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Effects of Beneficiation of Kaolin Clay Catalysts on Biodiesel Yield Using Used Cooking Oil (UCO)

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Abstract

The effects of both acid and base beneficiations on Kaolin clay catalysts (KCC) were investigated. Unmodified Kaolin clay can be used directly as catalysts or catalyst support for production of fatty acid methyl esters (FAME). Modification via calcination, acid or base beneficiation, addition of metal supports are often used to improve FAME yield. In this paper, 6M sulphuric acid was used to prepare the acid-beneficiated Kaolin clay catalyst. Also, 22.5% potassium hydroxide (KOH) was employed to prepare base-beneficiated Kaolin clay catalyst. Both beneficiated catalysts were characterized by FT-IR, SEM/EDX, XRD, TGA/DTA and BET. The acid-activated /beneficiated catalyst calcined at 600°C for 4h with reaction temperature of 120°C, catalyst loading of 3.5wt%, methanol to oil molar ratio of 9:1 and reaction time of 5h give the best yield of 67%, while base treated raw Kaolin clay catalyst with reaction temperature of 70°C, catalyst loading of 15wt%; methanol/oil molar ratio of 14:1 and reaction time of 3h give the best yield of 78%.

Keyword: Beneficiation, Acid beneficiation, Transesterification, Yield

1. Introduction

Effort must continually be geared towards the production of energy. The energy must be produced in the cheapest means possible. This is because energy is required in almost all activities of man. Activities such as production of social amenities, sports, transportation, establishment of industries, construction and infrastructural development. Conversional energies such as natural gas, petroleum derived fuels and coals, provide for over 70% of world's energy requirements, and are generally expensive. (Atika *et al*., 2019). The emission of greenhouse gases as a result of usage of fossil fuels and its attendant environmental problems for instance global warming is also of great concern (Fonseca *et al*., 2019, Borah *et al*., 2019). The reaction between vegetable oil or animal fats and primary alcohol (methanol) to produce biodiesel is very slow without catalyst; so synthesis of cost effective catalyst is required. Catalyst has been employed in the production of biodiesel and other catalyzed processes globally.

One of the major ways to reduce the cost of biodiesel production is to produce cost effective heterogeneous catalyst. This can be done by considering usage of either waste materials and naturally available materials.

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Examples of waste materials include egg shell, snail shell, animal bones, just to mention a few. The naturally available materials include kaolin clay and Lava Mountains. Kaolin clay is abundantly available in all part of the world. This informs its consideration for biodiesel production in this article. Kaolin clay consist of aluminum silicate compound together with traces of metallic oxides such as, Aluminum oxides, Silicon oxides (SiO_2), Potassium oxide (K_2O), Calcium Oxides (CaO), Titanium oxides (TiO_2), and Vanadium oxides (V_2O_5) and a host of others.

The average performance of about 51% yield of Fatty Acid Methly Ester (FAME) of the best performing kaolin clay (KC-600) catalyst without further treatment, need more improvement to further increase its FAME yield, hence the need for beneficiation. According to Alaba *et al.,* (2017) beneficiation is all treatment or process by which a targeted product is increased or improved. In this present work, FAME yield using kaolin catalyst was considered.

2. Experimental

2.1 Materials

The materials used consist of sieve kaolin clay (50µm - 150µm) already calcined at 600°C for 4h; using Used Cooking Oil (UCO) collected from N24 Brad street restaurants University Teknologi Malaysia (UTM), Malaysia. 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. A 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

This involved two (2) major stages: (a) Acid beneficiation (AB) of sieved calcinated kaolin clay catalysts (b) Base beneficiation (BB).

2.2.1   Acid beneficiation (AB) of sieved calcinated kaolin clay catalysts

Six (6) molar (6 M) of sulphuric acid (H_2SO_4) was prepared and 100ml of the acid were added to 10g of the sieved calcined kaolin clay catalysts in a conical flask with a cork to cover the content. The mixture was then placed on a hot plate and heated to 90°C for 4h with a continuous stirring using magnetic stirrer set at 300rpm. After 4h, vacuum machine connected to suction conical flask with funnel and a filter paper were used to rinse out the excess acid from the catalyst using distil water. Rising was continued until a pH of 5 was obtained using pH meter. The catalysts so obtained were kept in a hood fume to dry. The catalysts were then oven dried at 110°C for 12h. The catalysts were then re-calcinated at 550°C in a furnace for 2h. The catalysts so obtained were designated as acid-beneficiated (AB) kaolin clay catalysts ready to be used for transesterification study. The catalyst with calcination temperature at 600°C give higher yield than that calcined at 900°C.

2.2.2   Base beneficiation (BB)

This has two stages. (I) acid treatment step and (II)base beneficiation step

i)   **Step I**

Acid treatment of sieved calcined kaolin clay catalyst, a 100g of raw kaolin clay calcined at 600°C for 4h was treated with 250ml of 25% hydrochloric acid (HCL) for 4h and kept in a deep freezer at – 18°C. This is done to reduce the presence of metal impurities presence in raw kaolin clay sample. The catalyst was washed several time with distill water to filter out the excess HCL with filter paper and vacuum pump till pH of 4 was attained. The catalyst was then kept in hood fume till it was completely dried.

ii)   **Step II**

Base-beneficiation (BB) of sieved kaolin clay catalyst, a 100g of acid activated kaolin catalyst was dispersed in 250ml of x% of KOH for 18h at room temperature (X ranges between 20% - 30% KOH). After 18h, the excess KOH is filtered out using vacuum pump and filter paper. The wet catalyst was allowed to dry at 100°C in an oven for 8h. The dried catalyst was now calcined at 300°C for 5h. The catalyst obtained was regarded as base-beneficiated kaolin clay catalysts. Based on preliminary experiments 22.5% of KOH gave the optimum yield of biodiesel and is maintain in this research work.

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. 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. The crude biodiesel was 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 distilled water was added to remove any trace of unreacted methanol and glycerol still remaining. The water and biodiesel 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.

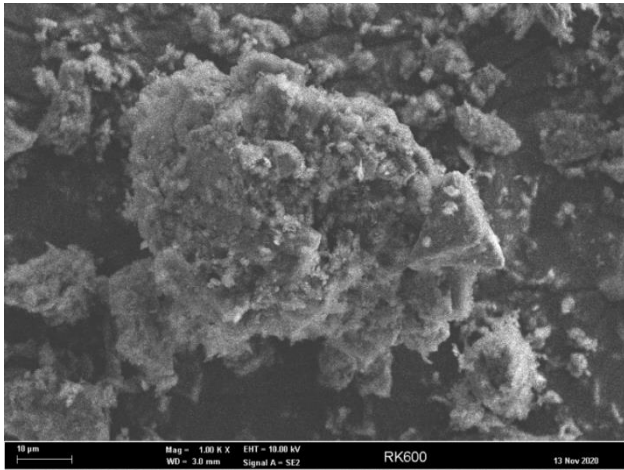$$Yield\% = \frac{Mass\ of\ biodiesel\ (g)}{Mass\ of\ oil\ used\ (g)} \ X \frac{100}{1}$$

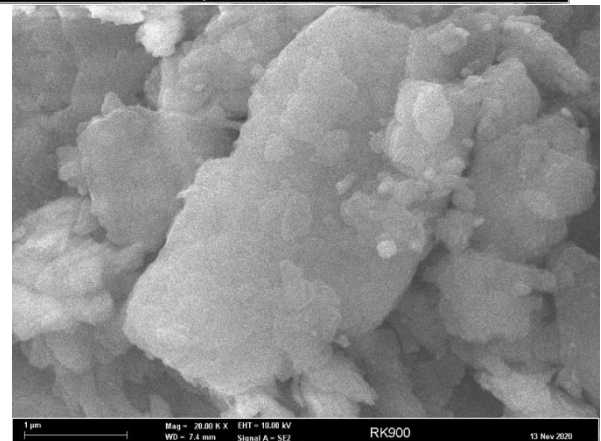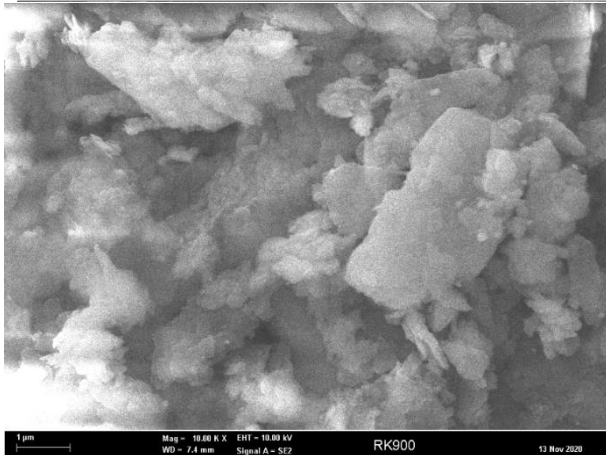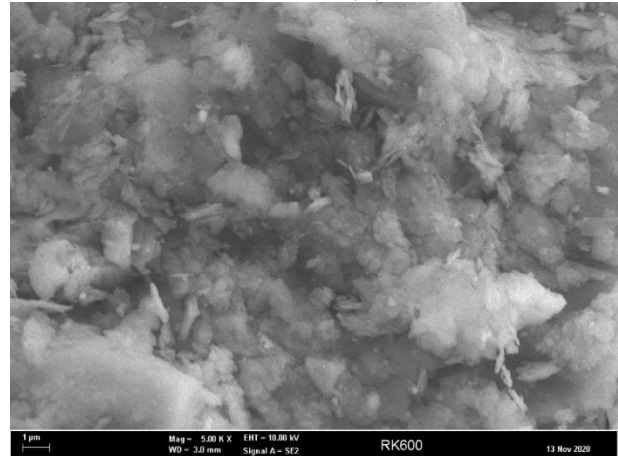## 3. Result and Discussion

3.1 Catalyst characterization

3.1.1 The Scanning Electron Microscopy (SEM) result of Acid beneficiated catalyst pretreated at 900°C and 600°C respectively at different magnifications.

For 900°C

a (i)   a (ii)
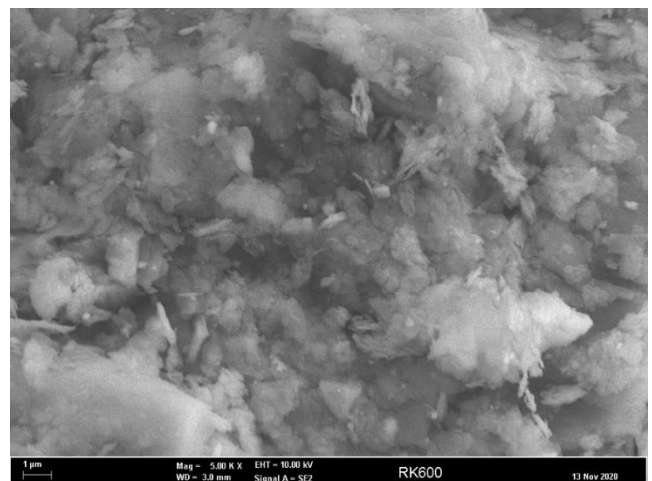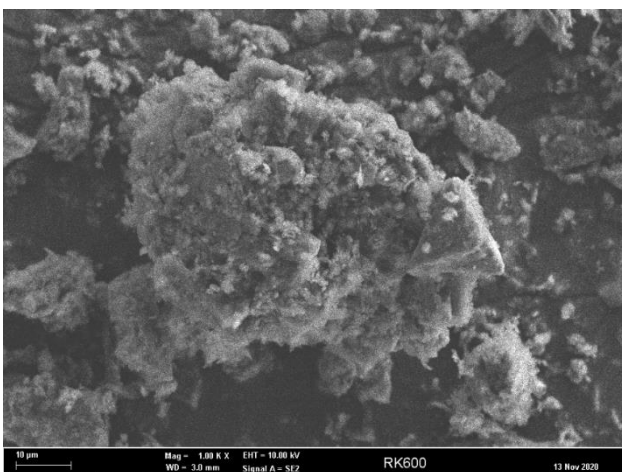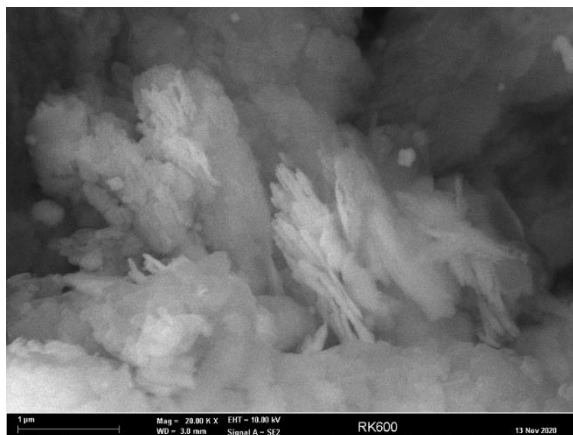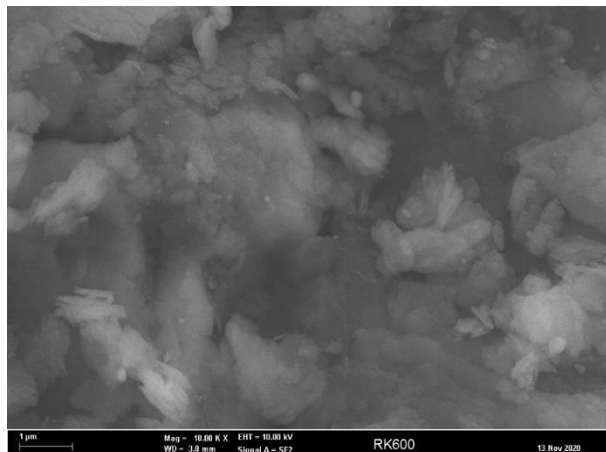

a (iii)

a (iv)

Fig 1 a (i), a(ii), a(iii), a(iv) Raw kaolin clay(150µm-53µm) SEM images of acid beneficiated kaolin clay after pre-treatment at 900ºC and calcined at 550ºC for 2h (RK-AB 900/550ºC) at different magnifications

For 600°C

b (i) b (ii)

b (iii)

b(iv)

Fig 2. b (i), b(ii), b(iii), b(iv) Raw kaolin clay(150μm-53μm) SEM images of acid beneficiated kaolin clay after pre-treatment at 600ºC and calcined at 550ºC for 2h (RK-AB 600/550ºC) at different magnification

Comparing the SEM images of acid beneficiated catalyst for both 600°C and 900°C at 10μm magnifications in Fig. 1 and 2. There are void spaces between particles, with bigger particles aggregating together, particularly, with acid beneficiated catalyst produced at 600°C. These limited spaces for movement during reactions. Even though the average molecular spaces between particles allowed for moderate movement and diffusion for both reactants and products. This is in agreement with the work of Thangearaj *et al.,* (2019). This explains the reason for better performance between acid beneficiated catalyst and those not beneficiated. Other magnifications reflected the same pattern.

3.1.2 BET result for both Acid and Base Beneficiated Catalyst
Table 1. BET Results of Acid Beneficiated Catalyst for RK-AB 900/550ºC, RK-AB 600/550ºC

Catalyst	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
RK-AB 900/550ºC	137.2838	0.200236	5.8342
RK-AB600/550ºC	58.4842	0.235418	9.2618

The BET result of acid beneficiated catalysts Table 1 contains two different catalysts. Generally, BET is used to determine the textural properties of any given catalyst, in this case TriStar II 3020 Version micomeritics instrument cooperation was used to test for surface area, total pore volume and average pore diameter. Even though catalyst RK-AB 900/550ºC has specific surface area of 137.284m2/g as compared with 58.5m^2/g, the synergetic properties of catalyst RK-AB600/550ºC with the specific surface area of 58.5m^2/g, pore volume 0.23542cm^3/g and pore diameter of 9.3nm give a better FAME yield of 67%. There was increased yield from kaolin clay catalyst 51% to 67% after acid beneficiation. There is still need to consider base beneficiation on kaolin catalysts. The increase in yield after acid beneficiation is in line with the work of (Alaba *et al*., 2017).

Table 2 BET Results for Base beneficiated catalyst pretreated at 600ºC of B(K/K+)/300ºC [5h],

Catalyst	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
B(K/K$^+$)/300ºC [5h]	12.5617	0.088252	28.1019

For the production of base beneficiated (BB) kaolin clay catalysts. The sieved kaolin clay (150μm-53μm) calcinated at 600°C for 4h were used. After the two steps involved which are (a) acid treatment and (b) base entrapment using 22.5% KOH for 18h, to produce B(K/K+)/300°C [5h] catalyst. This catalyst was subjected to transesterification study to determine the performance in FAME production. The optimum parameters for base beneficiated catalysts are: temperature of reaction 50°C-120°C, methanol to oil molar ratio1:6-1:18, catalyst loading 3 wt%-18 wt%, and Time (h) 1-5h. The base beneficiated catalyst gave the optimum performance at reaction temperature 70°C, catalyst loading of 15wt%., methanol to oil molar ration of 14:1 and reaction time of 3h gave the best yield of 78%. This is in agreement with the work of Mohammed *et al.,* (2018).

3.1.3 FTIR Results for acid and base beneficiated catalysts
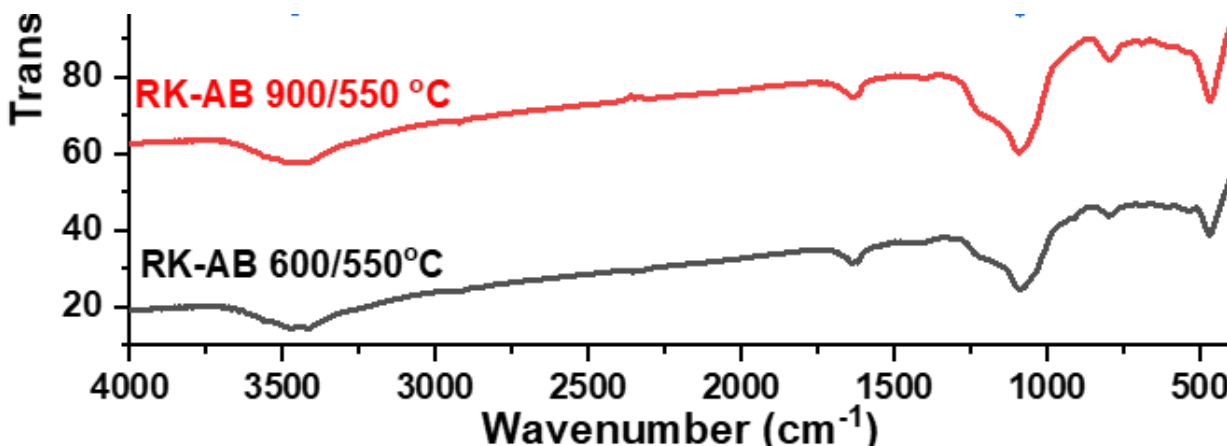

Fig 3 FTIR spectra for two samples of acid beneficiated (a) RK-AB 900/550°C (b) RK-AB 600/550°C

From Fig. 3 above, the FTIR spectra of acid beneficiated catalyst can be generated. See Table 3 below.

Table 3 FTIR spectra of acid beneficiated catalysts

S/N	FT-IR bands(cm⁻¹)	Assigned functional group
1	490	Zn-O bond
2	1125	C=O bond
3	1625	C=C stretch
4	3480	O-H stretching vibrations and water molecules

The FTIR Fig. 3 show the functional changes that occurs as a result of different calcination used for the raw catalyst, even though the wave gave a general pattern there was a reduction in broad band between 100 to 1500cm⁻¹. There is O-H stretching vibrations and water molecules around 3480 for the two catalyst. This require heating before usage. At 1125cm⁻¹, this will be assigned to stretching C-O of primary alcohol (Millar and Wil   952).
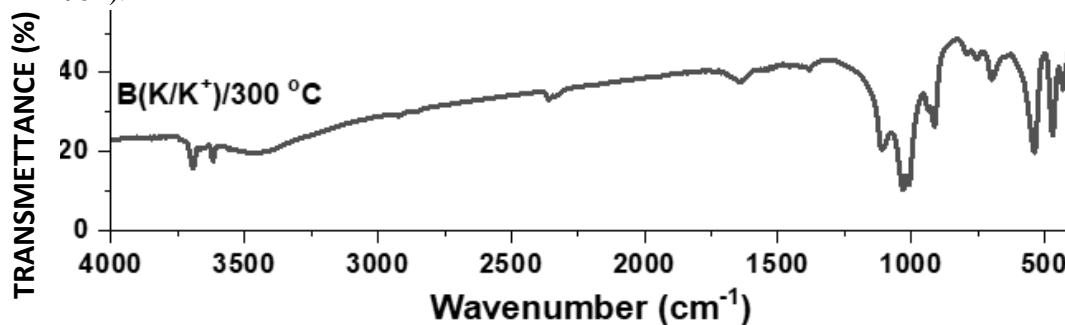

Fig 4 FTIR spectra for base beneficiated catalysts B(K/K⁺)/300°C

From Fig. 4 above, the FTIR spectra of base beneficiated catalyst can be generated. See Table 4 below.

Table 4 FTIR spectra for base beneficiated catalysts

S/N	FT-IR bands (cm^{-1})	Assigned functional group
1	3750-3700	O-H stretching vibrations and water molecules
2	3625	O-H stretching vibrations and water molecules
3	2376	Interlayer water molecules bonded to the hydroxyl ions
4	1625	C=C stretch
5	1375	OH bend
6	1000	C-C vibrations
7	520	Zn-OH translation

From Table 4 above, FT-IR bands (cm^{-1}) 3750 – 3700, 3652 all have O-H stretching vibrations and water molecules which are strong indication of production of methanol. 1625cm^{-1} stretch and 1375cm^{-1} OH bend are all strong indication for production of FAME and then Zn-OH translation 520cm^{-1} enhances the productions of FAME. The presence of many wavelike shape particularly at lower wavelength 520 – 1700cm-1 shows strong productions of FAME. These explains reasons for better performance compared to acid beneficiated catalyst (Millar and Wilkins, 1952).

4. Conclusion

The effect of acid and base beneficiations was investigated on kaolin clay catalyst treated at 600°C and 900°C respectively. The acid beneficiated catalyst were used in transesterification of UCO to produced biodiesel. The optimum variable for acid beneficiated was the catalyst pretreated for 4h with reaction temperature of 120°C, catalyst loading of 3.5wt%., methanol to oil molar ratio of 9:1 and reaction time is 4h give best FAME yield of 67%. The base beneficiated kaolin catalyst pretreated at 600°C for 4h, with temperature reaction of 70°C, catalyst loading of 15wt%., methanol to oil molar ratio of 14:1 and reaction time of 3h gives the best FAME yield of 78%. It can be concluded that base beneficiated catalyst gave a better yield compared with acid beneficiated catalyst.

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