

Synthesis and Evaluation of Biodiesel Using Calcined and Acid Modified Kono-Boue (Kb) Clays as Catalyst

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Abstract

The calcined and acid modified Kono-Boue (KB) clays have been used in the transesterification of palm oil to biodiesel for the first time. This was carried out by using raw, acid treated and calcined Kono-Boue clays as heterogeneous catalysts and sodium hydroxide (NaOH) as the control catalyst. The acid treated clay catalyst was prepared by adding 1% (1g) of concentrated hydrochloric acid (HCl) to 100g of the raw clay while the calcined clay was obtained by subjecting 30g of raw clay to 1 hour heating in a muffle furnace at 550^oC. Characterisations of the biodiesel product (i.e., specific gravity, kinematic viscosity, flash point, cloud point and acid value) were investigated using standard methods. The specific gravity, kinematic viscosity and cloud point of the biodiesel produced were all within those of ASTM biodiesel standard D6751:2012 while the flash points were slightly lower than that of ASTM biodiesel standard D6751:2012 but within the petroleum diesel EN 590:2004. The acid values of all the products (NaOH 0.2mgKOH/g; raw clay 0.3mgKOH/g; calcined clay 0.34mgKOH/g) were below 0.50mgKOH/g maximum except that of the acid treated clay catalyst whose acid value was 1.06mgKOH/g. The highest percentage yield obtained was 96.59% (calcined clay) while the least was 46.85% (raw clay). In addition, Gas chromatography-flame ionization detector (GC-FID) techniques were used to determine the composition of the methyl esters present in palm oil and biodiesel produced. The results of the GC-FID confirmed that the products were largely made up of fatty acid methyl esters (FAMES). These parameters were subjected to Analysis of variance (ANOVA) and the Duncan's multiple test and the results showed no strong significant differences ($P > 0.05$).

Key words: Kono-Boue clay; palm oil; transesterification; base catalyst; and Biodiesel

1.0 Introduction

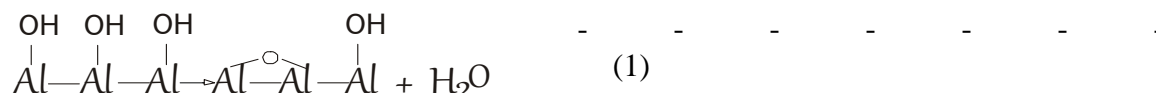
The environmental hazards that accompany fossil fuel utilization such as carbon (IV) oxide (CO₂) emissions and associated climate change due to combustion of such carbon sources, is a major concern to the society. Thus, recent research interests are channeled towards the study of biodiesel production as an alternative energy source (Saifuddin *et al.*, 2014; Irmawati *et al.*, 2014) to mitigate current CO₂ emissions and hence climate change. However, for biodiesel to be used as a viable and promising alternative source of fuel it needs to be constantly evaluated in terms of production cost efficiency, before it could fully substitute petroleum-derived diesel. Catalysts play significant roles in petroleum refining including

biodiesel product. However, most of the catalysts in use are quite expensive. Clay catalysts are cheap catalysts that are promising.

Clay deposits are found in several regions of the world. In Rivers State, one of the sites where clay resources are found is in Kono-Boue. The Kono-Boue (KB) clay is currently applied locally for pottery and building bricks by the inhabitants of Kono-Boue town.

Clays have different layered structures which are inter-related. These differences are due to the manner in which the silica tetrahedral and aluminium octahedral align in the structure. Naturally occurring clay such as kaolinite, hectorite and montmorillonite, have layer structures of octahedral and tetrahedral units. Aluminum occupies the octahedral site while silicon, the tetrahedral site (Atkin *et al.*, 2010). The numbers of other ions present are also responsible for the differences in the structure. The net negative charges possessed by the layers are neutralized by alkaline and alkaline earth metal ions such as Na^+ , K^+ , Ca^{2+} , etc., which occupy the inter lamellar space. Replacements of these interlamellar cations bring about modification of clays. Because these molecules can be bound to layer atoms the properties of clays, like acidity, pore size, polarity, surface area, and other characteristics that govern their performance as catalyst can be altered (Nagendrappa, 2010).

Clays function as Bronsted and/or Lewis acids, or as bases. Lewis acids and bases can be formed on exposed γ -alumina surface covered with molecules. When heated to about 100 to 150°C the water molecule desorbs leaving some hydroxyl (OH) group on the surface and this could act as Bronsted acids:



Increase in temperature condenses adjacent OH groups to liberate H_2O and this generates exposed Al^{3+} Lewis acid sites as well as O^{2-} Lewis base sites.

Biodiesel is one of the pioneering forms of alternative energy. It is a renewable, non-toxic, highly biodegradable and environmentally friendly bioenergy (Narasimharao *et al.*, 2007) which can be utilized in engines without any modification (Tazerout *et al.*, 2009; Saifuddin *et al.*, 2014). It was discovered by Rudolf Diesel in 1900 when he first proposed vegetable oil as an engine fuel (Shay, 1993; Lee *et al.*, 2009). Since vegetable oils or animal fats have high viscosity, i.e., $35\text{--}50\text{mm}^2\text{S}^{-1}$ (Thanh *et al.*, 2012), the viscosity should be lowered in order to use them in a common diesel engine. Thus, only the method of transesterification reaction reduces the viscosity of vegetable oils, and the products are collectively termed ‘biodiesel’ because they can be used either neat or blended with the petro diesel (Lee, *et al.*, 2009).

In the transesterification mechanism, triglycerides are reacted with alcohol such as methanol, which is a low molecular weight alcohol or other alcohols like ethanol and propanol to produce fatty acid methyl esters (FAMES) and glycerol (Guo and Fang, 2011; Irmawati *et al.*, 2014). Transesterification reaction takes place in the presence of homogeneous catalyst such as sodium hydroxide, NaOH or potassium hydroxide KOH, to produce biodiesel. The overall reaction between a triglyceride and an alcohol to methyl esters involves three consecutive and reversible steps with a diglyceride and a monoglyceride as intermediates in the process. When an acid or a base is used, a triglyceride molecule reacts with an alcohol molecule to produce a diglyceride, and a single FAME is liberated. Then, a diglyceride reacts with more alcohol to produce a monoglyceride and FAME and finally, a monoglyceride reacts further with alcohol to produce FAME, liberating the glycerol as by-product. However, the monoglyceride and diglyceride formed remained in the final biodiesel product (Irmawati

et al., 2014).

A lot of research has been carried out on the transesterification of palm oil to biodiesel using various solid heterogeneous catalysts. For instance, Kusuma *et al.*, 2013 studied the transesterification of palm oil to methyl esters (biodiesel) using KOH/zeolite as solid heterogeneous catalysts. Various process variables such as KOH concentration and reaction time were also studied in order to obtain maximum yield of biodiesel. The physical and chemical properties of their palm oil were determined using standard test methods and the results obtained were as follows: the density at 25⁰C was 0.9016g/cm³, kinematic viscosity at 23.4⁰C was 70.9 cSt, free fatty acid and flash point were 0.02 and 220⁰C respectively. The chemical composition of palm oil used was analysed using gas chromatography and the following fatty acid compositions of palm oil were obtained: lauric acid, myristic acid, palmitic acid, palmitoleic acid, oleic acid, linoleic acid, linolenic acid and arachidonic acid. Kumar *et al.*, 2012 reported the transesterification of palm oil to FAME using KOH loaded on Al₂O₃ and NaY zeolite supports as heterogeneous catalysts. They also reported transesterification of palm oil using CaO/Al₂O₃ composite catalyst. They found that both the calcination temperature and the amount of calcium oxide loaded on the support had significant positive effects on the biodiesel yield, showing maximum basicity and biodiesel yield of about 194 mmol/g and 94%, respectively. Transesterification of palm oil with methanol to form fatty acid methyl esters (FAME) had also been carried out, using silica loaded with potassium carbonate, K₂CO₃/SiO₂ as a solid base catalyst (Irmawati *et al.*, 2014). In their work, the FAME produced was characterized with gas chromatography (GC) where peaks corresponded to fatty acid methyl esters of palm oil. In a related work, Saifuddin *et al.*, 2014, investigated biodiesel production via alkaline transesterification using waste palm cooking oil and compared its chemical characteristics to conventional biodiesel. In their report, the highest yield of biodiesel was produced at a temperature of 55⁰C with a methanol to oil ratio of 6:1 and 1.0% KOH concentration. In another study, Dhanasekaran and Dharmendirakumar (2014) used frying palm oil to produce biodiesel by transesterification process. They also used the GC techniques to identify the fatty acid profile of the used frying oil and biodiesel. Their results show that the major fatty acid was linoleic acid with a mass percentage of 52.50%, followed by oleic acid with a mass percentage of 28.04%.

Other solid catalysts that have been studied and used for transesterification of vegetable oils include Suratthane black clay (SB) and Ranong Kaoline (RK) impregnated as catalysts (Jaimasith and Phiyalaninmat, 2007), calcium-zinc mixed oxide (Ngamcharussrivichai *et al.*, 2008), alkali and alkali earth metal supported on Al₂O₃ (Benjapornkulaphong *et al.*, 2009), K₂CO₃ supported on alumina silica (Lukic *et al.*, 2009), KOH supported on bentonite (Soetaredjo *et al.*, 2011), NaOH/Al₂O₃ catalysts (Taufiq-Yab *et al.*, 2011), Ca-based solid catalysts (Viriya-empikul *et al.*, 2012), and silica loaded potassium carbonate (K₂CO₃/SiO₂) catalysts (Irmawati *et al.*, 2014).

Although, other researchers have investigated clay obtained from other parts of the country as catalysts for biodiesel production, there is no report on the application of Kono-Boue clay in biodiesel production. For this reason, KB clay which is naturally occurring in Rivers State has been chosen to be studied. Therefore, this research seeks to examine the application of Kono-Boue clay in biodiesel synthesis from palm oil for the first time. The success of this study will provide a new source of cheap and easily available heterogeneous catalyst in our local industries and the world at large.

2.0 Materials and Methods

2.1 Materials

Kono- Boue clay was taken from Kono-Boue town situated on Latitude 4° 42' North of the equator and Longitude 7° 22' East of Greenwich meridian (Gbarakoro *et al.*, 2016) while four litres of palm oil was bought from Bori main market, all in the Khana Local Government Area of Rivers State, Nigeria. The chemicals and equipment used in the production of biodiesel was methanol, sodium hydroxide, and hydrochloric acid, muffle furnace, weighing balance and magnetic stirrer with heater.

2.2 Methods

2.2.1 Clay collection and preparation

The raw clay sample was dug and collected manually from a clay site at Kono-Boue town, Rivers State, Nigeria, with a shovel at a depth of about 50cm, and placed in a clean polythene bag. The clay sample was then oven dried at 110°C for 4 hours to ensure complete evaporation of the moisture content. The dried clay was milled and sieved through a British Standard Sieve (BSS) 100mm mesh. The fine grains obtained were used for the preparation. The clay sample was then subjected to two treatments, namely, acidification and calcination (thermal treatment). In the acid treatment, 1% (1g) of concentrated hydrochloric acid solution was thoroughly mixed with 100g of the raw clay. The calcined clay was obtained by subjecting 30g of raw clay to heating for 1 hour in a muffle furnace at 550°C.

2.2.2 Production of biodiesel

The method involved the use of Kono-Boue clay and NaOH as two different catalysts and a monohydric alcohol (methanol) as substrate. The biodiesel was produced using standard materials and under standard conditions. The mole ratio used was 6:1 methanol to palm oil and 0.70% NaOH and clay respectively to the palm oil sample. The NaOH pellet was weighed to get exactly 0.35g. The palm oil was heated to 50°C and a solution of sodium methoxide was added to the palm oil and stirred vigorously for 30 minutes using a magnetic stirrer. The mixture was then left to settle for 24 hours. After separation, the biodiesel was filtered off the glycerine which is the by-product. Thereafter, about 50ml of warm water was then used to wash the biodiesel to remove any excess glycerol and soap that remain in the funnel. This was done until clear water was seen below the product in the separating funnel. The washed sample of the biodiesel was dried to remove any trace of water still in the biodiesel. The quantity of biodiesel collected was measured and recorded in order to obtain yield. The above procedures were repeated using (i) Raw clay (ii) Acid modified clay and (iii) Calcined clay as catalysts.

2.2.3 Analysis of palm oil and biodiesel quality after production

The physical properties of palm oil such as specific gravity, viscosity, free fatty acid (FFA), moisture content and peroxide value and those of biodiesel such as specific gravity, viscosity, flash point, cloud point and acid value were determined using standard test methods.. The biodiesel products from all types of catalysts and the palm oil were analysed using Gas chromatography- Flame Ionisation Detector (GC-FID) technique. Gas chromatography-mass spectrophotometer (GC-MS) Nilst library search was also used for identification of the compounds present. The instrument used the column HP-530m x 0.32 micrometer x 0.25 micrometer Agilent GC-FID model 7820A, detector temperature 300°C, front inlet temperature 280°C, carrier gas flow 0.356ml/minute, pressure 10.95, and a run time of 32 minutes. The main purpose of this GC-FID analysis was to determine the composition of methyl esters present in each of the biodiesels produced as well as the palm oil. Statistical Package for the Social Sciences (SPSS) version 21 was the statistical software

used to analyse the results obtained from characterisation of biodiesel produced. Analysis of variance (ANOVA) was used to analyse the overall significance of the variables under consideration which were clay catalysts and physico-chemical properties. The Duncan's test statistics for multiple range tests was also used to support the ANOVA results.

3.0 Results and Discussion

3.1 Analysis of palm oil

The results of the palm oil analysis are presented in Table 1

Table 1: Characterization of palm oil

S/N	PARAMETER	TEST RESULT	NIS STANDARD (2000)
1	Specific gravity	0.896	0.895 – 0.90
3	Viscosity (cSt) (mm ² /sec)	42.8	40 - 45
3	Free fatty acid (%)	4.591	2 – 5
4	Moisture content (%)	0.125	0.2 – 0.5
5	Peroxide value (meqKOH/g)	1.961	10 maximum

The results obtained from the characterization of the palm oil showed that the specific gravity of the palm oil used for this research was 0.896. Kusuma *et al.*, (2013) also obtained a specific gravity of palm oil (0.9016). The palm oil used for the production of biodiesel had a viscosity of 42.8mm²/sec at 40°C (cSt) (Table 1). This value is in agreement with the viscosity of the palm oil used by Jaimasith and phiyanalinmat (2007), which gave values of 45.1mm²/sec at 37.8°C (cSt) and 7.88mm²/sec at 100 °C (cSt) respectively . The difference was due to the fact that viscosity is temperature dependent. It is high at low temperature and low at high temperature. The free-fatty acid (FFA) of the palm oil was low (4.591%). Esterification of the FFA gave the fatty acid methyl ester (FAME). The moisture content and peroxide value of the palm oil were 0.125% and 1.061meqKOH/g respectively.

3.2 Analysis of results from characterisation of biodiesel produced

The results of the characterisation of biodiesel produced are presented in Table 2

Table 2: Physico-chemical properties of palm oil methyl ester using sodium hydroxide (alkaline) and clay as catalysts

S/N	Properties	Biodiesel with NaOH	Clay catalyst			Petroleum diesel EN 590:2004	ASTM biodiesel standard D6751:2012	European biodiesel standards EN 14214:2012
			Raw clay	Acid Treated clay	Calcined clay			
1	Specific gravity	0.861	0.799	0.847	0.848	0.82-0.845	0.875-0.90	0.860-0.90
2	Kinematic viscosity @ 40°C(cSt) mm ² /s	4.2	3.2	4.1	4.0	2.0-4.5	1.9-6.0	3.5-5.0
3	Flash point (°C)	90	68	80	80	60-80 or 55 min.	93 or 130 min.	101 or 120 min.
4	Cloud point (°C)	11	5	10	10	-15 to 5	-3 to 12	
5	Acid value mgKOH/g	0.2	0.3	1.06	0.34	0.35	0.50 max.	0.50 max.

The characterization of biodiesel properties is listed in Table 2. It showed that Kono-Boue clay catalyst in this experiment produced biodiesel or esterified products. The biodiesel from the clays and the control (NaOH) gave the following properties: The specific gravity of the biodiesel produced was 0.861 (NaOH catalyst), 0.799 (raw clay catalyst), 0.847 (acidified clay catalyst) and 0.848 (calcined clay catalyst) whereas the specific gravity of palm oil used was 0.896. However, the European Biodiesel Standards EN14214:2012 for vehicle use is 0.860-0.90. Thus, there was a decrease in the specific gravity of esterification product compared to the raw material. This indicates that the product obtained was different from the feed. The specific gravity of the biodiesel produced was below the ASTM biodiesel standard D6751:2012 (0.875-0.90). However, that of the control (NaOH) fell within the range of European biodiesel standards EN 14214:2012. These values were close to the specific gravity of 0.880 obtained by Chopade *et al.*, (2012) and 0.880-0.888 obtained by Marwan *et al.*, (2015) for biodiesel but were higher than petroleum diesel EN 590: 2004 range of 0.82-0.845 except the one from raw clay (0.799).

Another important property in measuring the quality of biodiesel is viscosity, since it affects the operation of fuel injection in biodiesel engines. According to ASTM D6751:2012 standard, the standard range of viscosity for biodiesel is 1.9-6.0cSt at 40°C (Saifuddin *et al.*, 2014). Focusing on Kinematic viscosity at 40°C, it was found that the viscosities of the biodiesel produced were 4.2 mm²/sec (NaOH catalyst), 3.2 mm²/sec (raw clay catalyst), 4.1 mm²/sec (acid treated clay catalyst), and 4.0 mm²/sec (calcined clay catalyst). Compared to the viscosity of petro-diesel (2.0-4.5mm²/sec), the viscosities of the biodiesel with NaOH, acid treated and calcined catalysts were higher. The low value for the raw clay catalyst obtained may be due to the unreacted methanol which made it less viscous as compared to others whose methyl groups have been replaced. Saifuddin *et al.*, (2014) equally got a viscosity of 4.10cSt at 40°C while Marwan *et al.*, (2015) reported a viscosity of 3.825-4.655 at 40°C. The viscosities of the biodiesel also fell well within the standard range of ASTM D6751:2012 limits (1.9-6.0 mm²/s) and European biodiesel standards EN 14214:2012 (3.5-5.0).

The Flash points of palm oil diesel fuel was 90°C (NaOH catalyst), 68°C (raw clay catalyst) and 80°C (acid treated and calcined clay catalysts respectively). These values fell within the flash point of petro-diesel (60-80°C). The flash points of all samples were slightly lower than that of the ASTM D6751:2012 limit (93°C or 130 minutes) and European biodiesel standards EN 14214:2012 (101°C or 120 minutes). Since the flash points from this study is high (more than 65°C), therefore, this fuel is safe for handling and storage for a long period of time. With these high values of flash points, the biodiesel produced is considered as combustible. This confirmed that the storage of these samples would not constitute a fire risk.

The biodiesel obtained fell within the ASTM D6751:2012 limit for biodiesel cloud point (-3 to 12). However, it did not agree with the report of Jaimasith and Phiyalaninmat (2007) whose cloud point was 21.3 and 22.7°C. The values obtained from the palm oil biodiesel were 11°C (NaOH catalyst), 5°C (raw clay catalyst), and 10°C (acid treated and calcined clay catalysts) respectively. The values were higher but not enough to form wax when the fuel was cooled below room temperature. The average room temperature in this part of the world does not fall lower than 20°C, which is greater than the values.

The acid value was obtained as the milligram of potassium hydroxide necessary to neutralize the fuel acids in 1g of sample. The ASTM D6751:2012 standard and European biodiesel standards EN 14214:2012 values for pure biodiesel set the maximum acid value (acid number) at 0.50mgKOH/g respectively.

The evaluated acid value of palm oil diesel was 0.22 (NaOH catalyst), 0.30 (raw clay catalyst), 1.06 (acid treated clay catalyst) and 0.34 (calcined clay catalyst) respectively. The acid value obtained from the acid treated clay was higher due to acid treatment. The rest were below the recommended maximum of 0.50mgKOH/g.

The NaOH concentration as well as the acidified and calcined clay showed tremendous percentage yield for complete conversion of triglyceride into ester (Table 3). The inability of the raw clay to convert oil to ester might be responsible for low yield of ester. This could be due to unexposed active sites covered with associated water molecules within the raw clay or organics. However, the situation is different as the clay structure remained intact with less pore spaces upon acidification/calcination where acid creates channels due to removal of intercalating metal ions.

Table 3: Biodiesel percentage yields

Sample	% Yield (Biodiesel)	% Residue(Glycerine, Clay)
Biodiesel with NaOH as catalyst	91.42	8.57
Biodiesel with Raw Clay as Catalyst	46.85	53.14
Biodiesel with Acid Treated Clay as Catalyst	95.71	4.28
Biodiesel with Calcined Clay as Catalyst	96.57	3.42

The biodiesel products from all samples with catalysts were investigated by GC-FID analysis. The product identification was assigned as methyl ester. From the GC-FID analysis, Tables 4 -6 contained all the compound names identified by the GCMS Nilst library search. In Table 5, the biodiesel produced using NaOH as catalyst identified the compound names 7-hexadecanoic acid, methyl ester ($C_{17}H_{34}O_2$), hexadecanoic acid, methyl ester ($C_{17}H_{34}O_2$) and cis-13-octadecanoic acid, methyl ester ($C_{19}H_{36}O_2$) where the major peaks appeared at retention times 23.648, 23.925 and 25.672 respectively. The identification of these names as shown in Table 5 have also been reported previously by Saifuddin *et al.*, 2014, who used the library search report to identify the methyl esters.

The produced biodiesel from raw clay as catalyst (Table 5) equally contained pentadecanoic acid, 14-methyl-methyl ester ($C_{17}H_{34}O_2$), 9-octadecanoic acid (Z), methyl ester ($C_{19}H_{36}O_2$) and octadecanoic acid, methyl ester ($C_{19}H_{38}O_2$). The chromatogram of the produced biodiesel from raw clay as catalyst (Scheme 1) showed the highest peaks at retention times of 23.859, 25.550 and 25.739. These major compounds also contained in the FAME standard (Table 4). Saifuddin *et al.*, 2014, also reported the presence of these compounds (with similar retention times) in their work. Irmawati *et al.*, 2015, also reported the presence of heptadecanoic acid in their fatty acid composition of biodiesel produced.

The major peaks of the biodiesel produced using acid treated clay as catalyst showed highest peaks at retention times of 23.845, 25.511 and 25.739 with their respective compound names; pentadecanoic acid, 14-methyl, methyl ester ($C_{17}H_{34}O_2$), 9-octadecenoic acid (Z), methyl ester ($C_{19}H_{36}O_2$) and octadecanoic acid, methyl ester ($C_{19}H_{38}O_2$), as shown in Table 6. Similar results had been reported by Saifuddin *et al.*, 2014.

The GC-FID chromatogram of the biodiesel produced using calcined clay as catalyst recorded 23.902 and 25.596 as the retention times of the highest peaks (Scheme 2). The compound names that corresponded to these peaks are hexadecanoic acid, methyl ester ($C_{17}H_{34}O_2$), and 9- octadecenoic acid, (Z)-methyl ester ($C_{19}H_{36}O_2$) respectively (Table 6). Irmawati *et al.*, 2015, also reported the presence of methyl tetradecanoate acid (methyl myristate) in their work. These compound names also appeared in the palm oil and FAME standard (Table 4).

The fatty acid composition of palm oil was also investigated by using GC-FID analysis (Table 4). In the GC-FID chromatogram of palm oil, peaks of only the major compounds appeared at retention times of 23.858, 25.551 and 25.739 which corresponded to the compound names pentadecanoic acid-14-methyl, methyl ester ($C_{17}H_{34}O_2$), 9- octadecenoic acid (Z)- methyl ester ($C_{19}H_{36}O_2$), and octadecanoic acid, methyl ester ($C_{19}H_{38}O_2$) respectively. These results agreed with the results of Dhanasekaran and Dharmendirakumar (2014), and are most probably the case as they are the components present in the palm oil as documented and explained by Saifuddin *et al.*, 2014.

The ANOVA result output of the SPSS version 21 suggest no strong significance difference in the value of clay catalysts and physico-chemical properties; the F-value of 1.500 and a sig-value of 0.469 suggest near lack of significant difference. The Duncan's values are both greater than 0.05 (P-value), so it suggests a weak significance in the difference in value of the variables (raw, acid treated and calcined clay catalysts). Thus, the clay catalyst values for raw, acid treated and calcined have no strong significant difference. Statistically, they are the same.

Table 4: Standard for fatty acid methyl ester (FAME) from polyscience, a division of Preston Industries, Incorporated and GC-FID result of Palm Oil (Raw)

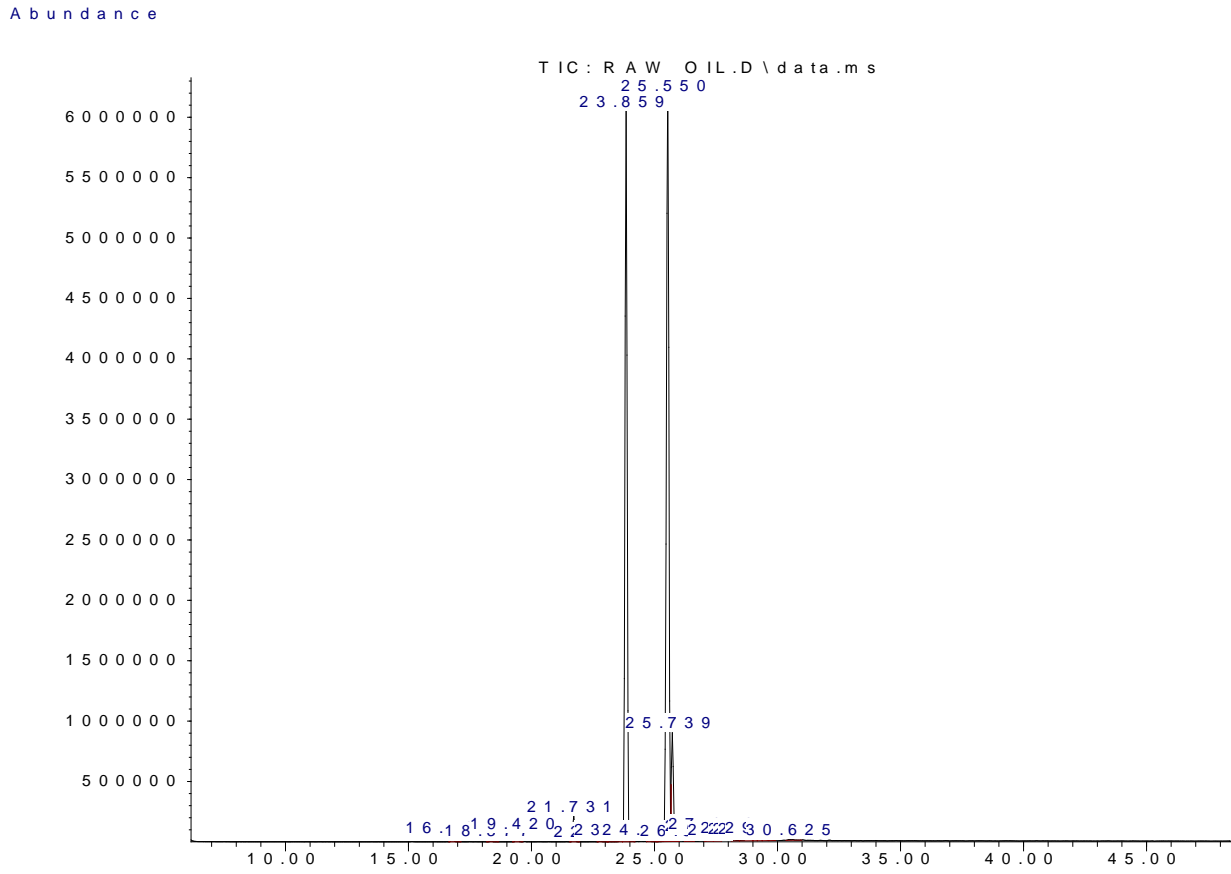
Peak #	Compound Name of FAME	Retention Time	Compound Name of Raw palm oil	Retention Time
1	Octadecanoic acid, methyl ester	13.792	Methyl tetradecanoate acid	21.731
2	Decanoic acid, methyl ester	17.138	Pentadecanoic acid-14-Methyl, methyl ester	23.858
3	Undecanoic acid, methyl ester	17.138	Eicosanoic acid,ethyl ester	24.476
4	Dodecanoic acid, methyl ester	19.733	Hexadecanoic acid, 15-methyl-, methyl ester	24.800
5	Tridecanoic acid, methyl ester	20.632	9-Octadecenoic acid,(Z)-,Methyl ester	25.551
6	Methyl tetradecanoate	22.075	Octadecanoic acid, methyl ester	25.739
7	Hexadecanoic acid, methyl ester	24.205	Ethyl -9-tetradecanoate	26.098
8	Heptadecanoic acid, methyl ester	24.885	Cis-vaccenic acid	27.304
9	Octadecanoic acid, methyl ester	26.119	Methyl 18-methylnonadecanoate	27.471
10	Nonadecanoic acid, methyl ester	26.684	Hexadecanoic acid,2-hydroxy-1-(hydroxymethyl) ethyl ester	29.128
11	Eicosanoic acid, methyl ester	27.500	E11 Hexadecenoic acid, ethyl ester	30.608

Table 5: GC-FID result of biodiesel with NaOH and raw clay Catalysts

Peak #	Compound Name (NaOH)	Retention Time	Compound Name (Raw clay)	Retention Time
1	Methyl tetra decanoate acid	21.761	Decanoic acid, methyl ester	16.796
2	7-Hexadecanoic acid, methyl ester	23.648	Dodecanoic acid, methyl ester	19.420
3	Hexadecanoic acid, methyl ester	23.925	Methyl tetradecanoate	21.731
4	n-Hexadecanoic acid	24.868	Pentadecanoic acid, 14-methyl-methyl ester	23.859
5	Cis-13-Octadecanoic acid, methyl ester	25.672	9-Octadecanoic acid (Z),methyl ester	25.550
6	Cis-Vaccenic acid	26.612	Octadecanoic acid, methyl ester	25.739
			Eicosanoic acid, methyl ester	27.476

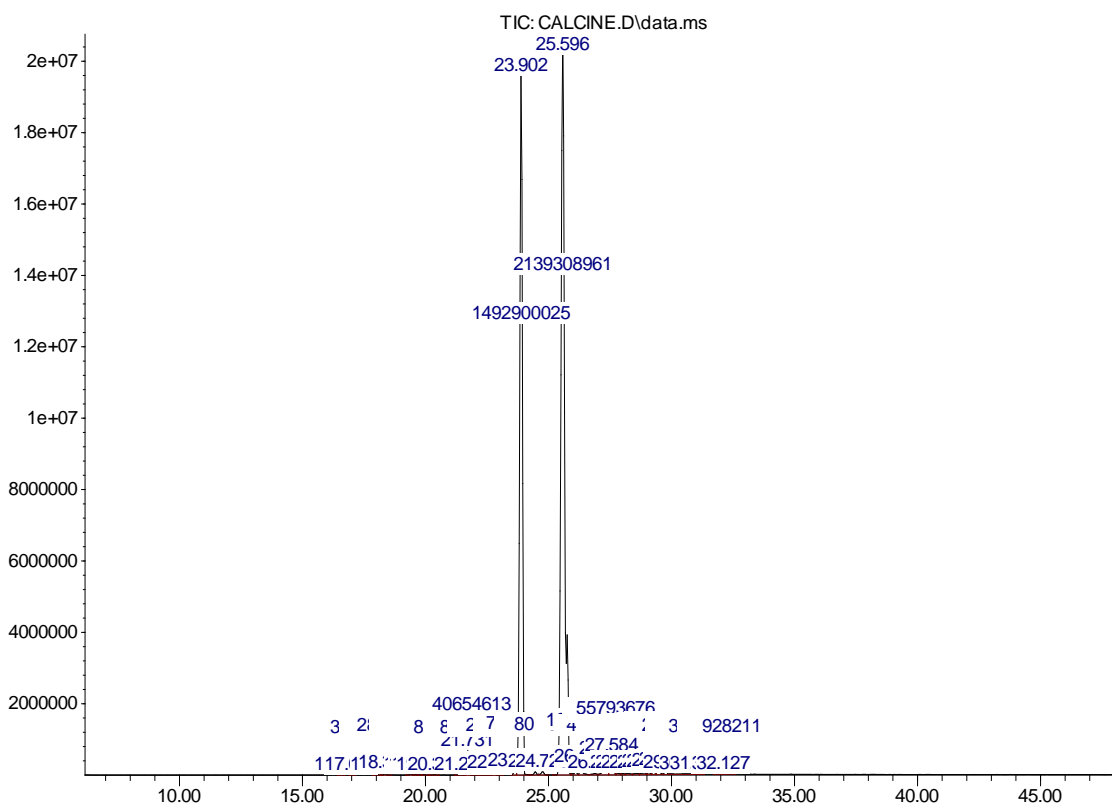
Table 6: GC-FID result of biodiesel with acid treated and calcined clay catalysts

Peak #	Compound Name (Acid treated)	Retention Time	Compound Name (Calcined)	Retention Time
1	Methyl 8-oxo octanoate	18.381	Methyl tetradecanoate acid	21.731
2	Decanoic acid, methyl ester	19.421	Hexadecanoic acid, methyl ester	23.902
3	Nonanedioic acid, dimethyl ester	19.746	9-Octadecenoic acid,(Z)-,Methyl ester	25.596
4	Methyl tetradecanoate	21.731	Octadecanoic acid, 10-oxo-, methyl ester	27.364
5	Pentadecanoic acid, 14-methyl, methyl ester	23.845	Nonanoic acid, methyl ester	27.584
6	9-Octadecenoic acid (Z), Methyl ester	25.511		
7	Octadecanoic acid, Methyl ester	25.739		
8	Methyl 8-methyl nonoate	27.509		
9	Oxirane octanoic acid, 3-Octyl,methyl ester cis isomer	28.265		
10	Phthalic acid, di(2-methylbutyl) ester	29.275		



Scheme 1: GC-FID Chromatogram of Biodiesel obtained from Palm oil using Raw Clay Catalyst

Abundance



Scheme 2: GC-FID Chromatogram of Biodiesel obtained from Palm oil using Calcined Clay Catalyst

4.0 Conclusion

The modified form of Kono-Boue clay has been used as a catalyst for the production of biodiesel from palm oil. The raw Kono-Boue clay produced poor grade and low yield biodiesel while in its modified form (calcined), it produced higher grade and better yield of approximately 97%. Therefore, Kono-Boue clay can be used as a solid catalyst in a modified form for biodiesel production from palm oil and as a heterogeneous catalyst in general. However, the ANOVA results and the Duncan's test statistics for multiple range tests suggested that the values of raw, acid treated and calcined clay catalysts have no significant differences ($P > 0.05$).

5.0 Recommendations

The following recommendations are made:

1. Modified calcined Kono-Boue clays should be used as catalyst of catalytic base for trans-esterification reaction by trans-esterification of palm oil to biodiesel since it is cheaper, more environmentally friendly, and did the same function as the NaOH.
2. Further studies on the characterization of Kono-Boue clays should be conducted in order to reveal the correlation between the catalytic properties and trans-esterification.

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7.0 References

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