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ORIGINAL ARTICLE

# Biodiesel Production from Waste Cooking Palm Oil using a $K_2O$-$CaO/\gamma$-$Al_2O_3$ Catalyst: Synthesis and Characterization

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## ABSTRACT

This study investigated the synthesis, characterization, and catalytic activity of a $K_2O$-$CaO/\gamma$-$Al_2O_3$ catalyst for biodiesel production from waste cooking palm oil via transesterification process. The catalyst was prepared by wet impregnation and activated at 700°C for 4.5 hours. It was characterized using XRD, FTIR, ICP-OES, and the Hammett indicator method. The stability of the catalyst was analyzed after using for four consecutive cycles by ICP-OES and it was determined that 18% K and 8.5% Ca leached into the reaction media at the end of the fourth cycle. Response surface methodology (RSM) in combination with central composite design (CCD) was used to optimize the operating parameters of the transesterification process. A 96% biodiesel yield was obtained under optimized reaction conditions of 12:1 methanol-to-oil ratio, 5.6 wt% catalyst loading, and 64°C reaction temperature in 3 hours of reaction time. Biodiesel was chemically characterized with $^{13}C$ NMR and $^{1}H$ NMR machine.

***Keywords:*** *Transesterification, Biodiesel, Wet impregnation, supported catalyst, waste cooking oil*

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## 1. Introduction

The search for an alternative renewable fuel is motivated by the depletion of petroleum together with instability in prices, the need for high energy security, heavy environment pollution brought by fossil fuel burning and global warming[1]. Biodiesel which is accepted as an attractive alternative fuel is prepared by transesterification of edible oil, non-edible oil and waste cooking oil with an alcohol in the presence of a catalyst[2]. The main challenge of biodiesel production is its high selling price. In particular waste cooking oil (WCO) is an excellent feedstock for biodiesel production as the use of waste cooking oil as biodiesel feedstock can reduce the cost of biodiesel production. Nevertheless, a vegetable oil subjected to thermal stress during frying can change its chemical and physical characteristics. The amount of heat and water in the frying increases the hydrolysis of triglycerides. Therefore, it causes a growth of the free fatty acids in the WCO. Moreover, oxidation and polymerization reactions cause an increment of the viscosity of waste cooking oil[3].

Direct use of vegetable oil is not applicable to most of actual diesel engines, as the high viscosity would damage the engine. In that case the transformation of the virgin oil to petroleum resembled fuels which is called biodiesel attract worldwide attention. Transesterification of oil is commonly catalyzed by acidic or basic catalysts either in homogeneous or heterogeneous state. Homogeneous catalysts could be basic or acidic. However, acid catalysts require too excess methanol to oil molar ratio, and only works effectively at higher temperature[4]. . Acid catalyzed transesterification reaction would generate more waste from neutralization reaction and are corrosive to the process equipment[5,6]. On the other hand, homogeneous base catalysts can provide higher activity and yield with in short reaction time than acid catalysts. But, the activity of these catalysts highly depend on presence of FFA and water. Also, homogeneous base catalysts are non-reusable and prone to emulsion formation. Biodiesel production process using homogeneous base catalysts includes transesterification of triglyceride followed by a downstream processing. Even though, homogeneous catalysts have managed to give better reaction rate, complicated downstream processing results in low production efficiency, high cost and more energy consumption[4]. To overcome these drawbacks, homogeneous catalysts have been replaced by heterogeneous catalysts. Heterogeneous catalysts have advantages over homogeneous catalysts from both economic and environmental point of view. They are more environmentally friendly as they present lesser waste during separation process. Cost reduction comes from their easier separation from the liquid phase and their long lifetime. Both solid acid and solid base catalysts have been used as catalysts in transesterification reactions. However, solid acid catalyst have demanded high reaction temperature and pressure that are not feasible from the economic point of view[5, 6]. Solid base catalysts present higher catalytic activity for transesterification of oil than solid acid catalysts. A variety of solid base catalysts have been used in transesterification reaction. These catalysts include mostly alkali, alkaline oxides, large-surface-area material supported alkaline oxides, basic zeolites, hydrotalcites and organic base catalysts[4]. Among these alkali and alkaline oxide solid base catalysts, calcium oxide (CaO) has been used widely in transesterification reaction. CaO has been studied due to its high basicity, low solubility in organic solvents, and low price. However, pure calcium oxide catalysts suffer poor mechanical strength which could cause separation problems and prone to leaching. Therefore, there is a need to develop efficient solid base catalysts with a high activity, highly basic, a large-surface-area and a sufficient mechanical strength. Loading effective strong basic elements and supporting on a high-surface area mechanically strong support has been a common and efficient way to find these kinds of catalysts. $Al_2O_3$, $SiO_2$and zeolites are among the most used supports due to their large surface areas, proper porosity, and stable structures. Different kinds of heterogeneous catalyst can be prepared following some methods. Most commonly, Supported and loaded catalysts for transesterification reaction have been prepared using an impregnation method of aqueous solution followed by drying and calcination[7, 8]. Even if several catalyst combinations have been used in biodiesel catalysis before, the exact ratios and the support material (γ-Al2O3), and the specific preparation method for conversion of waste cooking oil is lacking. Thus, this study focusses on the optimization (central composite design) of the reaction conditions (temperature, catalyst loading, methanol-to-oil ratio, reaction time) that lead to significantly improved biodiesel yields from waste cooking oil using a $K_2O$-CaO/ γ-$Al_2O_3$ catalyst. Also, response surface method (central composite design) was employed to optimize transesterification operating parameters.

## 2. EXPERIMENTAL

### Catalyst Synthesis and Characterization

Gamma alumina was prepared from Aluminum nitrate nonahydrate (Al $(NO_3)_3 \cdot 9H_2O$) and urea via a sol gel method[9]. $K_2O$-CaO/ γ-$Al_2O_3$ catalyst was synthesized by employing the method of impregnation: primarily, the measured weight of $CaCO_3$ (a precursor to CaO) (ca. 10%, 20%, 30% and 45% CaO by weight of γ-$Al_2O_3$) was dissolved in 50mL of distilled water under magnetic stirrer at room temperature. Then, the weighed mass of γ-$Al_2O_3$ powder was mixed with $CaCO_3$ solution and stirred over 4h to get CaO precursor uniformly deposited inside the pores and on the surface area of γ-alumina. Following this, $K_2CO_3$ (a precursor to $K_2O$) (ca. 35% $K_2O$ by weight of CaO) dissolved in 20mL of distilled water and added to the early made $CaCO_3$ and γ-$Al_2O_3$ solution. The mixtures were let dried in the oven at 105°C for 24h and at the end they were calcined at 700°C for 4:30h to liberate carbon dioxide, and physically absorbed and chemically bonded moisture. Activation employing calcination provided a catalyst having a composition approximately 35%$K_2O$-(10%, 20%, 30% and 45%) CaO /γ-$Al_2O_3$. All chemicals are of analytical grade and used without modification.

### Testing catalytic activity for catalyst screening

Catalyst screening was performed based on catalytic performance measured in converting waste cooking palm oil to biodiesel. The weight of $K_2O$ was kept constant at 35% by weight of CaO. But, the weight of CaO was varied i.e.10%, 20%, 30% and 45% by weight of γ- γ-$Al_2O_3$. Therefore, $K_2O$-CaO/γ-$Al_2O_3$ catalyst getting different CaO content was carefully tested to measure its catalytic capability in transforming waste cooking palm oil to fatty acid methyl esters at the reaction temperature, reaction time, methanol to oil molar ration, weight of catalyst to oil ratio and stirring rate of 65°C, 3h, 15:1, 6.5% and 480 rpm respectively. The values of those parameters were fixe based on the theoretical assumption of the boiling point of methanol (65 °C) and stoichiometric molar ratio of biodiesel reaction chemistries (3 :1). A Catalyst giving a better yield has been used for all experiments in this study.

### Surface area determination.

The surface area of γ-$Al_2O_3$ and $K_2O$-CaO/γ-$Al_2O_3$ solid catalyst were determined analytically through methylene blue adsorption method. Methylene blue was picked out because of its strong adsorption tendency over the surface of solids. The following formula was used to compute specific surface area:

$$S_g = \frac{N_A}{M_{MB}} q_m \sigma_{MB} \quad (1)$$

Where, $S_g$ is specific surface area($m^2/g$), $q_m$ is the maximum adsorption capacity (mg/g), $N_A$ is Avogadro's number, $M_{MB}$ is the molecular weight of methylene blue and $\sigma_{MB}$ is the area occupied by a single methylene blue molecule. The adsorption capacity obtained from linearized forms of Langmuir equation was used to compute the surface of area of the catalyst and gamma alumina as the area occupied by an adsorbed single methylene blue molecule is known which estimated to be 130 $Å^2$[10]

**FT-IR Analysis.**

Fourier transform infrared (FTIR) spectra analysis of the catalyst was done in the range of 4000-400 $cm^{-1}$ using Fourier transform infrared spectrophotometer (Perkin Elmer Frontier).

**XRD Analysis.**

Monochromatic x-ray (Bruker D8 X-ray diffractometer equipped with a Cu anode) as a source of radiation containing of Cu-Kα (λ = 1.5405 Å) with 40 kV power and 35 mA current was directed toward the sample. Each sample was scanned within the 2θ range of 10°-60° and intensity was measured.

**Basic strength of the catalyst.**

The basic strength of $K_2O$-$CaO/\gamma$-$Al_2O_3$ catalyst was determined by employing Hammett indicator experiment. The Hammett indicators used were phenolphthalein (pKBH+ = 9.3) and aniline (pKBH+ = 27). The basic strength of the catalyst was taken to be higher than the Hammett indicator that got a change in color[11].

**Biodiesel synthesis and characterization**

**Transesterification of waste cooking palm oil** : The experiments have been performed in a 250mL three necked round bottom glass reactor equipped with a water-cooled reflux condenser. Fifteen grams of waste cooking palm oil has been heated up to a desired temperature by the hot plate and stirred at 480 rpm by a magnetic stirrer; then the reaction was started by adding a desired amount of methanol and catalyst to the reactor, and stayed to react for 3hs. After the reaction was completed, catalyst, glycerol and biodiesel were separated in a separator funnel. Trace amount of methanol left in biodiesel was liberated off using a rotary evaporator.

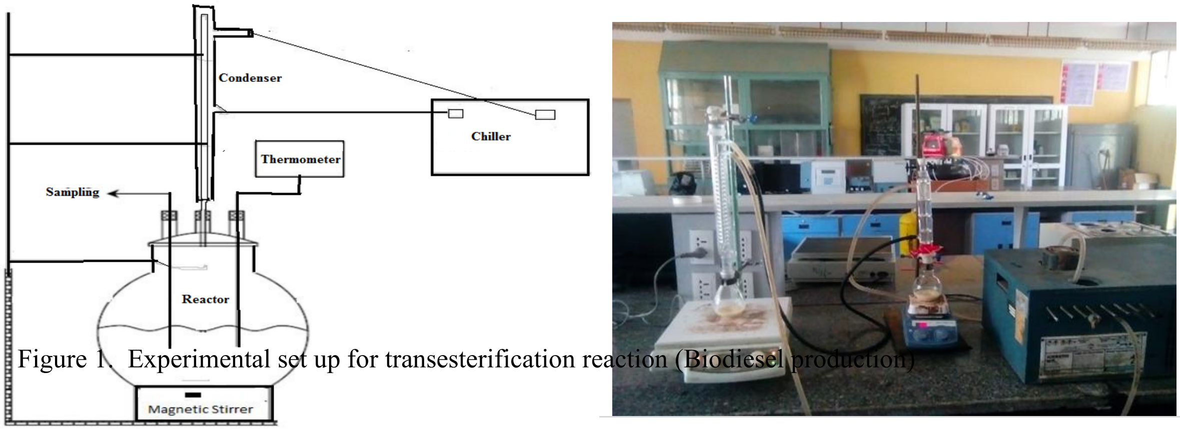


Figure 1. Experimental set up for transesterification reaction (Biodiesel production)

### Evaluating catalyst reusability.

The reusability of $K_2O$-$CaO/\gamma$-$Al_2O_3$ catalyst was tested to examine how many times could it keep its catalytic activity in transforming waste cooking palm oil to biodiesel at a high level of performance. Reusability was tested using the same catalyst in two ways i.e. using the catalyst repeatedly without applying catalyst reactivation and by involving reactivation of used catalyst. All the reusability tests have been performed at methanol to oil molar ratio, catalyst to oil mass ratio and temperature of 15:1, 6.5wt% and 65ºC respectively for 3h reaction time.

**Catalyst leaching** $K_2O$-$CaO/Al_2O_3$ solid base catalyst under operating conditions of methanol to oil molar ratio of 15:1, catalyst loading of 6.5 wt.% and reaction temperature of 65°C, was repeatedly used for four successive runs to check out if it can maintain its catalytic activity. Then, the leaching test of $K_2O$-$CaO/Al_2O_3$ catalyst was determined by ICP-OES (Optima 8000) instrument. Five catalyst samples were prepared for ICP-OES analysis. While the first sample was fresh catalyst, the rest were the catalyst used for the first, the second, the third and the fourth cycles

### Physical and fuel properties of biodiesel

Density (ASTM D1298), kinematic viscosity (ASTM D445), flash point (ASTM D93), pour point (ASTM D 97), saponification number (ASTM D94), water and sediment (ASTM D2709), copper strip corrosion (ASTM D130) and calorific value (ASTM D240) were determined according to ASTM standard procedures. Eevera T. et al. method was employed to determine cetane number[12]. Iodine number was determined using Wijs method.

### Chemical properties of biodiesel

### $^1$H-NMR and $^{13}$C-NMR study.

NMR analysis of the biodiesel sample obtained from waste cooking palm oil was performed using BRUKER Spectrospin 300 MHz spectrometer equipment.

### Design of experiment

Response surface methodology together with central composite design is an efficient way in modeling and analysis of quadratic responses with quantitative factors when the aim is optimization of the responses[13]. The experiment was designed using Design Expert software (version 7.0.0), which employs response surface methodology (RSM) combined with a central composite design. The objective of this study was to optimize the reaction conditions to enhance the yield of biodiesel. The factors selected for this study were methanol to oil molar ratio, catalyst to oil weight ratio and temperature, and biodiesel yield was the only response of the transesterification reaction(Table1).

**Table 1: Natural and coded variables**

| Natural variable | |
|---|---|
| 1. Methanol to oil molar ratio | Coded variable |
| 9:1 | -1.68 |
| 12:1 | -1 |
| 15:1 | 0 |
| 18:1 | 1 |
| 21:1 | 1.68 |
| 2. Catalyst to oil %wt. | Coded variable |
| 2.5 | -1.68 |

| | |
|---|---|
| 4.5 | -1 |
| 6.5 | 0 |
| 8.5 | 1 |
| 10.5 | 1.68 |
| 3. Temperature | Coded variable |
| 45 | -1.68 |
| 55 | -1 |
| 65 | 0 |
| 75 | 1 |
| 85 | 1.68 |

## 3. RESULTS AND DISCUSSION

### Catalyst Synthesis and Characterization

### Catalyst Screening

The yields of biodiesel obtained were 45.3%, 83.2%, 95.6% and 91.7% for 10, 20, 30 &45%CaO supported on $\gamma$-$Al_2O_3$ catalyst respectively at 35%$K_2O$ load. At low level of CaO loading the yield was smaller due to the absence of sufficient catalyst active sites. On the other hand, loading too much CaO over the support surface leads to the reduction of catalyst surface area which is responsible to the reduction of the yield. Therefore, for the rest of all experiments the catalyst with the composition of 35%$K_2O$-30%CaO/$\gamma$-$Al_2O_3$ has been chosen to be used as it has shown a better catalytic activity in converting waste cooking palm oil to biodiesel.

### Surface area of the catalyst

In this study, the Langmuir equation was used to investigate the adsorption isotherm of methylene blue to determine parameters that helped to evaluate the specific surface area of the support ($\gamma$-$Al_2O_3$) and the catalyst. The results are presented in table 2.

Table 2. Parameters of Langmuir adsorption equation and specific surface areas

| Dye | $\gamma$-$Al_2O_3$ | | | $K_2O$-CaO/ $\gamma$-$Al_2O_3$ | | |
|---|---|---|---|---|---|---|
| | $q_m$(mg/g) | b(L/mg) | $S_g$($m^2$/g) | $q_m$(mg/g) | b(L/mg) | $S_g$($m^2$/g) |
| MB | 69.54 | 0.76 | 170.25 | 23.15 | 0.15 | 56.13 |

As it is clearly seen in Table 2, the adsorption capacity of $K_2O$-CaO/ $\gamma$-$Al_2O_3$ solid catalyst was smaller than $\gamma$-$Al_2O_3$'s. Loading the active catalyst on the support got reduced significantly the surface area due to addition of $K_2O$ and CaO into the many pores of gamma alumina. This gives an evidence wherefore loading too much catalyst on the support reduces the catalyst surface area i.e. smaller surface area is often related to a reduced catalytic activity.

### FT-IR analysis.

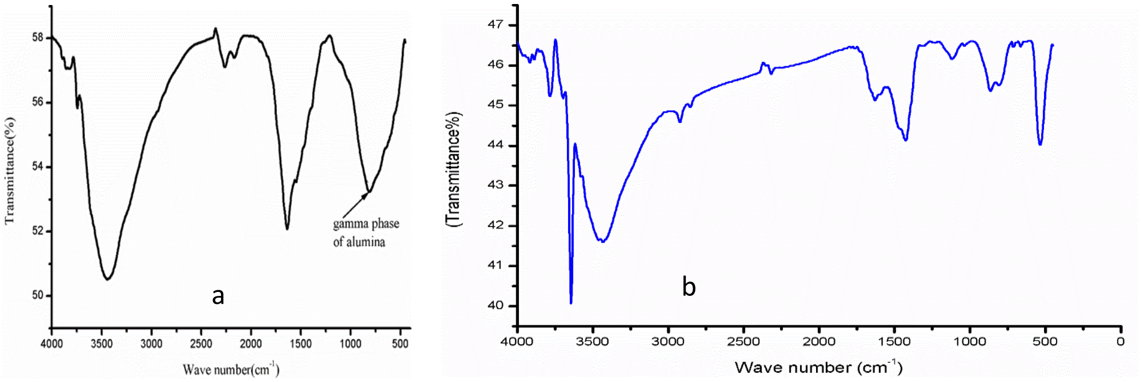
FT-IR spectrum of $\gamma$-$Al_2O_3$ powder is shown in Fig.2a. The band at 803 $cm^{-1}$ is specifically marked out to -AlO4 which indicates $\gamma$-$Al_2O_3$ contains a tetrahedral structure. This peak is attributed to the symmetric stretching vibrations of the Al–O–Al bonds[14]. The sets of bands detected from 3800 to 2700 cm$^{-1}$ is imputed to-OH stretching in which its source may probably belong to the different chemical compounds. As shown in Fig.2a, the band at 1633cm$^{-1}$ was resulted from the bending vibration of-OH picked up from the moisture. The small band centered at 1546 cm$^{-1}$ was ascribed by chemical sorption of $CO_2$, CO, $CO_3^{2-,}$ or $HCO_3^{1-.}$

The peaks in 400-1000 cm$^{-1}$ range (i.e. 803 cm$^{-1}$) has confirmed the formation of the γ-phase of alumina[14] as shown in Fig. 2a. The other peaks in the region of 2262 cm$^{-1}$ and 2166 cm$^{-1}$ may be due to an impurity from urea and aluminum nitrate nonahydrate left in the gamma phase. As shown in Fig.2b, the bands centered at 866 cm$^{-1}$ belongs to the bending vibrations of the Al–O–Al bonds[14] and the band at 1427cm$^{-1}$ belongs to C–O bonds from incompletely decomposed carbonate in CaO/γ-$Al_2O_3$. The band in the region of 500 cm$^{-1}$ i.e. 534cm$^{-1}$ and 875cm$^{-1}$ imputed to Ca–O bonds would really describe existence of CaO[15].

The strong and intense band at 3643cm$^{-1}$ corresponds to the O–H stretching vibration imputed to OH groups from calcium hydroxide. The manifold bands from 3800 to 2700 cm$^{-1}$ *(*Fig.2b*)* is ascribed to OH stretching which has been brought into existence from various sources into the surface of the activated CaO/$Al_2O_3$ i.e. mainly from absorbed moisture from the humid environment and the existed calcium hydroxide formed when CaO gets contacted with moisture. However, the CaO/$Al_2O_3$ catalysts showed intense and broad bands in the region of 1400-1600 cm$^{-1}$, which revealed the existence of mono and bicarbonates[16].

Fig. 2c has shown IR spectra of $K_2O$-CaO/γ-$Al_2O_3$. The bands from 3800 to 2700 cm-$^{1}$ is attributed to -OH stretching originated from manifold sources. The band located at 1630 cm$^{-1}$ is resulted from the bending vibration of OH. The existence of the band at 3458 cm$^{-1}$ is the results of–OH stretching vibration due to absorption of moisture. Another band at 3642 cm$^{-1}$ is the result of OH in Ca $(OH)_2$ formed when water is adsorbed by calcium oxide powder. The small band at 712 cm$^{-1}$ is due to Ca–O bond that confirms the presence of calcium oxide in the catalyst. Intense band at 1412cm$^{-1}$ is the results of C–O stretching from calcium carbonate.

The peak of K-O stretching vibration at 467cm$^{-1}$ is the confirmation to the presence of $K_2O$ in the catalyst complex[17, 18].In addition, there are two bands at around 1540 and 1400cm$^{-1}$, which are attributed to the vibrations of $CO_2$, CO, $CO_3^{2-}$ ions[19]. In the spectrum of the catalyst shown in Fig.2c, the band at 841cm$^{-1}$ is assigned to -AlO4 with tetrahedral coordination that indicates the presence of Al-O-Al framework[19].



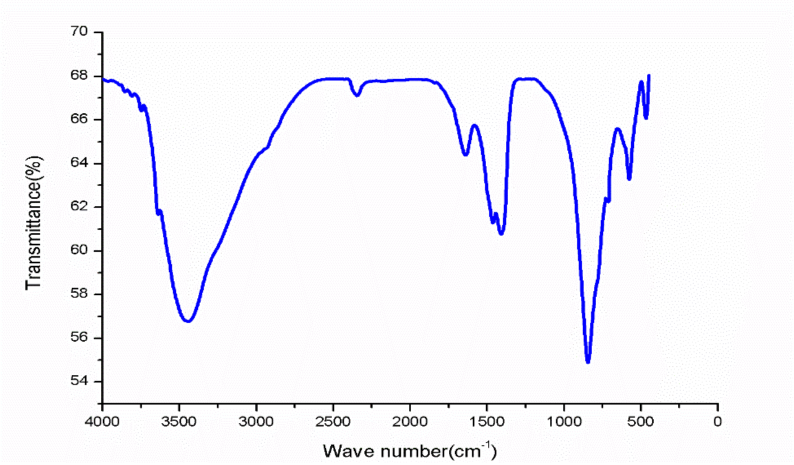


Figure 2. IR spectra of a) γ-$Al_2O_3$, b) CaO/γ-$Al_2O_3$, c) $K_2O$-CaO/γ-$Al_2O_3$ catalyst

**X-ray diffraction (XRD).**

X-ray diffraction (XRD) analysis has been conducted on activated catalyst to assure the existence of potassium oxide, calcium oxide and gamma alumina in the catalyst complex. The XRD patterns of $Al_2O_3$, CaO/$Al_2O_3$ and $K_2O$-CaO/$Al_2O_3$ are shown in Fig.3. The XRD pattern of gamma $Al_2O_3$ shows the diffraction peaks at 25.5, 37 and 46 of 2θ [14]. However, these peaks are not quite clear to mean that gamma alumina made was more amorphous. Powder X-ray diffraction typical peaks found at 2θ = 32.23, 37.34 and 53.93, belong to CaO supported on gamma alumina with corresponding d-values of 2.75, 2.39, and 1.69 respectively[20].

As shown in fig.3 the diffraction pattern displays a distinguishing feature of peaks at 18°,34°, 47.2°and 50.8° correspond to calcium carbonate ($CaCO_3$) and diffraction peak at 2θ of 29.4° might belong to calcium hydroxide ($Ca(OH)_2$)[21]. The absence of potassium oxide peaks in the $K_2O$-CaO/γ-$Al_2O_3$ pattern indicates that crystallites are too small and dispersed[20].

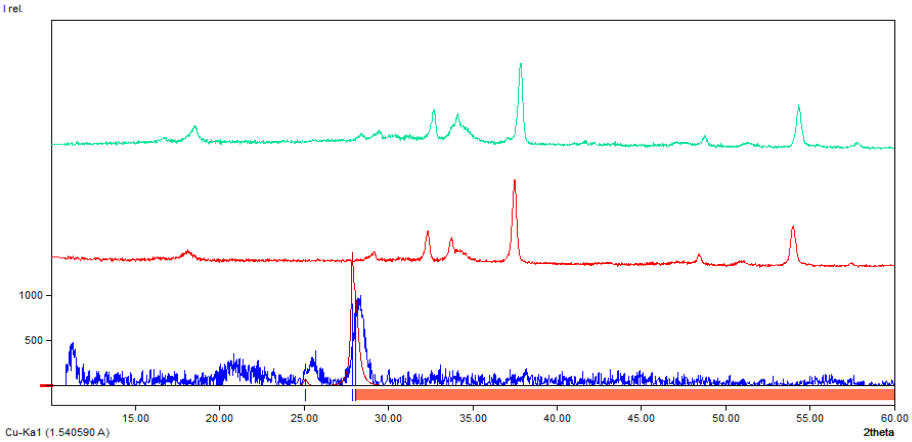


Figure 3. X-ray diffraction (XRD) patterns of γ-$Al_2O_3$ (blue pattern), CaO/ γ-$Al_2O_3$ (red pattern) and $K_2O$-CaO/ γ-$Al_2O_3$ (green pattern

**Basic strength of the catalyst**

The basic strength of the bare CaO catalyst is (8.2 < pKBH+< 10.1) determined by using Hammett indicators[22]. The basic strength of potassium oxide doped calcium oxide supported on gamma Alumina lied with in 9.3 and 27 (9.3 <pKBH+ <27). This showed that dopant $K_2O$ improves the basic strength of CaO which may be attributed to the increase in the number of basic sites in the lattice. An increase in the number of basic sites is supposed to occur by means of the exchange of $Ca^{+2}$ to K+ during calcination, helping to the generation of $O^{-2}$ anion or it is believed to be caused by the formation of O− centers via substitution of $Ca^{+2}$ ions by $K^+$ ions into calcium oxide lattice. The base strength of every catalyst has to be as high as enough in such a way that a proton gets abstracted from the methanol to make carbonyl group attacking methoxy anion to mean that base strength is more important factor[22].

## Characterization of Biodiesel

To examine the fuel properties of biodiesel produced from waste cooking palm oil: density, viscosity, flash point, iodine number, cetane number, copper strip corrosion, acid value, calorific value, pour point, cloud point, water and sediment and sulphated ash were determined. The values of these fuel properties are found to be acceptable according to Biodiesel ASTMD6751 and Biodiesel EN14214 standards. The extent of waste cooking palm oil conversion and the presence of fatty acid methyl esters in biodiesel was confirmed using $^1$H-NMR and $^{13}$C NMR analysis.

### Physicochemical properties of fuel.

Table 3. Fuel properties of waste cooking palm oil biodiesel: methanol-to-oil ratio=12:1, catalyst loading =5.6 wt%, and reaction temperature = 64°C

| Fuel properties | Diesel | Biodiesel ASTMD6751 | Biodiesel EN14214 | Test method(ASTM) | This study |
|---|---|---|---|---|---|
| Density 15ºC(kg/m$^3$) | 850 | 880 | 860-890 | D1298 | 875 |
| Viscosity at 40ºC(mm$^2$/s) | 2.6 | 1.9-6 | 3.5-5 | D445 | 4.57 |
| Cetane number | 40-55 | Min. 47 | Min. 51 | D613 | 57 |
| Calorific value(MJ/kg)) | 42-55 | - | 35 | D240 | 41.44 |
| Pour point(ºC) | -35 | -15 to 16 | | D97 | 5 |
| Copper strip corrosion(3h@100ºC) | 1 | Max. 3 | Min. 1 | D130 | D1b |
| Water and sediment(%V) | 0.05 | Max. 0.05 | Max 0.2 | D1796 | 0.015 |
| Sulphated ash(%w/w) | | Max.0.02 | 0.02 | D874 | 0.0011 |
| Flash point(ºC) | | 60-80 | | D130 | 90 |

### Chemical Properties

### $^1$H-NMR Analysis

$^1$H-NMR was used to figure out the extent of waste cooking palm oil conversion and points out the presence of fatty acid methyl esters in biodiesel. In that case, the amplitude of $^1$H-NMR signal is in proper proportion to the number of hydrogen atom contained by the molecule. As shown in Fig.4, the occurrence of methyl esters in biodiesel is confirmed by the presence of two distinct peaks. The characteristic signal of methoxy proton (CH3O CO−) due to $-OCH_3$ was noticed as a singlet peak at 3.58 ppm and as a triplet signal of α-$CH_2$ protons at 2.22 ppm are cognizant that these are definite chemical structures to biodiesel in $^1$H-NMR spectrum. These two peaks are the distinct peaks for confirmation of methyl esters present in the biodiesel. A triplet signal at 0.82($-$ $CH_3$) ppm is accepted to be a terminal methyl proton where as a strong doublet signal(($CH_2$) n) set up at 1.23 ppm belongs to methylene protons and a small peak located at 5.26 ppm thanks to the presence of olefinic hydrogen of olefins (−CHCH). Without doubt the lack of signals from 3.9 to 4.5 ppm has shown absence of glycerol and the protons of allylic carbons of unsaturated FAMES ($-CH_2CH_2CHCH-$) from 2–2.1 for good in the biodiesel. Very small peak as expected to be at 2.7ppm correspond to unsaturated FAMES bis-allyl carbons ($-CHCHCH_2CHCH-$)[23]. A triplet signal at 1.55 ppm is due to β-carbonyl methylene protons in biodiesel[23, 24].

$^1$H-NMR be able to find out the conversion of waste cooking palm oil to methyl esters or the yield of biodiesel. The pertinent signals picked for integration were methoxy group in the methyl esters set up at 3.58 ppm and α-carbonyl methylene protons at 2.22 ppm[25].

The equation used to quantify the yield of transesterification reaction is:

$$C = (2A_{Me})/(3A_{\alpha\text{-}CH2}) * 100 \qquad (2)$$

Constants 3 and 2 from the above equation are derived from the fact that methanol derived carbon has three undetached protons and methylene carbon contains two protons. Integration value are determined from response signals in a spectrum by electronic configuration[24].

Using the equation (4.3):

$$C = (2*18.79)/(3*13.08) *100$$

$$C = 96\%$$

Therefore, the yield of transesterification reaction of waste cooking palm for this study using the above equation was found to be 96%.

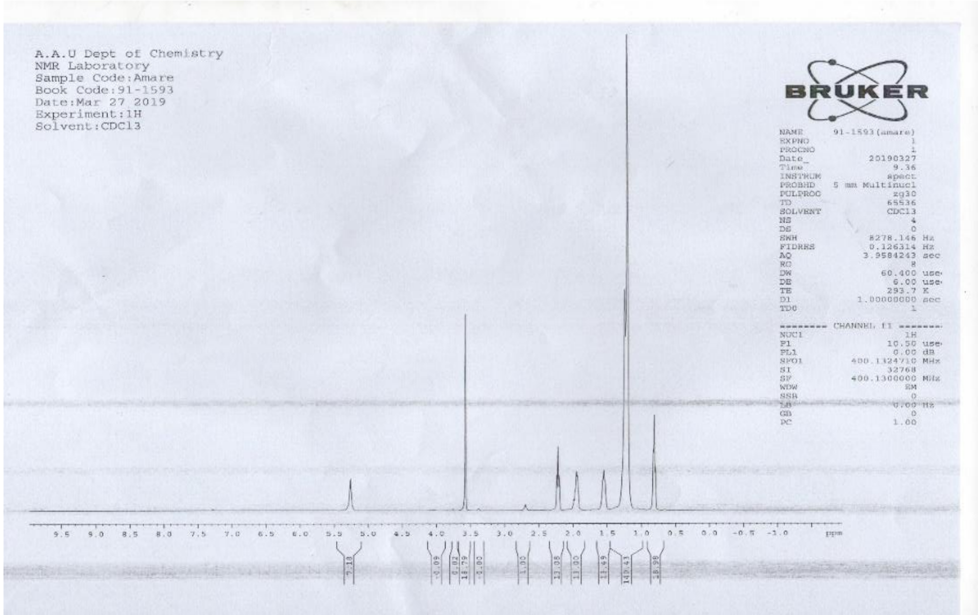


Figure 4. $^{1}$H-NMR result of waste cooking palm oil biodiesel: methanol-to-oil ratio=12:1, catalyst loading =5.6 wt%, and reaction temperature = 64°C

### $^{13}$C NMR analysis.

The $^{13}$C-NMR spectrum of waste cooking palm oil biodiesel is shown in Fig.5, which displays the determinant signals (−COO−) and C−O at 173.85 and 51.09 ppm as it is the distinct peaks to assure the presence of methyl esters in the biodiesel. This is related to carbon of carbonyl ester and methoxy group respectively. These signals are indicators to confirm the transformation of waste cooking palm oil to biodiesel by transesterification reaction. The signal placed at 13.94 ppm is due to terminal carbon of methyl groups and signals set up from 22.49 to 33.89 corresponds to methylene carbons found in the backbone of methyl esters of biodiesel chain. As show in Fig.5 a number of different singlet peaks between 127.79&129.92 ppm indicates the presence of unsaturated methyl esters in waste cooking palm oil biodiesel[26].

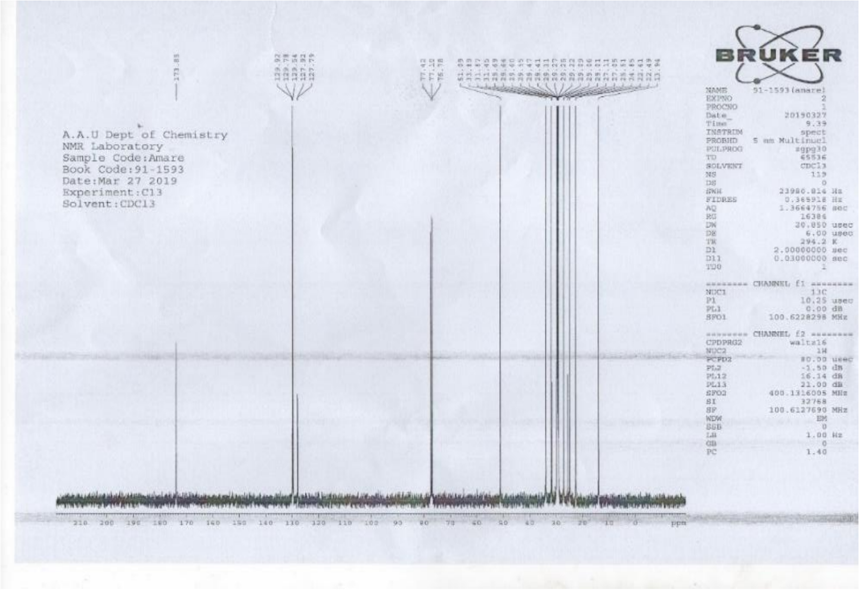


Figure 5. $^{13}$C-NMR spectrum of waste cooking palm oil biodiesel: methanol-to-oil ratio=12:1, catalyst loading =5.6 wt%, and reaction temperature = 64°C

## Effects of operating parameters on biodiesel yield

### Methanol to oil molar ratio.

Stoichiometry of the reaction clearly indicates that only three moles of methanol is demanded for every mole of triglyceride[27]. But transesterification reaction requires excess moles of methanol to shift the equilibrium to the right as the reaction is reversible. In this study a methanol to oil molar ratio of 12:1 was found to be the optimal value. Although higher methanol to oil molar ratio managed to give better results, getting surpassed optimal level of methanol to oil molar ratio caused lower biodiesel yield to occur as shown in Fig.6. This might be due to the dissolution of glycerol by-product in excessive methanol to form an emulsion which inhibits the reaction of methanol with oil in the presence of catalyst and due to catalyst leaching by excess methanol[23]. When glycerol is dissolved by excess methanol, it would drive the equilibrium back to the left, thereby lowering the yield of esters[28].

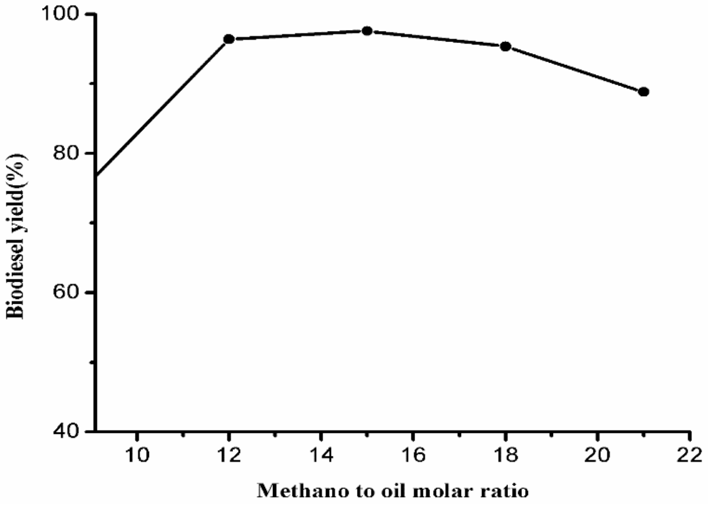


Figure 6. Effects of methanol to oil molar ratio on biodiesel yield:, catalyst loading =5.6 wt%, and reaction temperature = 64°C

**Temperature:** As it can be seen in the Fig.7, the temperature significantly increased biodiesel yield for the reason that the kinetic energy of the reactants becomes adequate enough relatively at higher reaction temperature. Furthermore, the yield of methyl ester increases with raising the temperature can also be attributed to the enhanced miscibility of oil-methanol, and viscosity of the oil decreases resulting into better contact of reactants. However, elevating temperature to a greater extent beyond optimal value has not given biodiesel yield as demanded as can be clearly seen in Fig.7. This could be attributed to the fact that at higher temperature (i.e. beyond 65°C) leads methanol vaporization and form bubbles which might inhibit the interfacial reaction[27]. The actual volume of methanol in the reaction media will reduce the interaction time of immiscible phases resulted in lower biodiesel yield[23].It also provide inadequate condensation of gas phase methanol into the reactor to lower actual acting volume of methanol at any time in the reaction media which consequently affect the reaction equilibrium[29].

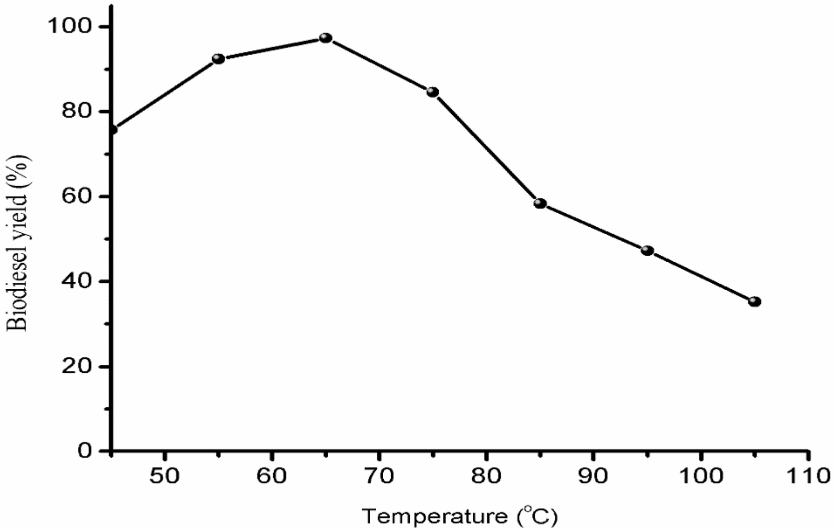


Figure 7. Effects of temperature on biodiesel yield: methanol-to-oil ratio=12:1 and catalyst loading =5.6 wt%,

**Catalyst loading**:

The increase in catalyst loading as shown in Fig.8 has increased biodiesel yield. This is attributed to the availability of sufficient number of active sites over the catalyst. Many reports revealed that biodiesel yield reached plateau when the catalyst loading exactly reached optimal level. Hence, letting further reaction to proceed might bring down the yield of biodiesel due to the increase in viscosity of the reaction media as clearly seen in Fig.8. Furthermore, mass transfer effect of solid catalyst on the reaction media would be one of the reasons wherefore the reaction does not reach at completion. The reaction medium consists of the two phase system (heterogeneous catalyst and immiscible reactants i.e. methanol and palm oil), in which the reaction would be slowed up when the catalyst loading is overreached as the reaction is usually a diffusion-controlled system. Beyond what is already stated adding more than enough catalyst can also cause to develop emulsion at time of transesterification reaction and brings difficulty during separation process as well[28].

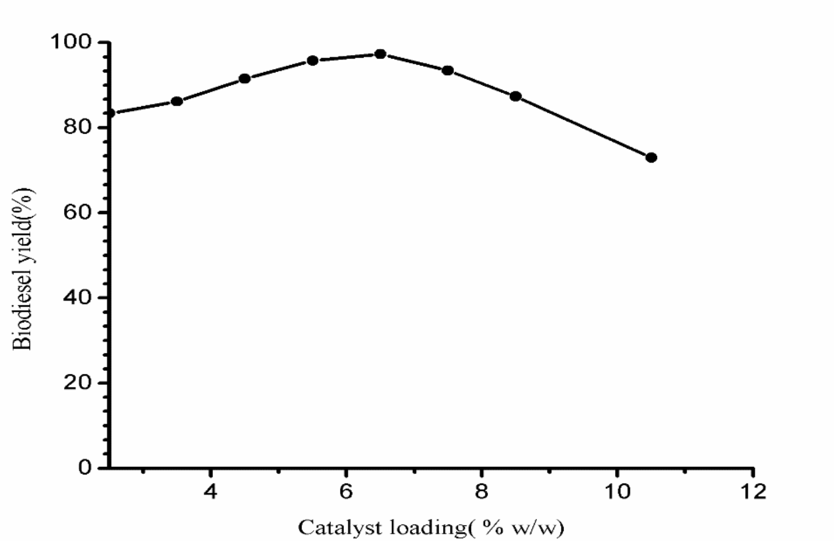


Figure 8. Effects of catalyst loading on biodiesel yield

**Effects reaction time at optimal condition*:*** methanol-to-oil ratio=12:1 and reaction temperature = 64°CTransesterification process depends on reaction time. However, longer reaction time does not always increase the conversion but favors the hydrolysis of esters which results in a reduction of product yield[30]. As observed in Fig.9, transesterification experiments for waste cooking palm oil were carried out between 0.5h and 8h reaction time. The yield of waste cooking palm oil rapidly increased with the reaction time ranged between 0.5h and 2.5h. For waste cooking palm oil transesterification reaction time of 2.5h for $K_2O$-CaO/γ-$Al_2O_3$ catalyst was sufficient to attain optimum biodiesel yield as shown in Fig.9 and remained constant up to 5h and then actually decreased very slowly after 5h reaction time because of the dissolution of formed glycerol in methanol for longer hours of reaction time, the portion of catalyst changed into calcium soap due to the possibility of reaction with free fatty acids, loss of biodiesel due to decomposition and during separation process[11].

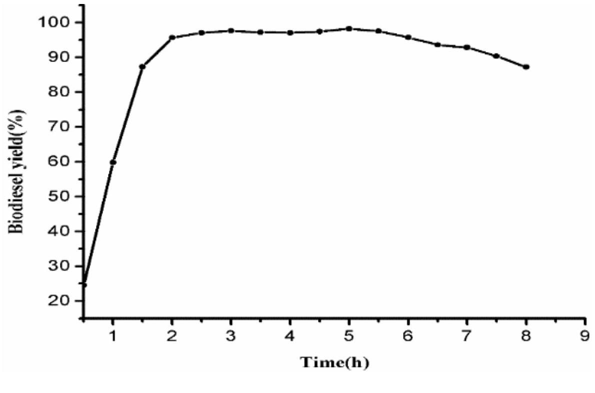


Figure 9. Effects of reaction time at optimal condition on biodiesel yield: methanol-to-oil ratio=12:1, catalyst loading =5.6 wt%, and reaction temperature = 64°C

**Biodiesel Yield Optimization with Response Surface Method**

A response surface methodology was used to develop a biodiesel model aimed at maximizing biodiesel production. The model's accuracy was assessed by comparing predicted yields with actual experimental results. The surface response optimization occurs at methanol-to-oil ratio of 12:1, catalyst loading of 5.6 wt%, and reaction temperature of 64°C. Multivariable regression analysis of data got found the following second-order polynomial equation with the determination coefficient (R-squared = 0.98 and adjusted determination coefficient (Adj R-squared=0.97):

$$\text{Yield}=-444.97+19.15M+15.95C+11.46T+0.68MC-0.065MT-0.19TC-0.68M^2-1.18C^2-0.075T^2$$

(3)

Where, M is methanol to oil molar ratio, C is catalyst to oil mass ratio and T is temperature.

The response surface and interaction effect plots of biodiesel yield depicted in Fig.10 point out the interaction effects of temperature, methanol to oil molar ratio and catalyst loading in biodiesel yield. Interaction of methanol to oil molar ratio with catalyst loading (M-C) and catalyst loading with temperature (C-T), methanol to oil molar ratio with temperature(M-T) and the square of each factor have statistically significant effect on biodiesel yield at the 95% confidence level. The interaction effect of temperature with methanol does not have as strong interaction effect as temperature with catalyst loading and methanol with catalyst loading do have. As most of the previous studies have stated catalyst loading, methanol to oil molar ratio and temperature have positive effect on biodiesel yield.

As it can be seen in Fig.10a&b at the low level of methanol to oil molar ratio as levels of the catalyst loading and temperature go to the optimal level up the yield reached a plateau. This biodiesel yield increment ends up somewhere at the optimum level and has begun getting down the yield back with an increase in the temperature and catalyst loading beyond optimum level attributed to the rise in reaction medium viscosity and the non-availability of sufficient methanol in the reactor respectively.

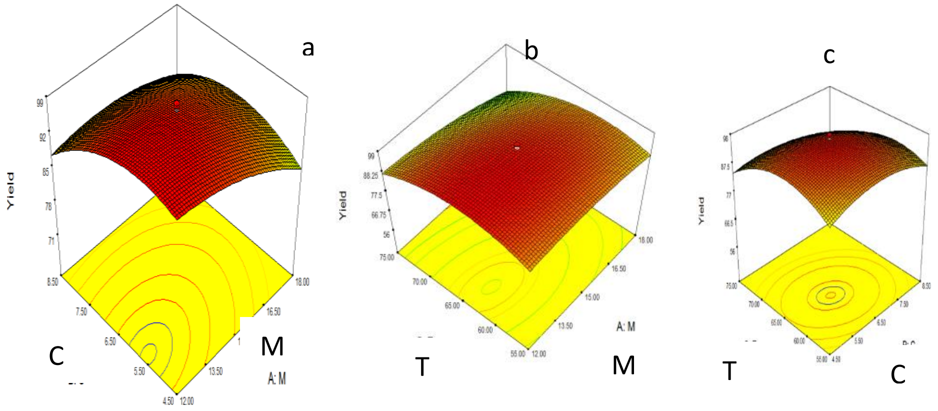


Figure 10. Response surface plots of: a) methanol to oil molar ratio with catalyst loading (M-C), b) methanol to oil molar ratio with temperature, c) catalyst loading with temperature (C-T)

As shown in Fig. 10c, it was found interesting that increasing catalyst loading together with temperature improved the yield vehemently due to the increase the number of active sites and the increase in kinetic energy of reactants.

**Evaluation of Catalyst Reusability**

It was found that the yield of biodiesel over the fresh catalyst was 96%. However, the biodiesel yield was 61.45% at the third cycle without employing reactivation and 69.8% at the fourth cycle by employing reactivation (i.e. calcination) after the end of each cycle. As shown in Fig.11, as the number of reaction cycle increases, biodiesel yield reduction is ascribed to the decrease in basic strength and amount of basic sites of over and over used $K_2O$-$CaO/\gamma$-$Al_2O_3$ catalyst. Catalytic activity may also decline when catalytic active surface is surrounded by poisons which ultimately reduce the contact of catalytic surface and reactants. As clearly seen in Fig.11, reactivating the catalyst can tremendously improve the yield of biodiesel as calcination has burnt impurities off from the active sites of the catalyst.

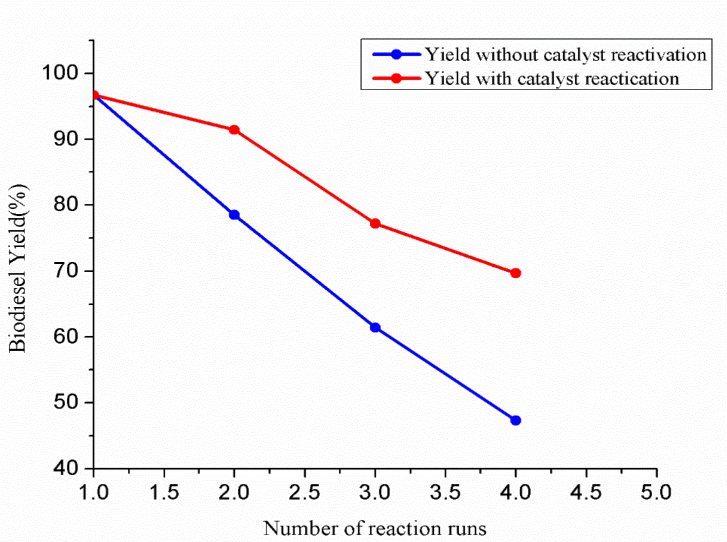


Figure 11. Evaluation newly prepared K2O-CaO/γ-Al2O3 catalyst reusability

## Catalyst Leaching

It was determined that a slight reduction in catalytic activity of $K_2O$-$CaO/Al_2O_3$ catalyst came to pass to give 96% biodiesel yield in the first run, 91.4% in the second run, 77.2% in the third run and 69.8% in the fourth run. The gradual decrease in catalytic activity of this recycled catalyst could be brought about by deactivation due to poisoning of active sites by the reaction mixtures, that can be reversible, and leaching of the active phase, that is irreversible, that lowers the number of active sites, in consecutive runs to the reaction media. $K_2O$-$CaO/Al_2O_3$ Catalyst leaching was explained by the leaching of $K^+$ and $Ca^{+2}$ into the reaction media during the reaction. The amount of calcium and potassium remained after the first and fourth cycles were measured to be 3.56mmol/g and 2.97mmol/g, for K and 5.43mmol/g and 5.03mmol/g for Ca respectively as shown in Table 4. These results provided an evidence that one of the main causes for the decrease in catalyst activity between consecutive runs are associated with $K^+$ and $Ca^{+2}$ leaching[31, 32]. The leaching of $K_2O$-$CaO/Al_2O_3$ solid catalyst was not too significant (can be reused more than four times) if the required catalyst loading is put into the reaction in each successive runs.

Table 4. Elemental analysis by ICP-OES of the fresh and reused $K_2O$-$CaO/Al_2O_3$

| Elements analyzed | Fresh catalyst | Reused catalyst | | | |
|---|---|---|---|---|---|
| | | 1st run | 2nd cycle | 3rd cycle | 4th cycle |
| K(mmol/g) | 3.62 | 3.56 | 3.44 | 3.23 | 2.97 |
| Ca(mmol/g) | 5.5 | 5.43 | 5.33 | 5.2 | 5.03 |

## 4. Conclusion

In this work, 35%$K_2O$-30%CaO/γ-$Al_2O_3$ solid heterogeneous base catalyst prepared via wet impregnation and calcined at 700°C for 4:30h in the furnace showed an excellent catalytic performance in transesterifying waste cooking palm oil. Based on a detailed inspection using response surface methodology (central composite design), the optimal operating parameters for transesterification of waste cooking palm oil to biodiesel for a well agitated reaction over a period of 3h were determined to be methanol to oil molar ratio of 12:1, catalyst loading of 5.6wt% and temperature of 64°C. At this optimal operating condition, the catalyst gave a maximum biodiesel yield of 96 %.

ICP-OES analysis of a recycled catalyst confirmed that leaching of the K and Ca active species from $K_2O$-CaO/γ-$Al_2O_3$ increased with the number of successive cycles. The leached active species came from the attack of the reaction media on $K_2O$ and CaO species found at the surface of the gamma alumina. An excellent catalytic capability for the most part to this catalyst attributed to heterogeneous catalytic performance though it cannot be winnowed out that homogeneous active species originating from leached ions did some homogeneous activity in transesterification reaction. This implies that this catalyst is relatively stable in the transesterification reaction of waste cooking palm oil to biodiesel. The transformation of waste cooking palm oil to biodiesel was affirmed by $^1H$ NMR and $^{13}C$ NMR analysis. The yield of 35%$K_2O$-30%CaO/γ-$Al_2O_3$ catalyzed transesterification of waste cooking palm oil biodiesel obtained at optimum operating conditions determined from $^1H$ NMR result was 96%.. The synthesized Biodiesel was characterized for the kinematic viscosity (4.57 $mm^2/s$), density (875 $kg/m^3$), pour point (5°C), flashpoint (90°C) and acid value (0.2 mg KOH/g), calorific value (41.44MJ/kg), cetane number (57), copper corrosion (1b), ash and sulphated ash (0.0011%w/w) suggesting as an excellent candidate for fuel application.

## Acknowledgment

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