# Effect of process variables on the transesterification process of palm oil sludge to biodiesel


## Abstract

In this research work, the optimum process variables (catalyst, methanol to oil ratio and reaction time) for transesterification of palm oil sludge (POS) to biodiesel were studied. The transesterification process was carried by mixture of palm oil sludge, methanol and catalyst with the help of magnetic stirrer at 300 rpm and at temperature of 60$^{o}$C. The catalyst used for the process was potassium hydroxide (KOH). One-Factor-at-A-Time was used to select the possible optimum levels of process variable that gives high biodiesel yield. The study was evaluated by five levels  of oil-to-methanol molar ratio (1:1 – 12:1), catalyst (0.1- 2 %) and reaction time (30 – 150 min).The optimum process variables for transesterification of palm oil sludge (POS) to biodiesel were methanol to oil molar ratio of 12:1, catalyst loading of 1.5wt% and reaction time of 30 min. An optimum biodiesel yield of 61.2% was obtained with reaction parameters such as a methanol to oil ratio of 12: 1, catalyst loading of 1.5 wt% and reaction time of 30 min. The biodiesel produced from transesterification of palm oil sludge meets the EN 14214 and ASTM 6751 standard



KEYWORDS: Biodiesel, Palm Oil Sludge, Transesterification, Catalyst and Methanol


## Introduction

Human activities are largely dependent on energy and due to the increase in population, there has been consistent demand in every arena for energy, all these resulted into high price of non-renewable energy (45). Production of fossil fuel causes some many problems such as human health problem, environmental degradation, global climate change, emission of greenhouse gases etc. ( 7; 29) . Increase in growth of the economy, consumption rate of energy, depleting of fossil fuel and negative effect of fossil fuel on the environment  led to search for alternative fuel in both developed and underdeveloped countries. Bio-diesel has been considered as one of the alternative energy that can replace fossil fuel (29; 37 ; 41). Biodiesel, which is also called mixture of fatty acid methyl esters (FAMEs) or fatty acid ethyl ester (FAEE) has been designed as one of the most renewable fuel and alternative fuel for diesel engine, it has many advantages over petroleum diesel, as it is a clean renewable fuel, biodegradable, nontoxic and produces less air pollutants with a lower smoke, airborne particle and carbon monoxide (17). Biodiesel can be used in diesel engines without requiring engine modification, its characteristics are similar to petroleum-based diesel fuels, it can be produced from edible and non-edible oil such as vegetable oils, palm oil, canola oil, soybean oil, sun flower oil and waste frying oil (14; 19). Biodiesel is obtained by esterification and transesterification of the edible and non-edible oil with alcohol in the presence of a catalyst. Esterification process involves reducing the free fatty acid in the oil by reacting the oil with methanol and sulfuric acid to obtain (excess water and oil) while, transesterification process involves the reaction between lipid (waste cooking oil) and in the presence of catalysts to form esters and by product (glycerol) (18; 35). The most common used of alcohol is methanol because it's cheaper. Biodiesel has good fuel properties such as high flashing point, high cetane number and good lubrication. The main two types of catalysts use in transesterification process are homogeneous and heterogeneous catalyst, these catalysts are classified into two such as acid catalyst sulfuric acid or hydrochloric acid ($H_2SO_4$ or HCl) and alkali catalyst potassium hydroxide or sodium hydroxide(KOH or NaOH) (33).The reaction rate for homogeneous alkali catalyst is higher than heterogeneous catalyst and the reaction occur at reduced time ,for acid-catalyst it requires high volume of methanol, longer reaction time and it is also corrosive(15).The preferable catalyst for transesterification is alkali catalyst because it is faster and cheaper and it does not required more time which will result into high energy consumption. The major barrier of commercialization of biodiesel is the cost of feedstock which led to the high cost of production. Generally the feedstock used for biodiesel production is edible oil which makes its more expensive than petroleum diesel and not competitive, It is reported that approximately 70%-85% of the total biodiesel production cost arises from the cost of the raw material (51). Everywhere in the world, there are huge amount of waste oil generated from food canteen, food processing industries and fast food restaurants, if all these wastes are discharged into the environment it will result into environmental degradation and pollution (38). There is need to explore way to reduce the high cost of production and solve the major environmental pollution caused by the wastes. Therefore waste oil such as palm oil sludge was used as an alternative feedstock to reduce the production cost of biodiesel and utilization of these wastes oil solve the major environmental degradation posed by the wastes. Many researchers have worked on biodiesel production from palm oil sludge using heterogeneous catalyst, acid catalyst and also gives report on the optimum condition of the process reaction. (22) worked on free fatty acid removal on sludge of palm oil using heterogeneous solid catalyst derived from palm empty fruit bunch. The researcher investigated the activity of catalysts from biomass waste derived from palm empty fruit bunch. The main objectives of the research was to evaluate the effect of process variables on the esterification reaction by varying several parameters, i.e. the molar ratio of methanol to SPO catalyst to oil (8:1 - 14:1), the amounts of catalyst (0.5 - 5 wt. % SPO), and the reaction temperatures (40 - 60 $^{o}$C). (23) Worked on production of biodiesel from sludge palm oil by esterification process using P-toluenesulfonic acid (PTSA) as acid catalyst in different dosages in presence of methanol to convert free fatty acid (FFA) to fatty acid methyl ester (FAME). The researchers studied the influence of P-toluenesulfonic acid (PTSA) dosage (0.25-10% wt/wt), molar ratio of methanol to SPO (6:1-20:1), temperature (40-80 $^{o}$C), reaction time (30-120 min) on batch esterification process of SPO. They monitored the effects of those parameters on the yield of crude biodiesel and conversion of FFA to FAME. While very few researchers worked on homogeneous catalyst for the transesterification of biodiesel from palm oil sludge. (24) Worked on biodiesel production from sludge palm oil by two-step processes. The researcher worked on converting the free fatty acid to fatty acid methyl ester followed by a transesterification process using an alkaline catalyst. The aim was to determine the optimum conditions for pretreatment process by esterification and the highest yield of biodiesel at optimum conditions of pretreatment by esterification. The aim of this research work was to determine the possible optimum levels of process variables use for biodiesel produced by transesterification of palm oil sludge mixed with homogeneous catalyst and alcohol for statistical optimization. The objectives of this study was to characterized the physico-chemical properties of palm oil sludge and evaluate the possible optimum levels of process variables for statistical optimization that can be used for estimating maximum production of biodiesel.

## MATERIAL AND METHODS

### 2.1 Sample collection and feedstock preparation

Palm oil sludge (POS) was collected from various locally palm oil processing place in Ogbomosho, Oyo state, Nigeria. Methanol, sulphuric acid, propanol, potassium oxide and phenolphthalein were obtained from a chemical store in Ibadan, Oyo state, Nigeria. A round bottom flask was used as a reactor and magnetic stirrer with hot plate was used as a stirring and heating medium. The palm oil sludge was heated at $70^0$C, thereafter the hot palm oil sludge was filtered using filter paper in order remove its impurities, suspended particles and inorganic materials present in the waste oil. The palm oil sludge was filtered to avoid impairment of oil quality causing reduction in the productivity of the transesterification reaction and also to avoid generation of undesirable by-products that will hurt the final product (12). The palm oil sludge used for this research work are shown in plate 2.1


**Plate 2.1: Sample of palm oil sludge**

## 2.2 Chemical characterization of the Palm Oil Sludge

The chemical characterization of the palm oil sludge and biodiesel produced were analyzed chemically according to the ASTM standards. Properties analyzed were density, viscosity, acid index, iodine index, saponification value, waste content (%), free fatty acid (%), flash point and pour point.

### 2.2.1 Determination of density and dynamic of palm oil sludge and biodiesel

Density of palm oil sludge and biodiesel at $15^oC$ were determined by gravimetric analysis, 25ml waste frying oil was measured with a glass cylinder and the mass of the oil was determined by electronic scale. The density was calculated using equation (1).

$$\rho = \frac{m}{v} \qquad (1)$$

$m$ [g] is weight of the sample; $v$ [$cm^3$] volume of the sample.

### 2.2.2 Determination of viscosity of palm oil sludge and biodiesel

The viscosity measurement was carried out according to ASTMD- 445. The viscosity of palm oil sludge and biodiesel were measured by a falling-ball viscometer. The falling-ball viscometer was used to measure the viscosity of liquid by measuring the time required for a ball to fall under gravity through a sample-filled tube that is inclined at an angle. The average time of ten testes were taken in this experiment. The viscosity and kinematic viscosity can be determined by equation (2a) and (2b).

$$\eta = k * t * (\rho_{ball} - \rho_{medium}) \qquad 2a$$

$$\upsilon = \frac{\eta}{\rho} \qquad 2b$$

Where, $\eta$ is the dynamic viscosity [g/cm. s], $\upsilon$ is the kinematic viscosity [g/cm, s], *k* is the geometrical constant of the ball[$m^2$], t is the fall time through the tube [s], $\rho_{ball}$ is the density of the ball [$g/cm^3$] and $\rho_{medium}$ is the density of the medium [$g/cm^3$], $\rho$ is the density of the sample [$g/cm^3$].

### 2.2.3 Determination of refractive index of palm oil sludge and biodiesel

The refractive index of a medium is a measure of how much the velocity of a wave is reduced inside that medium. In this experiments the Abbe refractometer was used to measure the refractive index. The light ray pitched on the interphase of phases then it was refracted. The impact angles, rebound and the refraction were measured between a ray running perpendicular to the phase interface. Ray break is a result of differences in the speed of light in both phases. Refractive index is the ratio of the speed of light in phases, the light passes through. Its principle is the detection of limit angle fracture (βmax), which is the maximum possible angle fracture where the angle of impact is close to $90^o$.

### 2.2.4 Determination of saponification value of palm oil sludge and biodiesel

The saponification value was determined according to ASTM standards D-5558. The saponification value was obtained by washing 2 grams of oil into excess alkaline solution of potassium hydroxide and then titrating the excess alkaline solution mixed with oil with 0.5N hydrochloric acid. The saponification valve was calculated based on the equation 3 below

$$SV = \frac{3\times56.1\times1000}{(MMW\times3)+92.09-(3\times18)} \qquad 3$$

Where:

S.V. is saponification value defined as mg KOH per g of sample

MMV is mean molecular weight, 3 is the number of fatty acids per triacylglycerols

56.1 is molecular mass of KOH (g/mol), 1000 is conversion of units (mg/g)

92.09 is molecular mass of glycerol (g/mol), 18 is molecular mass of water (g/mol)

### 2.2.5 Determination of acid value of palm oil sludge and biodiesel

Acid value was determined according to ASTM-D 1980. The acid value is the number of milligrams of KOH required to neutralize all acid in 1g of sample. The acid value was determined by titration of the sample (oil or Biodiesel) dissolved in the mixture of ethanol-toluene with a standardized titration solution of KOH. In this method, a weighed amount of the sample (oil or Biodiesel) was added into a flask and it was dissolved in an ethanol-toluene mixture; phenolphthalein was added as an indicator. KOH was used as titrant solution. The titration process was stopped when the solution turned into pink color. The acid value (AV) was calculated using the equation below:

$$AV\left(\frac{mgKOH}{g}\right) = \frac{56.1 \times C_{KOH} \times V_{KOH}}{m} \qquad 4$$

Where: 56.1 is the molecular weight of the solution employed for titration (g/mol).

$V_{KOH}$ is the consumption during titration (ml).

$C_{KOH}$ (mol/1) is the concentration of the titration **KOH** solution; m is the weight (g) of the analyzed sample.

### 2.2.6 Determination of iodine number of palm oil sludge and biodiesel

This was determined according to the ASTM standard-5554. The iodine value was obtained by weighing 0.5 g waste frying oil and pour into Erlenmeyer flask. 10 ml of chloroform solution and 25 ml of Hanus solution (Iodine-Bromide Reagent) were added, shaken until all oil were well blended and kept in a dark room for 30 minutes. 10 ml of 15% KI solution was added. Titration was done with a solution of 0.1 N $Na_2S_2O_3$ and the indicator used was 1% starch. The titration was stopped when a clear solution was obtained.

$$\text{Iod Number} = \frac{(b-a) \times NNa_2S_2O_3 \times 12.69}{g} \qquad 5$$

Where:

a = Number of ml of solution for the titration of the sample, b = Number of ml of solution for blank titration

### 2.2.7 Determination of free fatty acid of palm oil sludge

The free fatty acid of waste frying oil was done according to the procedure reported by (54).The free fatty acid was determined by titration of the sample (oil) dissolved in the mixture of propanol- phenolphthalein indicator with a standardized titration solution of KOH. In this method, 5g of oil was dissolved in 25 ml of propanol then 5 drops of phenolphthalein indicator was added to the oil-propanol solution, thereafter the oil-propanol solution with phenolphthalein indicator was titrated by 0.1N KOH solution until the colour of the solution turn to pink colour. The free fatty acid (FFA) was calculated using the equation below:

$$\%FFA = \frac{V \times M \times N}{m \times 10} \qquad 6$$

V = Number of KOH solution (ml), M = Molecular weight of oleic acid (g/mole)

N = Normality number of KOH (g/L), m = Weight of waste frying oil (g)

### 2.2.8 Determination of pour and flash points of biodiesel

The pour and flash points were determined according to the ASTM standard D97, D25100-8 ad D56, respectively.


**Plate 2.2: Free fatty acid titration**

**Plate 2.3: Color comparison before and after FFA titration**

### 2.3.9 Determination of the amount of methanol to oil ratio use for the process.

The molecular weight of the oil was determined using the equation (7) below:

$$M = \frac{56.1 \times 1000 \times 3}{SV - AV} \quad (7)$$

SV =Saponification Value, AV=Acid Value, M=Molecular Weight of the oil,
Thereafter the amount of methanol was determined by using Equation (8)

$$M = \frac{O \times b \times MWM}{a \times MWO} \quad (8)$$

O=Amount of oil, M=Amount of methanol, MWO=Molecular weight of oil
MWM=Molecular weight of methanol, a=molar ratio of oil, b=molar ratio of methanol

## 2.3 Experimental Procedure

### 2.3.1 Desacidification of palm oil sludge by esterification reaction

The esterification reaction was done according to the procedure reported by (54).100ml of palm oil sludge (POS) was measure and heated at 60$^{o}$C, then sulphuric acid (0.14ml) and methanol (55ml) were added to the palm oil sludge, the mixture was pour into round bottom flasks and then stirred with magnetic stirrer at 800rpm for 60mins thereafter the mixture was allowed to settle in a separation funnel for 2hrs in order to achieve 2 distinct liquid phases (water at the top and preheated oil at the bottom).

### 2.3.2 Transesterification of treated palm oil sludge

The transesterification reaction was carried out in accordance with the procedure of Aworanti *et al.* ( 8). Different amount of methanol and catalyst which are shown in Table 2.1-2.2 were weighed and mixed vigorously with magnetic stirrer in order for the catalyst to be dissolved and form potassium methoxide solution. Constant volume of pretreated palm oil sludge (100ml) was heated to 60$^{0}$C, then potassium methoxide solution formed was poured gently into the heated palm oil sludge (POS) in a round bottom flask. The entire mixture was stirred with hot plate magnetic stirrer at 300 rpm and the temperature was maintained at 60$^{o}$C. The reaction time for the process were also varied and this are shown in the Table (2.3). After the process, the mixture was poured into a separating funnel and kept for 24hours so as to separate the glycerin from the biodiesel. The separation segment are glycerol layer at the bottom and biodiesel layer at the top. Thereafter the physicochemical properties of biodiesel derived from the transesterification of POS was determined and compared with European norms biodiesel. The apparatus set-up for the biodiesel production are shown in plate 2.4. The samples of biodiesel produced are shown in plate 2.6. The biodiesel yield of the transesterification process was calculated using Equation (9)

$$Biodiesel\ yield(\%) = \frac{MBP}{MWFO\ Used} \times 100 \qquad 9$$

**MBP**=Volume of biodiesel produced (ml); **MWFO**=Volume of waste frying oil (ml)

**Table 2.1: Percentage of Catalyst used for each Run at Constant Reaction Time and Molar Ratio.**

| Run | Catalyst (wt %) | Time (min) | Ratio |
|---|---|---|---|
| 1 | 0.1 | 90 | 1:9 |
| 2 | 0.5 | 90 | 1:9 |
| 3 | 1 | 90 | 1:9 |
| 4 | 1.5 | 90 | 1:9 |
| 5 | 2 | 90 | 1:9 |

**Table 2.2: Oil to Methanol Molar Ratio used for each run at Constant Catalyst and Reaction Time**

| Run | Catalyst (wt %) | Time (min) | Ratio |
|---|---|---|---|
| 1 | 1.5 | 90 | 1:1 |
| 2 | 1.5 | 90 | 1:3 |
| 3 | 1.5 | 90 | 1:6 |
| 4 | 1.5 | 90 | 1:9 |
| 5 | 1.5 | 90 | 1:12 |

**Table 2.3: Reaction Time used for each run at Constant Catalyst and Molar Ratio**

| Run | Catalyst (wt%) | Time (min) | Ratio |
|---|---|---|---|
| 1 | 1.5 | 30 | 1:12 |
| 2 | 1.5 | 60 | 1:12 |
| 3 | 1.5 | 90 | 1:12 |
| 4 | 1.5 | 120 | 1:12 |
| 5 | 1.5 | 150 | 1:12 |

**Plate 2.4: Biodiesel production set-up**



**Plate 2.5: Biodiesel-Glycerin separation from palm oil slugde**


**Plate 2.6: Sample of biodiesel produced from palm oil sludge (POS)**

## 2.6 Experimental Design

One-factor -at-a time (OFAT) approach was developed to evaluate the possible optimum level of the operating parameter for statistical optimized that can be used for evaluating maximum production of biodiesel fuel. The ranges of the operating parameters used are stated in Table 2.4

**Table 2.4: Ranges of Operating Parameters for One-Factor-at-a-Time (OFAT) Analysis**

| Factors | | Ranges | | | | |
|---|---|---|---|---|---|---|
| Operating Parameters | Units | 1 | 2 | 3 | 4 | 5 |
| Catalyst | wt% | 0.1 | 0.5 | 1 | 1.5 | 2 |
| Methanol:oil | Ratio | 1:1 | 3:1 | 6:1 | 9:1 | 12:1 |
| Reaction Time | Mins | 30 | 60 | 90 | 120 | 150 |

## RESULTS AND DISCUSSION

### 3.1 Physicochemical characterization of palm oil sludge used in biodiesel production.

The result of the properties of palm oil sludge analyzed in this study is as presented in Table 3.1, it was observed that the free fatty acid values of the sample was more than 2%, which justifies pretreatment (esterification) of the samples in order to reduce the free fatty acids in the palm oil sludge (1). The high free fatty acids content in the palm oil sludge (25.25%) can result into soap formation in the presence of potassium hydroxide during transesterification reaction of the oil. Studies also shown that high FFA reduces catalyst effectiveness and decreases the production yield (50; 1). (21;56) reported the free fatty acid value of palm oil sludge to be 74.8% and 22.3%. In this work the water content in the palm oil sludge was 0.03% which was less than 0.05%. The results obtained are within the range reported in the literature (0.05%) (43). Presence of water content in palm oil sludge is an important issue which also affect the biodiesel yield. Presence of high water content in the oil during transesterification reaction has negative effect on free fatty acid. High water content in the palm oil sludge lead to soap formation when it is reacted with catalyst during transesterification reaction (39; 48; 55). Also hydrolysis is formed during transesterification reaction, due to the presence of high water content in the palm oil sludge samples and this increases the free fatty acid in the oil (58). These two properties (water content and free fatty acid) in oil can reduce the effect of catalyst and lower the biodiesel yield (13;39). To avoid the saponification reaction, hydrolysis and reduction in catalyst, the oil must be heated at a particular temperature in order to remove the water, then pretreatment of this oil by the esterification reaction with sulfuric acid in the presence of methanol was required to reduce the free fatty acids (FFA) to the limit necessary to achieve the transesterification reaction. The density of palm oil sludge used for the transesterification reaction was 976 kg/m$^3$. The results obtained are within the range reported in the literature (0.9625 g / ml and 0.9772 g / ml) (46). Comparing this literature value with the density values of palm oil sludge in this research work, we concluded that there is no significance difference with values reported in the literature. It was observed from the result that the oil density decreased from 976kg/m$^3$ to 857 kg/m$^3$ after transesterification reaction and this has a significant impact on the viscosity value of the biodiesel i.e the viscosity decreased from 42.45mm$^2$/s to 5.35mm$^2$/s. The kinematic viscosity value of the palm oil sludge used for the research work was 42.45 $mm^2/s$ (16) reported the viscosity value of palm oil sludge to be 41$mm^2/s$, which is in the range with the viscosity value of palm oil sludge used in this research. Density, specific gravity and kinematic viscosities have been described as one of the most basic and most important properties of fuel because some important performance indicators such as cetane number and heating values are correlated with the parameters ( 4; 6; 57).The saponification number of palm oil sludge used for this research work was 191.6 mgKOH/g. The saponification number indicates the amount of potassium hydroxide (KOH) needed to saponify (converted to soap) one gram of oil. (3) reported that the saponification number of palm oil sludge ranges from 173.82 to 197 mg KOH / g oil. The saponification number of palm oil sludge used in this work falls within the literature report. The acid value of the palm oil sludge for this work was 50.50 mgKOH/g. The acid value is one of the most important properties used to determine biodiesel quality and the percentage of free fatty acids contained in each oil (28). It shows the amount of corrosive acid as well as oxidation products present in the oil. From literature the acid value should be lower than 0.50 mgKOH/g specified by ASTM standard (52). Comparing this result with the literature it shows that the palm oil sludge used in this research work has a very high acid value. Therefore the oil must be pretreated in order to reduce free fatty acids. The iodine value of palm oil sludge was 56.40$gI_2$/100g. The results obtained are within the range reported in the literature (40 – 55.7 $gI_2$/100g) (3). This indicate that the iodine value indicates the amount of this compound which can absorb the palm oil sludge in unsaturated bonds, that is, the larger the index value the greater adsorption on the double bonds present in the oil (5).

**Table 3.1: Physico-chemical Properties of palm oil sludge used for transesterification experiment**

| **Parameters determined** | **Palm oil sludge** |
|---|---|
| Viscosity at 40$^oC$ ($mm^2/s$) | 42.45 |
| Density ($kg/m^3$) | 976 |
| Free fatty acid (%) | 24.25 |
| Specific gravity at 15$^oC$ $g/cm^3$ | 0.976 |

| | |
|---|---|
| Acid number mgKOH/g | 50.50 |
| Iodine value $gI_2$/100g | 56.40 |
| Saponification value mgKOH/g | 191.6 |
| Water Content (%) | 0.03 |

### 3.3 Physical Property of Biodiesel Produced

The physical property of pure biodiesel was determined by ASTM standards to ensure that the following important factors in the fuel production process by transesterification are satisfied: complete transesterification reaction, complete esterification of FFA, removal of glycerol, removal of catalyst and removal of alcohol.

**The value of fatty acid number of biodiesel product**

The result of free fatty acid of biodiesel production from palm oil sludge was 0.32 mg/KOH. According to the data of ASTMD-6751, the maximum value of free fatty acid in biodiesel is 0.8 mg/KOH. The result shows that the biodiesel product has a value that is in accordance with the standard. The acid value is one of the most important properties for biodiesel quality check. High acid value can cause sediment in the fuel system and corrosion of the media. The higher the acid value the lower the quality of biodiesel (40; 42).

**Iodine value of biodiesel product**

The result of iodine number of methyl ester from palm oil sludge was 55.8$gI_2$/100g. The result of the analysis shows that iodine number in biodiesel from synthesis according to standard biodiesel value determined by SNI (31; 40). If the iodine value of biodiesel produced is higher than the standard of 115 $gI_2$/100 g it will lead to polymerization and formation of deposits in injector's nozzle and piston rings at the start of combustion.

**Density value of biodiesel product**

The result of density of transesterification process from palm oil sludge was 857 kg/$m^3$. The results obtained meets the EN14214 and ASTMD-6751 standard. Density provides information on how the fuel will work in diesel engines. High density value indicate some impurities in the biodiesel (42).The use of high temperature during the transesterification reaction will increase the saponification reaction.

## Viscosity value of biodiesel product

The result of viscosity value of biodiesel from palm oil sludge was 5.38 $mm^2/s$. The result of the analysis falls within the specification range of the ASTM D-6751 standard. Viscosity is defined as fluid resistance to the flow rate of a mm-sized capillary. If the viscosity value is high it will lead to formation of oxidized polymeric compounds and this can lead to the formation of gums and sediments that clog the filters in the engine (10).

## Acid value of biodiesel product

Based on result obtained, the acid number of biodiesel produced from palm oil sludge falls within the range of the ASTMD-6751 standard. Acids can be formed when traces of water is presence in the biodiesel which result into hydrolysis of the esters to form alcohol and acids (10). The acid number increases with an increase in peroxides because the esters first oxidize to form peroxides which then undergo complex reactions, including a split into more reactive aldehydes which further oxidize into acids. Acid number indicates the level of free fatty acids (FFAs) present in biodiesel. Acid value lower than 0.5 mg KOH/g is ideal as fuel for vehicle. A high acid value can have a strong solvency effect on rubber seals and hoses in the engine, thereby causing premature failure. It may also be left deposits, which can clog the fuel filter or drop fuel pressure.

## Flash Point and Pour Point

Flash point is the temperature at which biodiesel burns when in contact with ignition source. The value of flash point of the biodiesel produced from palm oil sludge was 180 $^oC$. This value fall within the range of biodiesel flash point standard (ASTM D6751). Pour point has been described as an important parameter for low temperature operation of a fuel also the lowest temperature at which fuel can flow. It is the temperature at which wax becomes visible when the fuel is cooled and it is sufficient to gel the fuel (6). The value of pour point of the biodiesel produced from palm oil sludge was -5 $^oC$. This value fall within the range of biodiesel pour point standard (ASTM D6751). Lastly the appearances of the biodiesel produced was noticed, it was observed that the biodiesel produced from palm oil sludge was brown in colour.

**Table 3.3: Properties of biodiesel produced from WFCO and WFPO**

| Properties | POS biodiesel | EN14214 | ASTMD-6751 |
|---|---|---|---|
| Acid value mgKOH/g | 0.17 | 0.50 | <0.8 |
| Free fatty acid (%) | 0.32 | | 0.8 |
| Density at 32$^{o}$C (kg/m$^{3}$) | 857 | 860-900 | 875-900 |
| Kinematic viscosity at 40$^{o}$C (mm$^{2}$/s) | 5.38 | 3.5-5.0 | 1.9-6.0 |
| Pour point($^{o}$C) | -5 | - | -15 to 10 |
| Flash point ($^{o}$C) | 180 | 120 | >130 |
| Iodine value g$I_2$/100g | 55.8 | 120 | - |
| Biodiesl Yield (%) | 61.2 | >96.5 | >96.5 |

## 3.4 Effect of Catalyst Percentage on Biodiesel Yield

The result of the effect of catalyst loading on transesterification of palm oil sludge to biodiesel using 9:1 methanol to oil ratio, stirring rate of 300rpm and temperature of 60$^{o}$C for 90 min are shown in Figure 3. 1. It was observed from the graph that biodiesel yield increases with increase in catalyst loading up to 1.5 wt%. It was noticed that yield increases to 35% when the catalyst loading increases up to 1.5 wt% at 90 min, while it decreases to 28% above 1.5 wt%. The optimum catalyst that gives the highest biodiesel yield was 1.5wt%. It was noticed from the result that the yield of biodiesel increased slightly when the amount of catalyst increased from 0.1%-1.5% and biodiesel yield reduced drastically when the catalyst was increased to 2%.

However, an increase in catalyst amount up to 1.5 wt% increases the total number of active sites, resulting in an increase in biodiesel conversion (30;44), while an increase in catalyst loading above 1.5 wt% makes the reactant and catalyst mixture too viscous which leads to problems with mixing and poor diffusion of the reactants, resulting in a decrease in the biodiesel yield (9; 30; 34; 53) . Decrease in yield may also be attributed to the fact that the solubility of methanol in oil is low and increasing catalyst loading provides more active sites to adsorb the products consequently, the yield of biodiesel decreases (26). Also the low biodiesel yield at catalyst loading above 1.5 wt% may be due to the attainment of mass transfer limitation (rate determining step) between the reactant and catalyst (59). KOH concentration 1.5 % (in relation to palm oil sludge mass) can therefore be taken as optimum for KOH-catalysed palm oil sludge transesterification with methanol under reaction conditions of 60º C temperature, 90 minutes duration.

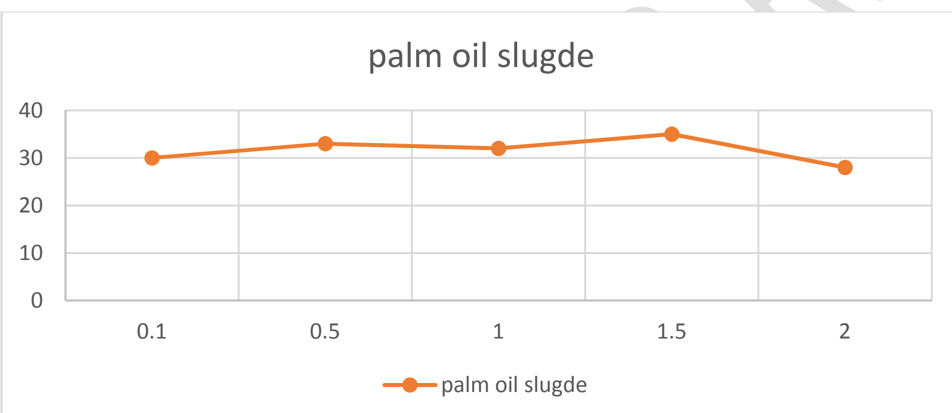


**Figure 3.1: Effect of catalyst loading on the process of transesterification using POS.**

### 3.5 Effect of Methanol/Oil Molar Ratio on Biodiesel Yield

The effect of varied molar ratio of palm oil sludge to methanol on the yield of biodiesel from transesterification of palm oil sludge are shown in Figure 3.2. Thus, this parameter was optimized by carrying out the transesterification reaction with various methanol to oil ratios (1 : 1, 1 : 3, 1 : 6, 1:9 and 1 : 12) using a catalyst loading of 1.5% and at a time of 30min and temperature of 60$^{o}$C. It was observed in Figure 3. 2, that methanol to oil ratio (12:1) gave the highest biodiesel yield of 61.2%. It was noticed that biodiesel yield increased as the methanol to oil ratio increased from 1:1 to 12:1 but it was a gradual increment. Thus, the optimum molar ratio was 12:1 and this can be used for the production of biodiesel from palm oil sludge under a magnetic stirrer heating system, especially with the application of KOH catalyst and methanol. The methanol to oil ratio is another important factor which affects the biodiesel yield. In order to increase the biodiesel yield and to keep the equilibrium on the right side of the reaction, it is necessary to increase the methanol in the reaction (25). Hypothetically, every mole of biodiesel is a result of one mole of methanol and 1/3 of a triglyceride mole from the transesterification response. Stoichiometrically, 3 mol of methanol is required to one mol of glyceride (55).

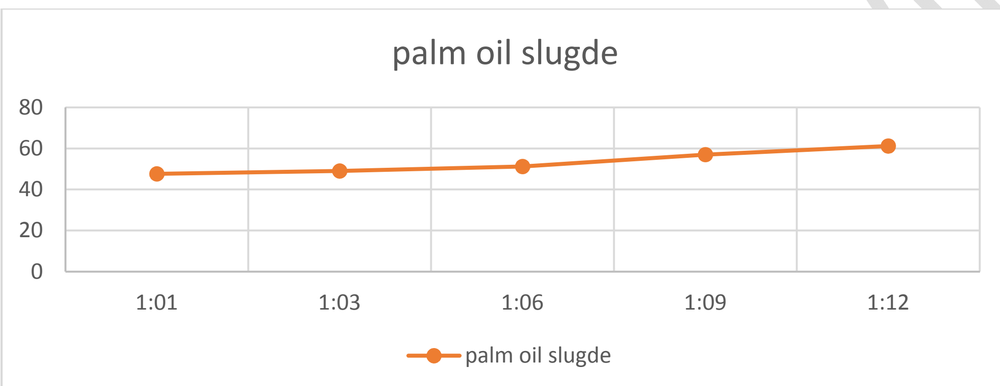


**Figure 3.2: Effect of methanol/oil molar ratio on the process of transesterification using POS**

### 3.6 Effect of Reaction Time on Biodiesel Yield

The influence and effect of reaction time on biodiesel yield was examined under the following operating conditions: 1.5 wt%, temperature of 60°C and molar ratio of 12:1 and the biodiesel yield obtained at different time intervals are shown in Figure 3.3.The experimental result shows that the yield decreased with time, the highest yield of 61.2% was achieved at 30 min as shown in Figure 3. 3. The yield deteriorated after 30 min because hydrolysis of esters may start to occur with a further increase in the reaction time, which results in more fatty acids forming soap (20). Additionally, a back reaction may take place after reaching the equilibrium since the reaction is reversible, subsequently decreasing the yield (2; 12; 28; 36; 53; 60). An optimum biodiesel yield of 61.2% was obtained with reaction parameters such as a methanol to oil ratio of 12 : 1, catalyst loading of 1.5 wt% and reaction time of 30 min.

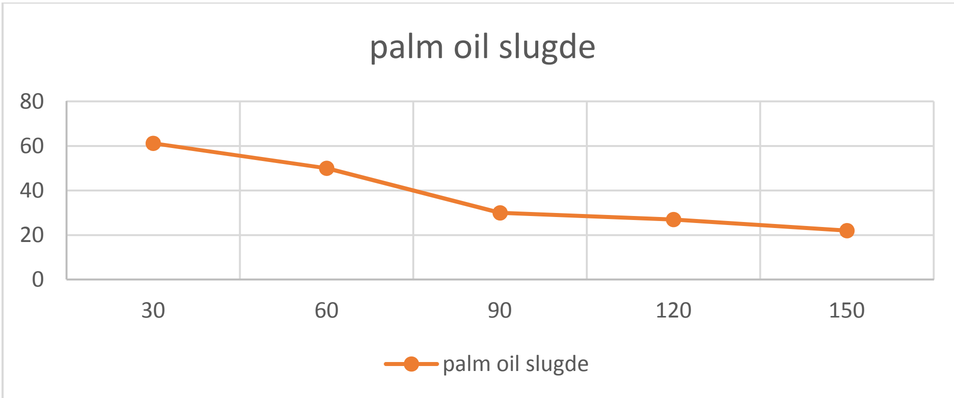


**Figure 3. 3: Effect of reaction time on the process of transesterification using POS.**

## Conclusion

The aim of this project was to determine the optimal reaction conditions on transesterification process. One factor at a time was used to determine the optimal condition that can be used to produce biodiesel from palm oil sludge. The optimum conditions for producing biodiesel were: methanol to the oil (12:1), amount of catalyst loading (1.5 wt %), and reaction time (30 min). The optimum yield of biodiesel was 61.2% obtained from transesterification process of palm oil sludge. Also, increase in the operational parameters (methanol to oil molar ratio and catalyst) and decreased in reaction time, increased the biodiesel production rate, biodiesel production potential and these subsequently increased the biodiesel yield. The product characterization meet the requirements the American Standard (ASTM) for biodiesel fuel. The result of the characterization shows that the reaction complete transesterification and esterification of FFA, removal of glycerol, removal of catalyst and removal of alcohol also, the lower viscosity value of the final product is an indication of completion of reaction and removal of heavy glycerol.

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