order to maintain thermal and oxidation stability. The iodine value of APO is less than 100gI_2/100g showing that it is non-drying oil. The saponification value is a bit high confirming its high free fatty acid which will result in readily formation of soap with homogeneous catalyst. The high flash point of the oil indicates that the oil is not flammable while the low values of cloud point and pour point show that the oil can be stored for a long time without oxidizing.

3.2 Characterization of the catalyst

3.2.1 Physiochemical properties of the synthesized catalyst

The physical properties of the raw clay catalyst and thermally modified clay catalyst are presented in Table 2. From the table, it could be observed that the properties of the clay catalyst improved after thermal activation. The surface area of the raw clay increased after thermal activation and this may be attributed to breaking of bonds which resulted in shrinkage of the pores and consequently decreased the pore size.

Table 1: Physicochemical properties of APO

S/N	Physicochemical properties	African pear seed oil
1	Specific gravity	0.930
2	Acid value (mgKOHg)	5.49
3	Free fatty acid (FFA) (%)	2.75
4	Spanofication value (mgKOH/g)	130
5	Iodine value (gI_2/100g)	24.23
6	Kinematic viscosity at 40^oC (mm^2/s)	7.8
7	Peroxide value	4.6
8	Flash point	230
9	Cloud point	-3
10	Pour point	13
11	Moisture content (%)	7
12	Refractive index	1.46
13	Oxidation stability 11^oC (Hour)	5
14	Molecular weight	868.8

Table 2: Physiochemical properties synthesized clay catalyst

Parameters	Raw clay	Thermally activated clay (TAC)
Surface area (m^2/g)	286.3	487.6
Pore size (nm)	4.523	2.647
Total pore volume (cm^3/g)	13.67	25.3
Bulk density(g/cm^3)	2.4	1.92

3.2.2 X-ray fluorescence analysis of the clay catalysts

The chemical composition of the raw clay and thermally activated clay used in this study is summarized in Table 3. The main compositions of the clay are Si, Al, Ti and Fe. The clay has high amounts of SiO_2, Al_2O_3 and Fe_2O_3. The modification of the raw clay by heat slightly increased the quantity of SiO_2, Al_2O_3 and reduced the quantity of Fe_2O_3 classifying the modified clay as Brønsted and Lewis acids. The activation consequently, enhanced the amount and strength of Brønsted and Lewis acid sites (Sani et al. 2014).

3.2.3 Fourier Transform Infra red (FTIR) analysis of the catalysts

Fourier transform infra-red (FTIR) spectroscope of the raw clay catalyst and the acid modified clay catalysts was done to ascertain the functional groups present in them and depicted in Table 4. Comparing the raw clay to the thermal activated clay it could be observed that there were no significant changes in intensity of the bands 998.9 and 685 cm^{-1}, suggesting that the structural changes attributed to the modifications are small. According to Zatta et al. (2013), the FTIR bands at 998.9, 909.5, and 685 cm^{-1} are attributed to Al–OH–Al, Al–OH–Mg and Al–OH–O–Si vibrations respectively. Moreover, the raw clay and thermally activated clay have good peak in a region of 3652.8 – 3693.8cm^{-1}containing Alumina and silicate that can be assigned to Bronsted acidity and 450-685 cm^{-1}containing silicate which can be assigned to Lewis acidity. The appearance of peak 1640cm^{-1}in activated clay containing alumina indicates the increase in the strength of the Bronsted active site. These peaks assignments were done based on the previous works by Jacques (2015) and Onukwuli and Ude (2018). These results suggest that the clay catalyst used performed as both Bronsted and Lewis acids.

Table 3 X-ray fluorescence (XRF) of clay catalysts

	Concentration (wt%)	
Elements	Raw clay	Thermal activated clay
Na_2O	0.000	0.000
MgO	0.321	0.386
Al_2O_3	23.123	23.565
SiO_2	57.115	57.403
P_2O_5	0.310	0.311
SO_3	0.246	0.269
Cl	0.018	0.019
K_2O	0.080	0.089
CaO	0.756	0.773
TiO_2	4.217	4.098
Cr_2O_3	0.028	0.030
Mn_2O_3	0.055	0.052
Fe_2O_3	13.682	12.963
ZnO	0.023	0.021
SrO	0.025	0.023

Table 4: FTIR analysis of the catalyst

	Group Frequency (cm^{-1}) of catalyst		Functional group/Asigment
S/N	Raw clay	Thermally activated clay (TAC)	
1	450 -685	451-685	Si-O-Si deformation
2	752.9	749.2	Aliphatic chloro compounds, C-Cl
3	797.7	797.7	Aliphatic chloro compounds, C-Cl
4	909.5	909.5	Aromatic C-H out-of-plane bend, Al-OH-Al
5	998.9	998.9	Vinyl C-H out-of-plane bend, Al-OH-Mg
6	1118.2	1118.2	Organic siloxane/silicone (Si-O-C), Si-O
7	-	1640	Conjugated ketone, Al-O-Al
8	2009.0	-	Cyanide ion
9	3652.8	3652.8	Double bond C = C, primary alcohol –OH stretch
10	3693.8	3693.8	Double bond C = C, Al-O-Si-O

3.2.4 Scanning electron microscopes (SEM) of the clay catalysts

The morphologies of the raw clay catalyst and thermally activated clay catalyst were ascertained by SEM as shown in Figures 1 and 2 respectively. Micrographs of the clay catalyst samples synthesized by thermal activation showed increase in number of pores and decrease in pore size on the clay. For the thermal activated clay, the formation of more pores on the clay particles was observed and this supports the fact that it has more surface area with lower pore size.



Fig. 1 SEM image of raw clay catalyst

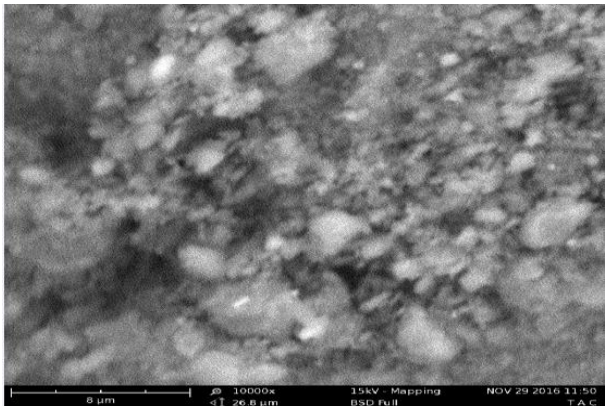

Fig. 2 SEM image of thermal activated clay catalyst

3.2.4 X-ray diffraction pattern of the clay catalysts

Figures 3 and 4 present XRD of the raw clay and thermal activated clay catalyst respectively. It is observed that raw clay contains kaolinite, quartz and muscovite confirming the presence of alumina and silica but after thermal activation it contains quartz and phengite which characterized the montmorillonite group. This suggests that the clay belongs to kaolinite group but behaved as montmorilloniteclay after activation.

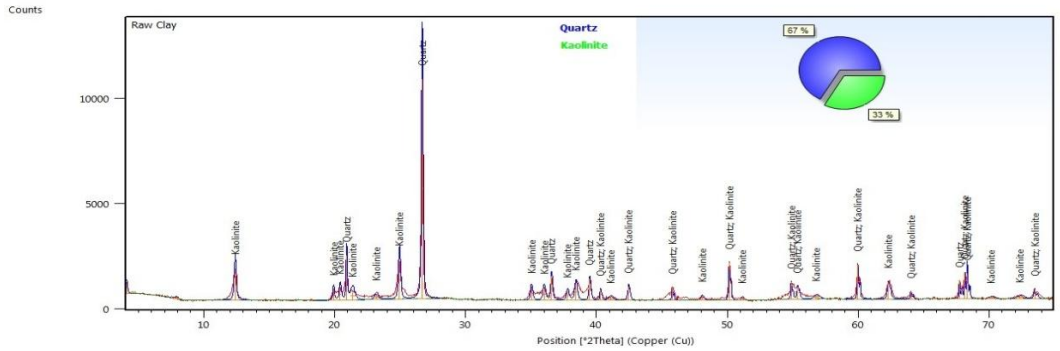

Fig. 3 XRD of raw clay

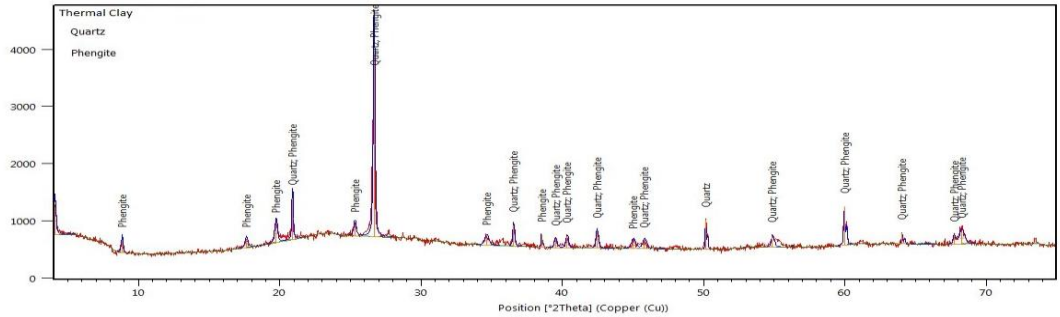

Fig. 4 XRD of acid activated clay catalyst

3.3 Effects of process parameters on biodiesel yield

3.3.1 Effect of time on biodiesel yield

In this work, the effect of reaction time from 1hr to 5hrs on the reaction yield at other reaction conditions of temperature of 55°C, catalyst conc. of 3wt%, methanol/oil molar ratio of 12:1 and speed of 300rpm using thermally activated clay catalyst is presented in Figure 5. It was found that higher yieldoccurred at reaction time of 3hrsand beyond it the yield decreased. The reaction was very slow due to diffusion of methanol and triglyceride into the active site of the catalysts is slow and this led to decrease in the biodiesel yield after 3hrs.This phenomenon may be due to reversible reaction of transesterification resulting in loss of esters.

3.3.2 Effect of catalyst concentration on biodiesel yield

In a chemical reaction, the bonds holding the reactants together must first be broken before the reaction can begin. Breaking bonds requires energy, and the minimum energy needed to start a reaction is referred to as activation energy. Catalysts provide alternative reaction pathways for breaking and remaking of bonds. The activation energy for this new pathway is often less than the activation energy of the normal pathway. Thermally activated clay catalyst was used as heterogeneous catalyst for the transesterification reaction in this study. The effect of catalysts concentrations expressed as weight percentage of the African pear seed oilon the production yield is depicted in Figure 6. The reaction conditions were temperature of 55°C, methanol/oil molar ratio of 12:1, speed of 300rpm and time of 3hrs.From the figure, it could be observed that the yield of methyl ester increased with increase in catalyst weight up to 3 wt% and then began to decrease. Increasing the catalyst weight beyond the catalyst weight of 3 wt% led to the decrease in ester yield. This may be due to excess catalyst causing dispersion and mixing problems, thereby inhibiting the formation of end product (Zhang et al. 2003).

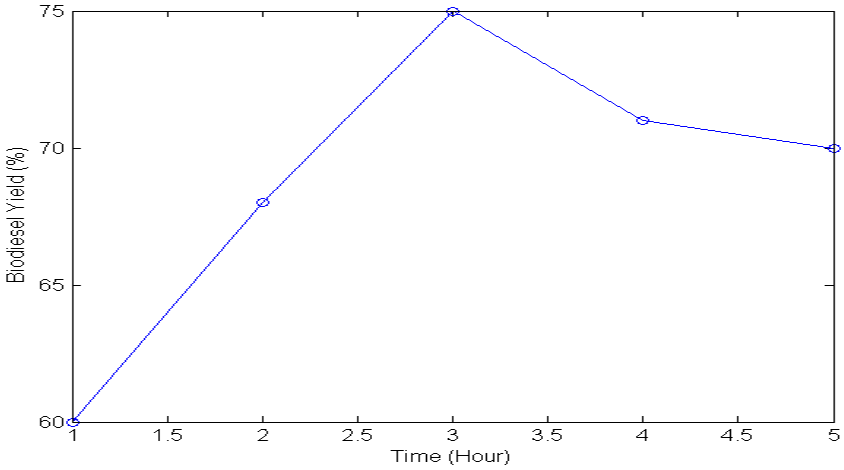

Figure 5: Effect of time on biodiesel.

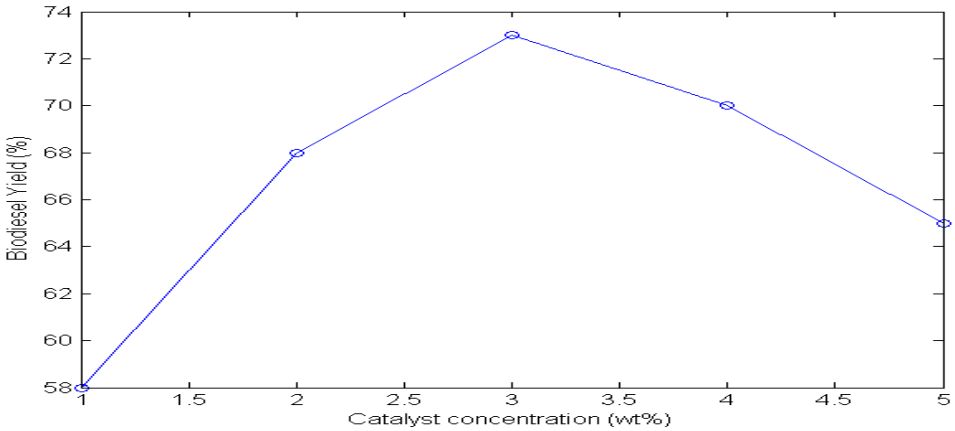

Figure 6: Effect of catalyst concentration.

3.3.3 Effect of methanol/oil molar ratio on biodiesel yield

The effect of methanol/oil molar ratio of 6:1 to 14:1 on the yield of methyl esters was investigated at reaction conditions of temperature of 55°C, speed of 300rpm, time of 3h and catalyst conc. of 3 wt % and shown in Figure 7. The result indicated that methanol oil molar ratio has significant impact on biodiesel yield. The maximum ester yield was obtained at a methanolysis of oil molar ratio of 10:1. The higher molar ratio results in higher rate of ester formation. The yield reduced when the molar ratio was beyond 10:1. This may be due to decrease in the catalyst activity with increase in methanol content and difficulty in glycerol separation. The results obtained are in agreement with the reports of earlier works of Zhang et al. (2003).

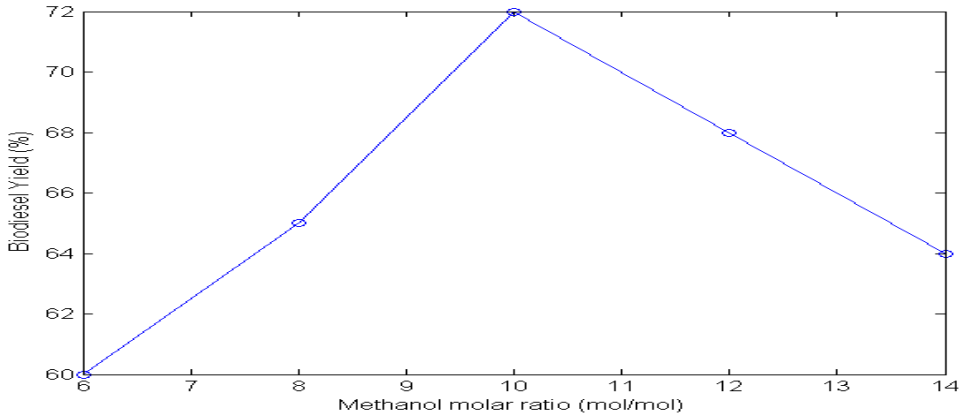

Figure 7: Effect of methanol/oil molar ratio.

3.3.5 Effect of temperature on biodiesel yield

The effect of temperature on the yield of the transesterification reaction of African pear seed oil with thermally activated clay was studied at the reaction temperatures of 45, 50, 55, 60, 65 and 70°C with other reaction conditions of speed of 300rpm, time of 3hrs, catalyst conc. of 3 wt % and methanol/oil molar ratio of 10:1. As shown in Figure 8, the reaction rate was slow at low temperatures, but biodiesel yield first increased and then decreased with the increased of the reaction temperature beyond 60°C. Generally, a more rapid reaction rate could be obtained at high temperatures, but at high temperatures, methanol was vaporised and formed a large number of bubbles, which inhibited the reaction on the two-phase interface. Similar result was reported by Liu et al. (2008).

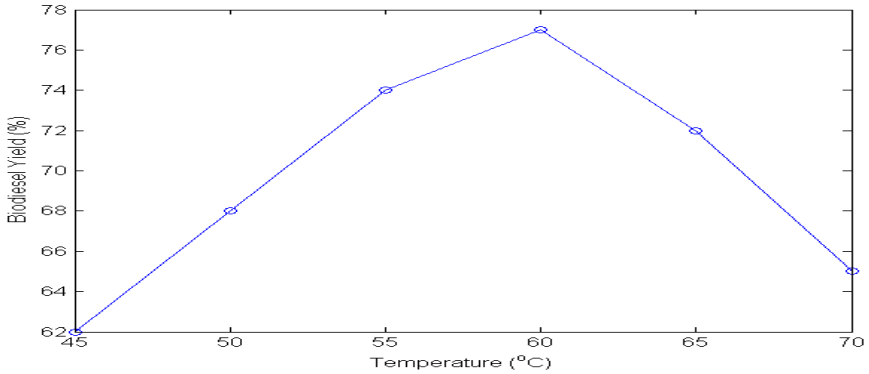

Figure 8: Effect of temperature.

3.3.6 Effect of speed of agitation on biodiesel yield

In this study, methanolysis was conducted with different rate of stirring such as 100, 200, 300, 400 and 500 revolutions per minutes (rpm). The reaction was carried out at conditions of time of 3hrs, catalyst conc. of 3 wt %, methanol/oil molar ratio of 10:1 and temperature = 60°C.The yield of methyl esters produced fromAfrican pear seed oil with thermally activated clay catalyst at different rate of mixing is shown in Figure 9. It was observed from the figure that the reaction of methanolysis was low at 100rpm and only exhibited a yield which was difficult to separate. The yield was maximum at 300rpm. But the increase in the stirring time beyond 300rpm witnessed decrease in the yield. This indicates that the backward reaction may have been favoured when mixing intensity was accelerated.

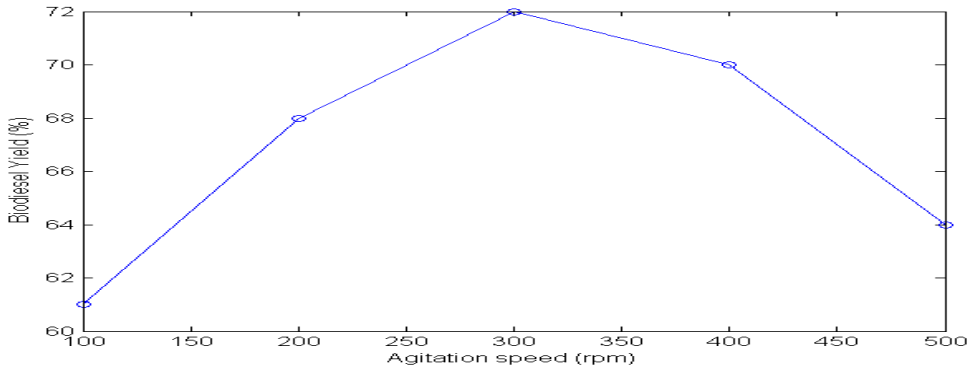

Figure 9: Effect of agitation speed.

3.4 Fuel properties produced with optimal conditions

Table 5 gives a summary of all the fuel properties analyzed and the limits that they were compared with (ASTM standards). It was observed that the properties of biodiesel produced are within the acceptable limits and can be used in an internal combustion engine without modification.

Table 5Biodiesel properties of APO methyl esters compared with ASTM limits

PROPERTY	UNITS	ASTM METHODS	APO FAME by TAC	ASTM LIMITS
Density	kg/m^3	ASTM D-1298	860	830-880
Kinematics Viscosity	Cst	ASTM D-445	3.6	1.6-6.0
Flash Point	^oC	ASTM D-93	177	≥130
Pour Point	^oC	ASTM D-97	2	+15 max
Cloud Point	^oC	ASTM D-2500	1.3	
Acid Value	mgKOH/g	ASTM D-974	0.3	≤ 0.80
Low Heating Value	MJ/kg		40.1	≥ 35
Aniline Point	(^oC)	ASTMD4737	175	
Higher Heating Value	MJ/Kg		51	
Oxidative stability	Hour	ASTM D6751/ EN 14112	5.0	3 min
Cetane number		ASTM D-130	52	47 min

4.0 Conclusion

The purpose of this study was to investigate the potential of producing biodiesel from economical and environment-friendly waste materials in order to make the process affordable and consequently expand the use of biodiesel all around the world. The oil used was extracted from African Pear Seed by solvent extraction using n-hexane. The clay employed in the transesterification was thermally activated at 800°Cand characterized. A reasonable amount of oil was extracted from the seed and it has good characteristics for biodiesel production using heterogeneous catalyst. The clay catalyst was identified to belong to kaolinite group and possessed Bronsted and Lewis acid active sites. The catalyst converted the African Pear Seed oil (APO) in the presence of methanol to biodiesel which canbe compared withstandard quality of biodiesel. The biodiesel produced has qualities within the acceptable limits for biodiesel.

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