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Biodiesel Production from Used Cooking Oil (UCO) using Kaolin Clay Catalyst: Effects of Calcination Temperature

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Abstract

In this study, the catalysts were prepared and categorized as KC-raw and calcined catalysts. These are: RKC, KC-600 and KC-900. They were used directly in trans-esterification reactions without further treatment to determining its performance in producing fatty-acid methyl esters (FAME). The Kaolin clay sample treated at calcination temperature of 600℃ (KC-600) for 4hours with reaction temperature 120 o C; catalyst loading of 3.5 wt% and methanol / oil ratio of 9:1 gave the highest yield of 51.09%. The catalysts KC-raw; KC-300; KC 600 and KC 900 where characterized using scanning electron microscopy (SEM) and energy- dispensive x-ray spectroscopy (EDX). Branauer-emmett-teller (BET), thermographic analysis (TGA) and differential thermal analysis (DTA). Fourier transform infrared spectral (FT-IR). X-ray fluorescence spectral (XRF) was also used to detect chemical composition of the catalysts and to gain insight into the structural changes that occurred at different calcination temperature which in turn determine their performance in trans- esterification reaction.

Keyword: Raw Kaolin Clay (RKC), Kaolin Clay Calcined at 300 °C (KC-300), Used Cooking Oil (UCO), Transesterification, Kaolin Clay Catalyst (KCC)

1. Introduction

The demands for continuous search of green energy which is environmentally friendly and cost effective cannot be over emphasized. The problems associated with current conventional energies such as coal, fossil fuel and natural gases are enormous and of global dimension [1-2]. Some of these problems are: Global warming and its attendant consequences for example flooding and loss of agricultural produce leading to hike in food production. Greenhouse gas emission. Non-renewability of most petroleum-based energy and price instability in energy market globally. [3-4].

Several materials have been synthesized and developed as solid heterogeneous catalysts for the production of Fatty Acid Methyl Esters (FAME). But as a result of high cost of production and other stringent conditions for their optimal performance, lower percentages of application and utilization were recorded in current world's energy requirements which are mostly in America, Europe and Asian nations [5].

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According to [6] the major factors that determine the cost of FAME production are chemical feedstock [12%] and type of oil feedstock used. (75%). In this paper the naturally abundant kaolin clay which is present in almost all parts of the world and Used Cooking Oil. (UCO) which is available in all standard restaurants and eateries were exploited [7].

Kaolin clay consist essentially of hydrated Aluminia – silicate compound ($Al_2Si_2O_5(OH)_4$ and mixture of other metallic oxides such as Al_2O_3, SiO_2, K_2O, CaO, TiO_2, V_2O_5, Cr_2O_3, Fe_2O_3, ZnO, CaO, Rb_2O, and SrO, just to mention a few [8]. The presence of these metallic oxides justifies their use as heterogeneous catalysts in trans-esterification reaction [9].

It is a known fact from review of most work done for decades in solid catalyst of highly selective, functional and reusable catalysts for biodiesel production depends essentially on scientific manipulations and combinations of this variables Viz: size reduction through crushing to produce micro to nano-particles to enhance surface areas, alteration of calcination temperature; changes of trans-esterification reaction temperature; contacts between reactants and or pre-treatment of the feedstock as the case may demand [10-11]. A combination of those variables were exploited in this study which are crushing of Kaolin clay catalyst (KCC) to obtain the desired size reduction to increase the surface area, effects of calcination temperature on the already crushed (KCC) and alteration of trans-esterification reaction temperature (30° – 180°C) [12]. The reaction parameters such as oil to methanol ratio. Time of reaction in (h). Catalyst loading were investigated and optimized. The KCC catalyst; KC-RAW; KC-300; KC-600 and KC-900 were characterized using SEM / EDX; BET; TGA/DTA XRD; FITR and XRF.

2. Experimental

2.1 Materials

The Raw kaolin catalyst was collected from Kutigi deposit in Niger state, Nigeria. Used Cooking Oil (UCO) was collected from N24 Brad street restaurants Universiti Teknologi Malaysia (UTM). Methanol used has a percentage purity (Assay by G.C) $\geq$ (99.5%). Water content by karl fisher $\leq$ 0.1%; purchased from elite advance material Sdn Bhd Selangor, Malaysia. 15cm diameter filter papers through 0.2 micron produced and packaged in Malaysia were used for UCO filtration. The molecular weight (MKL). Acid value, and moisture content of UCO used are 859.95g/mol; 0,78mgKOH/g; and 0.0603%.

2.2 Catalyst preparation

The raw Kaolin clay collected from Kutigi Niger state, Nigeria was dried in an oven at 105°C overnight before being crushed with mechanical crusher at Geology Department UTM Malaysia. The dried grounded raw kaolin clay was sieved on a mechanical shaker to obtain 53µm – 150µm particle size. About 1kg of the sieved clay was kept in an air tight container and labelled as Raw-clay. 100g each of sieved raw clay sample were measured and heated in a furnace in the temperature range of 300° – 900°C for 4h. Each of the calcined clay were kept in an air tight container and labelled as KCC – 300 for the one calcined at 300°C for 4h; KCC – 400 for the one calcined at 400°C for 4h until the last sample labelled at KC – 900 in a similar pattern were obtained. These catalysts were subjected to methanolysis without further treatment to determine their FAME yield.

2.3 Catalyst characterization, equipment used and condition

The chemical composition of both raw and some selected calcined clay were analyzed using X-Ray Fluorescence machine (XRF). The surface morphology (texture) of the various samples were determined using Scanning Electron Microscopy (SEM)> The Fourier Transform Infrared (FT-IR) was used to discover the various functional groups contained in the catalyst. X-Ray diffraction (XRD) was done via Cu Kx (X = 0.154nm) as a radiation (Rigaku Denki, Japan) to determine the structural characteristics and phase changes in the sample. The Branauer –Emmet – Teller (BET) was used to determine the surface area, pore-size and pore-volume of the catalyst sample with AUTOSORB – 1 – MP.IR spectral Japan. The Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) were used to determine the thermal stability of the catalyst. That is the measure of weight changes as a result of temperature changes using (TGA/SI) T85 (Mettler-toledo) at heating rate of 10k/min till 90°C was attained.

2.4 Experimental procedure

Used Cooking Oil (UCO) was pre – treated and used in trans-esterification reaction. A 250ml, three-necked round bottomed flask connected with a reflux condenser to prevent methanol from escaping from the reactor most especially at higher temperature was used. A pre-determined amount of UCO based on preliminary experiments was measured and poured into the round bottomed flask. 33ml of methanol and 3.5wt% of clay catalyst were added and stirred using magnetic stirrer at 550rpm for all the experiments. The reactor was seated in a Silicon oil-bath and heated accordingly. Timing begins whenever each batch has reached the desired temperature. For optimal performance of each set of the experiments, the clay catalyst was accurately measured and heated in an oven at 105°C for 30mins to remove any possible moisture (water) before being charged into the reactor. The temperature of reaction (30° – 180°); reaction time (0.5 – 5h), catalyst loading (0.5wt – 15wt%) and oil methanol molar ratio of (1:1 – 1:15) were studied to determine the optimal condition for biodiesel yield.

2.5 Transesterification study

At the end of each experiments, the mixtures were filtered with filter papers and vacuum pump to remove the clay catalyst. Then the remaining mixtures were transferred to a separating funnel and allowed to settle. Two major layers were noticed, one of fatty acid methyl ester (FAME) on top and secondly glycerol at the bottom of the crude biodiesel poured into centrifuge tube ready to be centrifuged. After centrifuge at 4000rpm for 10mins, the clear biodiesel were then poured into a separating funnel and equal amount of pure distilled water was added to remove any trace of unreacted methanol and glycerol still remaining. The water and bio-diesel mixture were allowed to settle and the water drained off. The biodiesel was then heated on a hot plate to remove any possible water/ moisture content still remaining and the yield calculated.

$$Yield\% = \frac{Mass\ of\ biodiesel\ (g)}{Mass\ of\ oil\ used\ (g)}\ X\ \frac{100}{1}$$

3. Result and Discussion

3.1 Catalyst characterization

The chemical composition contained in the raw kaolin clay, (RKC), KC-600 and KC-900 were determined by X-Ray fluorescence (XRF) and presented in Table 1 below. The XRF results revealed that the major component of the RKC, are Aluminum oxide (Al_2O_3), Silicon Oxide (SiO_2) and Titanium Oxide (TiO_2). which are 33.4, 62.4 and 2.04% respectively. After calcination of the raw clay at 600°C a similar trend was observed with KC-600 showing (Al_2O_3); (SiO_2) and (TiO_2) as 32, 63.6 and 2.16% respectively. Also, KC-900 maintained the similar trend of (Al_2O_3); (SiO_2) and (TiO_2) as 33.3, 59.3 and 3.43% respectively. The result of RKC is in close agreement with the work of [13] for kaolin clay. Alaba et-al [13] calcined kaolinite clay at 600°C and obtain close result with KC-600 of XRF analysis.

Table 1. Chemical composition of RKC, KC-600 and KC-900 catalysts X-ray fluorescence (XRF).

Compound	Weight (wt%)		
	RKC	**KC- 600**	**KC- 900**
Aluminum Oxide (Al_2O_3)	33.3	32.0	33.3
Silicon Oxide (SiO_2)	62.4	63.6	59.3
Potassium Oxide (K_2O)	0.884	0.831	1.16
Calcium Oxide (CaO)	0.0202	0.0198	0.0441
Titanium Oxide (TiO_2)	2.04	2.16	3.43
Vanadium Oxide (V_2O_5)	0.0718	0.0813	0.0138
Chromium Oxide (Cr_2O_3)	0.0079	0.0078	0.0053
Manganese Oxide (MnO)	ND	0.0027	ND
Iron (III) Oxide (Fe_2O_3)	0.999	1.07	1.53

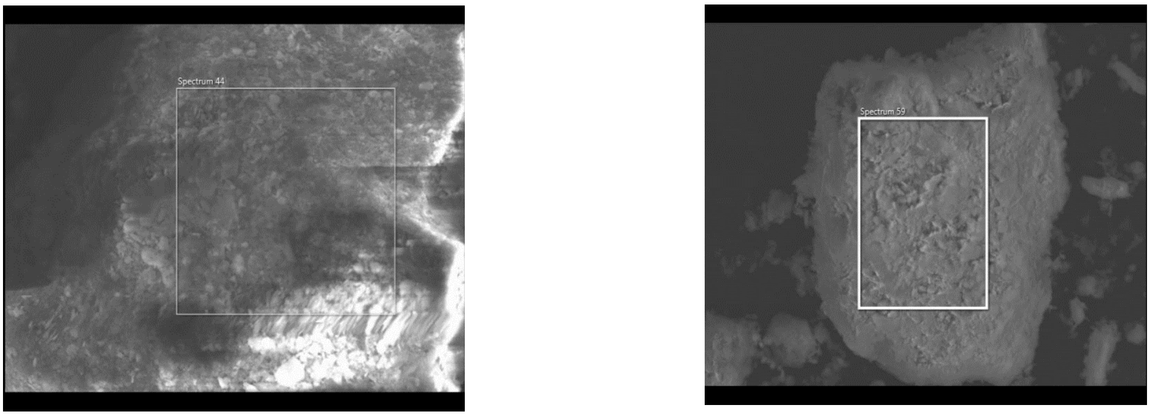
Zinc Oxide (ZnO)	0.0033	0.0043	0.0076
Rubidium Oxide (Rb_2O)	0.0043	0.0043	0.0056
Strontium Oxide (SrO)	0.0056	0.0059	0.0084
Yttrium Oxide (Y_2O_3)	0.0096	0.0101	0.0132
Zirconium Oxide (ZrO_2)	0.162	0.165	0.217
Europeaum Oxide (Eu_2O_3)	0.0220	0.0187	ND
Barium Oxide (BaO)	0.0046	0.0051	0.0464
Hafnium Oxide (HfO_2)	0.0032	0.0040	0.0060
Loss on ignition (LOI)	0.0625	0.01	0.9126
Total	100	100	100

The presence of vanadium (iv) oxide (V_2O_5), Calcium Oxide (CaO) and Titanium Oxide (TiO_2) though in smaller amounts have been reported to give high yield in the production of FAME [14-15]. The clay sample also contains Iron (iv) Oxide (Fe_2O_3) which have been reported to give high yield in biodiesel production [16]. The presence of the metal oxides justifies their usage in synthesizing active heterogeneous catalysts.

3.1.1 Scanning Electron Microscopy (SEM)

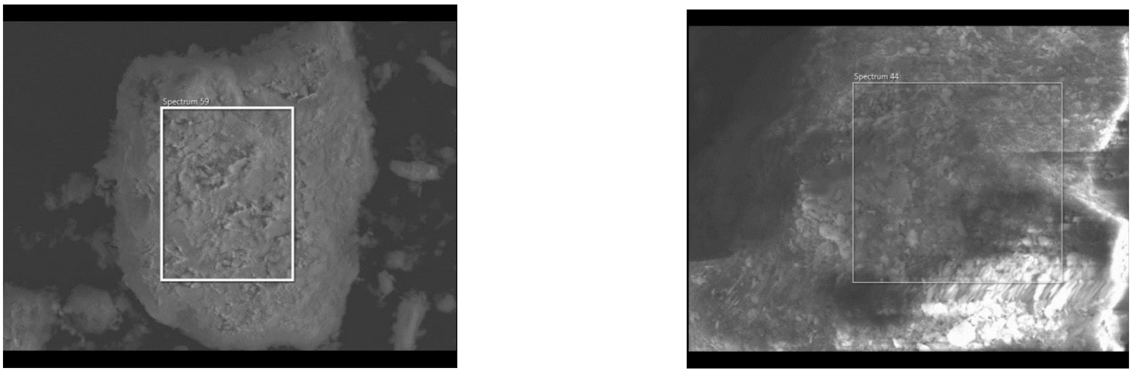
This is generally used to determine the morphology, crystal structure and material make ups of materials. The SEM images of the raw kaolin and calcined catalysts are shown in Figures 1 to 4. The images at magnification of 20,000 X shows presence of both small and large particles with small particles aggregating together and voids visible on all the catalyst. The low FAME yield noticed with catalyst calcined at temperatures lower that 600ºC is attributable to presence of oxygen (O_2) and carbon (iv) oxide (CO_2) occupying the available pore spaces preventing the reactants from gaining contact with each other and as a result preventing the reaction from taking place. (Olutoye and Hameed, 2013). These pores were essentially free for calcination at higher temperature as observed in Figures (3) & (4) as the gases evolves at higher temperatures.

Scanning Electron Microscopy (SEM) result for kaolin clay catalysts



1. SEM image for raw kaolin clay catalysts

2. SEM image for KC-300 catalysts



3. SEM image for KC-600 catalysts

4. SEM image for KC-900 catalysts

Figures 1- 4 SEM images for (1) Raw kaolin clay (2) KC-300 (3) KC-600 (4) KC-900 catalysts.

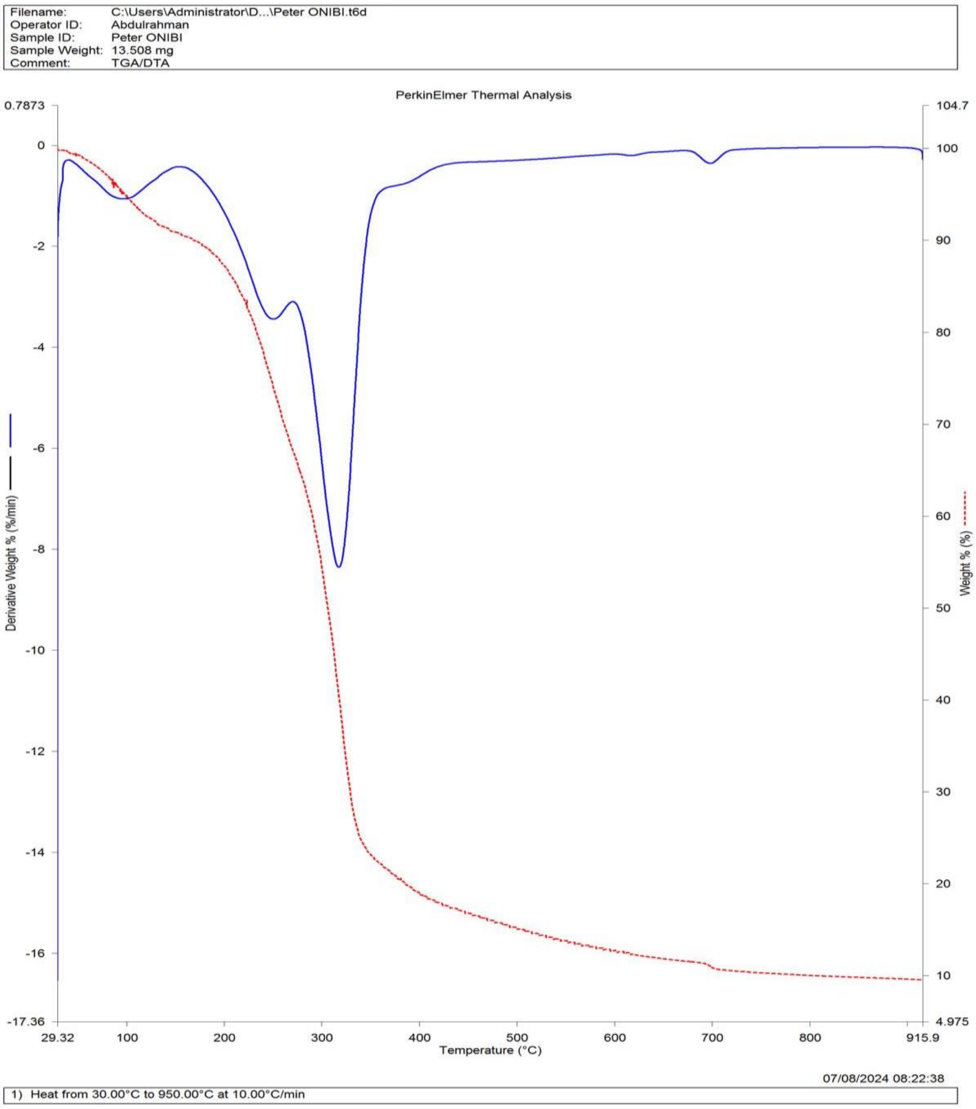


Fig 5 Thermogravimetric and Differential Thermogravimetric Aanalysis of RKC from 30ºC to 915ºC

The TGA and DTA profiles depicted in Figure 5 alluded to this fact. Two major points of decompositions were noticed around 81ºC and 574ºC showing points of evolution of adsorbed gases from the catalysts as temperature increases.

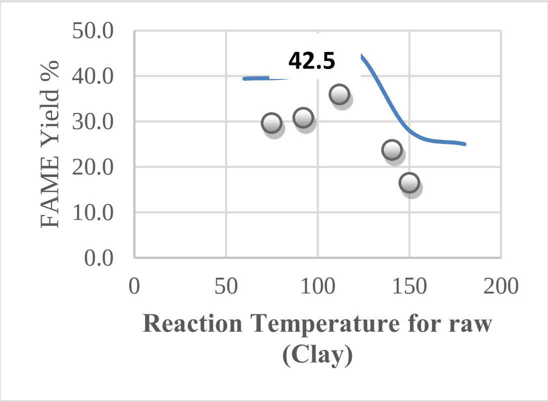
The major stability was noticed when the temperature increased from 504ºC to 915ºC. Though the plateau was not fully achieved, it can be concluded that Kutigi Kaolin clay can be safely calcined between 504ºC to 915ºC (Olutoye & Ahmed, 2013) [9].

3.2 Effect of calcination temperature on transesterification reaction of calcined clay catalysts.

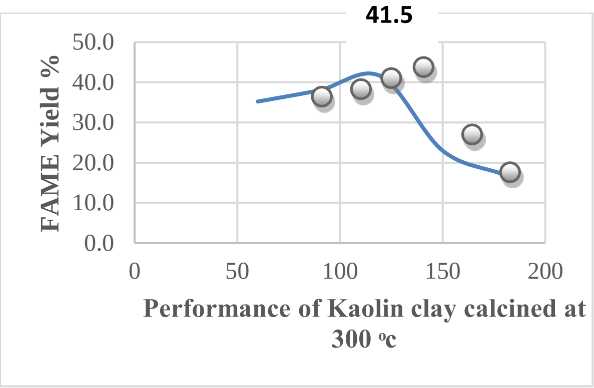
The raw kaolin clay (RKC) was subjected to different calcination temperatures ranging from 300ºC – 900ºC at constant time of 4h and designated as different catalysts. The transesterification reaction of calcined clay catalyst at different calcination temperatures, KC-300, KC-400; KC-500; KC-600, KC-700; KC-800 and KC-900 were carried out to determine the FAME yield at constant reaction time of 5h, methanol/oil ratio of 9:1; catalyst loading of 3.5wt% and reaction temperatures of 60ºC – 180ºC.

The different parameters used were determined based on previous work on the kaolin clay catalysts. Fig 6. Shows the performance of FAME yield at different temperatures. Also the RKC, KC-300, KC-400 and KC-500 gave yields lower than the average. (I.e. 50%). But for raw kaolin clay calcined at 600ºC for 4h gave the best yield of 51.09%; at reaction temperature of 120°C, with all other parameters remaining constant. The reason for this improved performance is due to elimination of PO_4, CO_2, CO, and SO_2 at temperatures greater than 550°C (where complete calcination takes place). The XRF results also confirmed this.

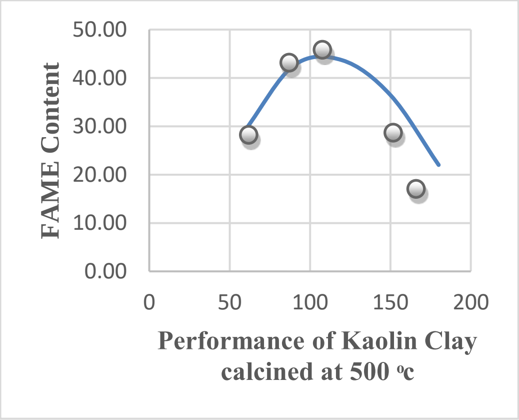
(a)



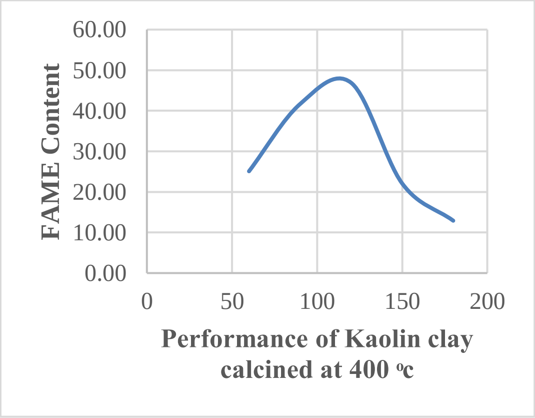
(b)



46.9



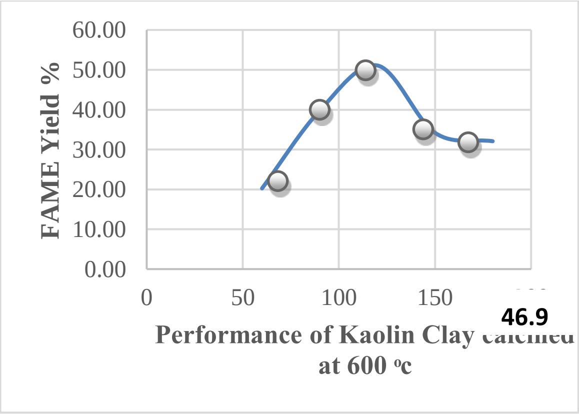
(c)



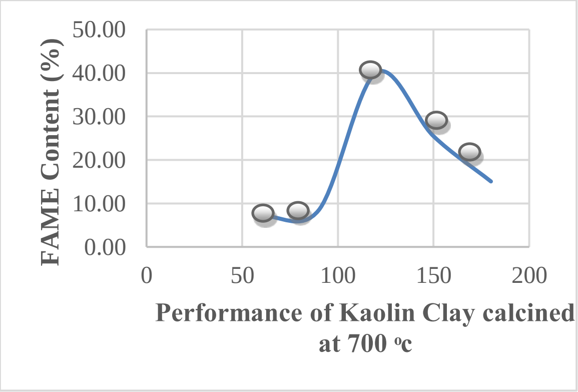
(d)

51.0

40.0



(e)



(f)

40.05

18.98

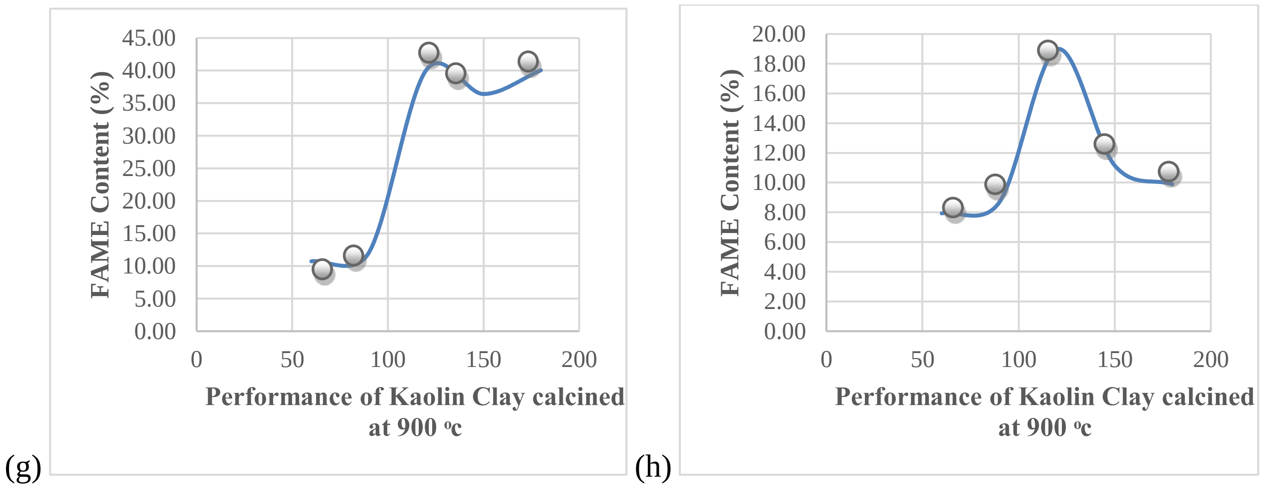


Fig. 6 Performance of raw kaolin catalyst and calcined catalysts at different reaction temperature of 60°C – 180°C

Table 2 Results of EDX of RKC, KC-300, KC-600 and KC-900

	RKC	**KC-300**	**KC-600**	**KC-900**
Element	Wt%	Wt%	Wt%	Wt%
C	13.00	13.01	13.12	7.53
O	58.41	56.26	55.42	53.88
A1	13.01	5.67	14.21	8.71
Si	14.07	24.40	15.66	28.68
K	0.11	0.07	0.26	0.16
Ti	0.79	0.39	0.79	0.65
Fe	0.60	0.19	0.05	0.40
Total	100.00	100.00	100.00	100.00

The synergetic effective of K, Ti, and Fe in KC-600 catalyst have been established to be active in FAME production which are accumulatively higher in KC-600 catalyst. (Alaba *et al.*, 2017; Olutoye *et al*., 2016; Olutoye and Hameed 2013)

Table 3 BET Result for RKC, KC-300, KC- 600 and KC- 900

Catalyst	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
RKC	10.7968	0.080866	283.191
KC-300	6.1676	0.101786	577.1757
KC- 600	41.3147	0.135003	130.700
KC- 900	0.4580	0.093845	8, 196.081

The synergetic effect or better surface area, pore volume, pore diameter for KC- 600 catalyst was responsible for its best performance in transesterification studied.

3.3 Effect of temperature of reaction

The reaction temperatures were steadily increased from 60°C to 180°C while other parameters remained constant for all the kaolin clay catalysts studied. The results show that there were steadily increased in biodiesel yield from 60°C – 120°C after which the yield begins to reduce. Many authors reported similar results. [17].

3.4 Reusability of the best performing Catalyst

In the production of any commercially viable, cost effective, heterogeneous catalyst, the reusability of such catalyst must be guaranteed. This accessed the performance of the catalyst after each successive experimental run. Five circles of experimental runs were done for the best performing catalyst. The reaction conditions remained the same (i.e. reaction time of 5h, methanol to oil molar ratio of 9:1; catalyst loading of 3.5wt% and optimal reaction temperature of 120ºC) The catalysts were retrieved after each run, washed with fresh methanol until no trace of glycerol is seen. Then re-washed with hexane to remove oil molecules. The recovered catalyst was then left to dry in an oven at 110ºC overnight. The catalyst was then used again for the next trans-esterification reaction. The reduction in yield after the fifth circles was just 8.6% showing that the catalyst was stable to maintain its activity after five circles.

4. Conclusion

The effects of calcination temperature were studied in kaolin clay catalyst and used in trans-esterification of UCO to produce biodiesel. The optimal variables that give the best yield are kaolin clay catalyst calcined at 600ºC for 4h, with optimum catalyst loading of 3.5wt%, methanol to oil molar ratio of 9:1, reaction temperature of 120ºC, and a reaction time of 5h. The catalyst proves to be stable over five successive runs. A welcome discovery in developing cost-effective heterogeneous catalyst that can be produced in any part of the world because of the availability of materials involved and method of production employed.

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