*Biotechnology Journal International*

***23(2): 1-14, 2019; Article no.BJI.48733***
***ISSN: 2456-7051***
*(Past name: British Biotechnology Journal, Past ISSN: 2231–2927, NLM ID: 101616695)*

# Effect of Process Variables on the Transesterification Process of Palm Oil Sludge to Biodiesel

**O. A. Aworanti[1], A. O. Ajani[1*], S. E. Agarry[1], K. A. Babatunde[1] and O. D. Akinwunmi[1]**

*[1]Department of Chemical Engineering, Biochemical Engineering and Biotechnology Laboratory, Ladoke Akintola University of Technology, P.M.B. 4000, Ogbomoso, Nigeria.*

***Authors' contributions***

*This work was carried out in collaboration among all the authors. Author OOA designed the study, wrote the protocol and performed the laboratory work with her project students. Author AOA managed the literature searches. Author SEA wrote the first and revised draft of the manuscript and Authors KAB and ODA managed the analyses of the study. All authors read and approved the final manuscript.*

***Article Information***

DOI: 10.9734/BJI/2019/v23i230076
Editor(s):
(1) Dr. Joana Chiang, Department of Medical Laboratory Science and Biotechnology, China Medical University, Taiwan.
Reviewers:
(1) Ibrahim Shehu Shema, Umaru Musa Yar' Adua University, Katsins, Nigeria.
(2) João Gomes, ISEL – Lisbon Polytechnic, Portugal.
Complete Peer review History: http://www.sdiarticle3.com/review-history/48733

***Original Research Article***

***Received 22 February 2019***
***Accepted 01 May 2019***
***Published 15 July 2019***

## 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 60ºC. 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 methanol-to-oil 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 achieved maximum biodiesel yield were found to be methanol to oil molar ratio of 12:1, catalyst loading of 1.5wt% and reaction time of 30 min. At this optimum conditions the maximum biodiesel yield was 61.2%. The biodiesel produced from transesterification of palm oil sludge was characterized in order to determine the

**Corresponding author: E-mail: aoajani@lautech.edu.ng;*

properties of the product. The density of POS is 857.0 kg/m$^3$, kinematic viscosity of 5.38 mm$^2$/s, flash point of 180°C, pour point of -5°C, and Acid value of 0.17 mgKOH/g. The biodiesel produced from transesterification of palm oil sludge meets the EN 14214 and ASTM 6751 standard. Thus, this study will be helpful to determine an efficient and economical procedure for biodiesel production from non-edible raw materials with high free fatty acid.

*Keywords: Biodiesel; transesterification; homogenous catalyst; palm oil sludge; methanol.*

## 1. INTRODUCTION

Human activities are largely dependent on the use of energy. Due to the increase in world population, there has been consistent increase in demand for energy and this has resulted in high cost of non-renewable energy [1]. Production of fossil fuel causes many problems such as human health problem, environmental degradation, global climate change, emission of greenhouse gases etc. [2-3]. 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 [3,4,5]. 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 [6]. 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[7-8]. 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) [9-10]. 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 two types of catalysts that are used majorly in transesterification reactions or processes are homogeneous and heterogeneous catalysts. These two types can further be classified as acid catalyst (e.g. sulfuric acid ($H_2SO_4$) or hydrochloric acid (HCl)) and alkali catalyst (such as potassium hydroxide (KOH) or sodium hydroxide (NaOH)) [11]. With the use of alkali catalyst, the rate of transesterification reaction is higher than with the use of acid catalyst and the reaction occurs at reduced time [12]. In addition, transesterification with acid-catalyst requires high volume of methanol and longer reaction time [12].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 [13]. 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 [14]. 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. Hidayat et al. [15] 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). Hayyan et al. [16] 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. Hayyan et al. [17] 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.

## 2. MATERIALS AND METHODS

### 2.1 Sample Collection and Feedstock Preparation

Palm oil sludge (POS) was collected from various locally palm oil processing plant 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 70ºC, thereafter the hot palm oil sludge was centrifuge using centrifuge machine in order to remove its impurities, suspended particles and inorganic materials present in the waste oil. The palm oil sludge was filtered to avoid deterioration of oil quality causing reduction in the productivity of the transesterification reaction and also to avoid generation of undesirable by-products that will hinder the final product [18]. The palm oil sludge used for this research work are shown in Fig. 1.

### 2.2 Characterization of the Palm Oil Sludge

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

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

Density of palm oil sludge and biodiesel at 15$^o$C were determined by gravimetric analysis, 25ml waste frying oil was measured with a glass cylinder and the mass of the oil was determined using an electronic scale. The density was calculated using Equation (1) [19].

$$\rho = \frac{m}{v} \tag{1}$$

*m* [g] is mass of the sample; *v* [m$^3$] 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 (2) and (3) respectively (19)

$$\eta = k \times t \times (\rho_{ball} - \rho_{medium}) \tag{2}$$

$$\upsilon = \frac{\eta}{\rho} \tag{3}$$

Where, η is the dynamic viscosity (Pa- s), υ is the kinematic viscosity (Pa- s).

*k* is the geometrical constant of the ball (m$^2$), t is the fall time through the tube (s).


**Fig. 1. Sample of palm oil sludge**

$\rho_{ball}$ is the density of the ball (kg/m$^3$) and $\rho_{medium}$ is the density of the medium (kg/m$^3$), ρ is the density of the sample [kg/m$^3$).

#### 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. [19].

#### 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 mixing 4 grams of oil with 50 cm$^3$ alkaline solution of potassium hydroxide, the mixture was then heated in order to saponify the oil. The excess alkaline solution in the mixture was titrated with 0.5 N hydrochloric acid using phenolphthalein as indicator. A blank sample was also prepared and back titrated accordingly. The sample and blank titres ($V_1$ and $V_2$) were recorded. The saponification values of the samples were then calculated using Equation (4) [20- 21].

$$sv = \frac{[(V_2 - V_1) \times M \times 56.1}{W} \quad (4)$$

SV= Saponification value, $V_1$=Volume of Hydrochloric acid used for the sample,
$V_2$ = Volume of Hydrochloric acid used for the blank,
M = Molarity of the Hydrochloric acid, W = Weight of sample used,
56.1 = Molecular weight of Potassium hydroxide.

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

Acid values of the various vegetable oils were also determined by ASTM method (ASTM – D 644 and 974(00). 0.2 – 0.5 g of sample were weighed into 250 ml conical flask. 50ml of neutralized ethyl alcohol was added. The mixture was heated on a water bath to dissolve the sample. The solution was titrated against 0.1 M KOH using phenolphthalein as indicator. The acid value was determined after which the free fatty acid was calculated respectively as follows [22]:

$$\text{Acid Value} = \frac{A \times M \times 56.1^F}{W} \quad (5)$$

(Source $^{(F)}$: ASTM-D 974 (00))

Where, A = ml of 0.1 M KOH consumed by sample, M = Molarity of KOH W = weight in grams of the sample

$$\text{Then free fatty acid} = \frac{Acid\ Value}{2} \quad (6)$$

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

This was determined according to the EN 14104 standard. 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 $Na_2 S_2$

$O_3$ and the indicator used was 1% starch. The titration was stopped when a clear solution was obtained. The Iodine number was calculated using Equation (7) [23].

$$\text{Iod Number}=\frac{(b-a)\times N\times 12.69}{g} \quad (7)$$

Where:

a = Number of ml of solution for the titration of the sample,
b = Number of ml of solution for blank titration
N= $Na_2\,S_2\,O_3$

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

The pour and flash points were determined according to the ASTM standard D2500 and D93, respectively.

#### 2.2.8 Determination of the amount of methanol to oil ratio

The molecular weight of the oil was determined using the Equation (8) [24] below:

$$M=\frac{56.1\times 1000\times 3}{SV-AV} \quad (8)$$

SV =Saponification Value, AV=Acid Value, M=Molecular Weight of the oil,

Thereafter the amount of methanol was determined by using Equation (7)

$$M=\frac{O\times b\times MWM}{a\times MWO} \quad (9)$$

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 Syviengkham [25].100 ml 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 800 rpm 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.* [26]. One-factor -at-a time (OFAT) approach was used to evaluate the possible optimum level of the operating parameters that can be used for the production of maximum biodiesel yield. The ranges of the operating parameters used as stated in Table 1. Different amount of methanol and catalyst which as shown in Table 1 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 (100 ml) was heated to 60ºC, 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 on the 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 shown in the Table (1). After the process, the mixture was poured into a separating funnel and kept for 24 hours 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 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 Fig. 2. The samples of biodiesel produced are shown in Fig. 4. The biodiesel yield of the transesterification process was calculated using Equation (9)

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

MBP=Volume of biodiesel produced (ml); MWFO+M=Vol. of waste frying oil+Methanol (ml)

## 3. RESULTS AND DISCUSSION

### 3.1 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 2, it was observed that the free fatty acid values of

**Table 1. Ranges of operating parameters for one-factor-at-a-ime (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 |

**Fig. 2. Biodiesel production set-up**

**Fig. 3. Biodiesel-glycerin separation from palm oil slugde**

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 [27]. 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 [27,29]. Hayyan et al. [28] & Usam et al. [30] 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%) [31]. Presence of water content in palm oil sludge is an important issue which also affect the biodiesel yield. Presence of high


**Fig. 4. Sample of biodiesel produced from palm oil sludge (POS)**

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 [32,33,34].

Hydrolysis will also occur 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 [35]. These two properties (water content and free fatty acid) in oil can reduce the effect of catalyst and lower the biodiesel yield [36-37]. To avoid the occurrence of saponification reaction, hydrolysis and catalyst reduction, the oil must be heated at a particular temperature in order to remove the water. Thereafter, pretreatment of the oil by esterification reaction with sulfuric acid in the presence of methanol is required so as to reduce the free fatty acids (FFA) to the limit that is 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) [38]. 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 976$kg/m^3$ 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 0.0425 Pa-s to 0.00535 Pa-s. The kinematic viscosity value of the palm oil sludge used for the research work was 0.0425 Pa-s. El-Araby et al. [39] reported the viscosity value of palm oil sludge to be 0.041 Pa-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 [40,41,42].

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. Anine et al. [43] 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 [44]. 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 [45]. 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$gI_2$/100 g. The results obtained are within the range reported in the literature (40 – 55.7 $gI_2$/100 g) [43].

**Table 2. Properties of palm oil sludge used for transesterification experiment**

| Parameters determined | Palm oil sludge |
|---|---|
| Viscosity at 40°C (Pa-s) | 0.0425 |
| Density (kg/m$^3$) | 976 |
| Free fatty acid (%) | 24.25 |
| Specific gravity at 15°C g/cm$^3$ | 0.976 |
| Acid number mgKOH/g | 50.50 |
| Iodine value g$I_2$/100g | 56.40 |
| Saponification value mgKOH/g | 191.6 |
| Water Content (%) | 0.03 |

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 [46].

## 3.2 Physical Properties of Biodiesel Produced

The physical properties of pure biodiesel were 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.

### 3.2.1 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 [23,47].

### 3.2.2 Iodine value of biodiesel product

The result of iodine number of methyl ester from palm oil sludge was 55.8g$I_2$/100 g. The result of the analysis shows that iodine number in biodiesel from synthesis according to standard biodiesel value determined by SNI [23,48]. If the iodine value of biodiesel produced is higher than the standard of 115 g$I_2$/100 g it will lead to polymerization and formation of deposits in injector's nozzle and piston rings at the start of combustion.

### 3.2.3 Density value of biodiesel product

The density value of the biodiesel obtained from the transesterification process of palm oil sludge was 857 kg/m$^3$. This value 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 [47].

### 3.2.4 Viscosity value of biodiesel product

The viscosity value of biodiesel from palm oil sludge was 0.00538 Pa-s. The value of the analysis falls within the specification range of the ASTM D-6751. 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 [49].

### 3.2.5 Acid value of biodiesel product

Based on result obtained, the acid number of biodiesel produced from palm oil sludge was 0.17 mgKOH/g which 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 [49]. 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.

**Table 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 32ºC (kg/m$^3$) | 857 | 860-900 | 875-900 |
| Kinematic viscosity at 40$^o$C (Pa-s) | 0.0054 | 0.0035-0.005 | 0.0019-0.006 |
| Pour point($^o$C) | -5 | - | -15 to 10 |
| Flash point ($^o$C) | 180 | 120 | >130 |
| Iodine value gI$_2$/100g | 55.8 | 120 | - |
| Biodiesel Yield (%) | 61.2 | >96.5 | >96.5 |

#### 3.2.6 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 180ºC. 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 [41]. The value of pour point of the biodiesel produced from palm oil sludge was -5ºC. 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.

### 3.3 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 60ºC for 90 min are shown in Fig. 5. 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 [50,51], 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 [50,52,53,54]. 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 [55]. 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 [56]. 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 60ºC temperature, 90 minutes duration.

### 3.4 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 Fig. 6. 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 12 : 1) using a catalyst loading of 1.5% and at a time of 30min and temperature of 60$^o$C. It was observed in Fig. 6, 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 [57]. Hypothetically,

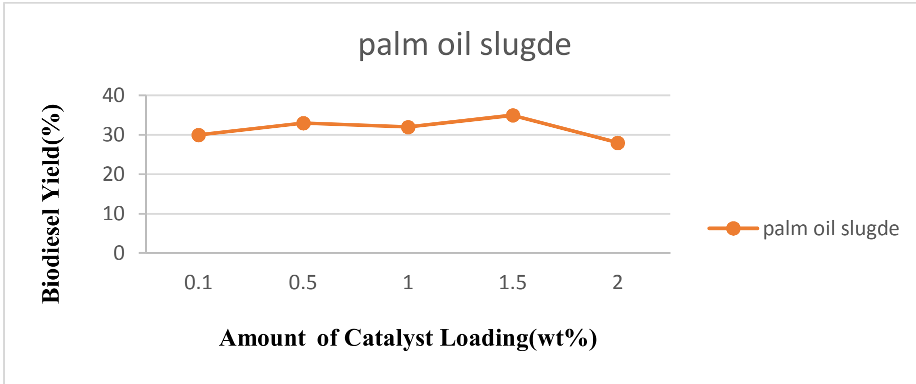


**Fig. 5. Effect of catalyst loading on the process of transesterification using POS**

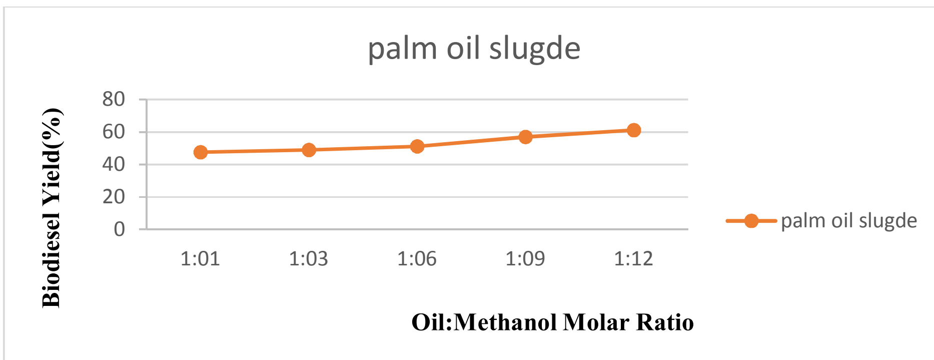


**Fig. 6. Effect of methanol/oil molar ratio on the process of transesterification using POS**

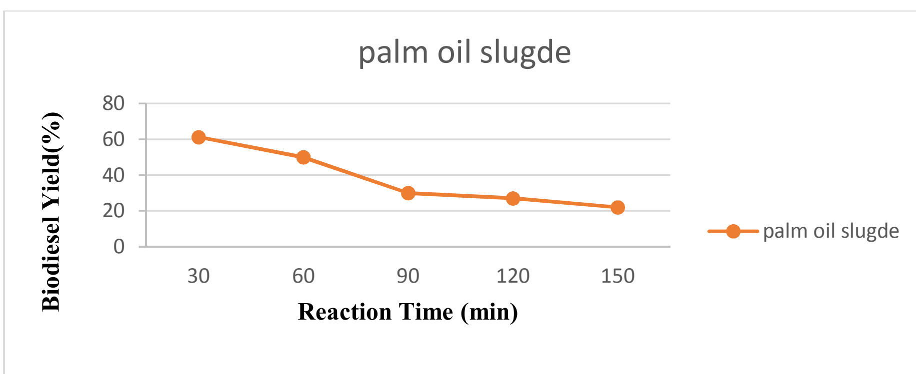


**Fig. 7. Effect of reaction time on the process of transesterification using POS**

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 produce one mol of glyceride [34].

### 3.5 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 Fig. 7.The experimental result shows that the yield decreased with time, the highest yield of 61.2% was achieved at 30 min as shown in Fig. 7. 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 [58]. Additionally, a back reaction may take place after reaching the equilibrium since the reaction is reversible, subsequently decreasing the yield [18,44,54,59,60,61]. 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.

## 4. 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.

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

## REFERENCES


1. Saleh AM, Kulkarni K. Production of biodiesel from waste cooking oil by using homogeneous catalyst. Int. J. Chem. Sci. 2014;12(3):941-951.
2. Atadashi IM, Aroua MK, Abdul Aziz AR, Sulaiman NMN. Refining technologies for purification of crude biodiesel. Applied Energy.2011;88:4239-4251.
3. Lee S, Shah YT. Biofuels and bioenergy: Processes and Technologies. CRC Press, Taylor and Francis Group, 6000 Broken Sound Parkway NW, Suite 300 Boca Raton, FL; 2013.
   [ISBN 978-1-4200-8955-4]
4. Minami E, Saka S. Kinetics of hydrolysis and methyl esterification for biodiesel production in two-step supercritical methanol process. Fuel. 2006;85:2479-2483.
5. Peterson DLR CL. Emissions Tests with an On-Road Vehicle Fueled with Methyl and Ethyl Esters of Rapeseed Oil, in ASAE International Winter Meeting, Paper No. 946532; 1994.
6. Evangelos GG. A statistical investigation of biodiesel physical and chemical properties and their correlation with the degree of unsaturation. Renewable Energy. 2013;50:858-878.
7. Dhar A, Kevin R, Agarwal AK. Production of biodiesel from high-FFA neem oil and its performance, emission and combustion characterization in a single cylinder DICI Engine, Journal Fuel Proc. Technol. 2012;97:118-129.
8. Freedman B, Pryde EH, Mounts TL. Variables affecting the yields of fatty esters from transesterified vegetable oils. Journal of the American Oil Chemists Society. 1984;61:1638–1643.
9. Filemon AU. Biofuels from plant oils. Published by the ASEAN Foundation, Jakarta, Indonesia. 2010, 1-6. 15) Hidayat Arif, Muflih A. Adnan and Diana. Free Fatty Acid Removal on Sludge of Palm Oil using Heterogeneous Solid Catalyst Derived from Palm Empty Fruit Bunch. International Journal of Renewable Energy Research. 2018;8(2):3-8.
10. Meher LC, Dharmagadda VSS, Naik SN. Optimization of alkali-catalyzed transesterification of pongamiapinnata oil for production of biodiesel, Journal of Bioresource Technol. 2006;97:1392-1397.
11. Lotero E, Liu Y, Lopez DE, Suwannakarn K, Bruce DA, Goodwin JA. Synthesis of biodiesel via acid catalysis. Ind. Eng. Chem. Res. 2005;44:5353–5363.
12. Dizge N, Aydiner C, Imer DY, Bayramoglu M, Tanriseven A, Keskinler B. Biodiesel production from sunflower, soybean and waste cooking oils by transesterification using lipase immobilized onto a novel microporous polymer. Bioresource Technology. 2009;100:1983–1991.
13. Sharma A, Melo JS, Prakash NT, Prakash R. Fuel properties of blend and biodiesel generated from acid oil using whole cell biocatalyst. Energy Sources, Part A: Recovery, Utilization and Environmental Effects. 2018;40(2):148-154.

14. Mittelbach M, Gangl S. Long term storage stability of biodiesel made from rapeseed and used frying oil. Journal of American Oil and Chemical Society. 2001;78(6):573-577.
15. Hidayat Arif, Muflih A. Adnan and Diana. Free fatty acid removal on sludge of palm oil using heterogeneous solid catalyst derived from palm empty fruit bunch. International Journal of Renewable Energy Research. 2018;8(2): 3-8.
16. Hayyan A, Alam MZ, Mirghani MES, Kabbashi NA, Hakimi NIN M, Siran YM, Tahiruddin S. Production of biodiesel from sludge palm oil by esterification process. Journal of Energy and Power Engineering. 2010;4(1):1-7.
17. Hayyan Adeeb, Md. Zahangir Alam, Mohamed ES, Mirghania Nassereldeen A. Kabbashi, Noor Irma Nazashida Mohd Hakimi, Yosri Mohd Siran, Shawaluddin Tahiruddin. Sludge palm oil as a renewable raw material for biodiesel production by two-step processes. Bioresource Technology. 2010;101:7804–7811.
18. Carlos A, Guerrero F, Andrés GR, Fabio ES. Biodiesel production from waste cooking oil. Biodiesel - Feedstocks and processing technologies. Dr. Margarita Stoytcheva (Ed.); 2011. [ISBN: 978- 953-307-713-0] In Tech. Available:http://www.intechopen.com/books/biodiesel-feedstocks-andprocessing-
19. Boris Ramos. Production of biodiesel from vegetable oils. Thesis, Master of Science, Department of Chemical Science and Technology School of Chemical Science and Engineering Royal Institute of Technology (KTH) Stockholm, Sweden. 2012;31-35.
20. Nielsen SS. Introduction to the chemical analysis of foods. 2002;183-204.
21. Milwidsky BM, Gabriel DM. Detergent analysis. A Handbook for Cost-effective Quality Control. 1982;187-234.
22. Ankapong Edward. Influence of physicochemical characteristics of vegetable oils on the quality of biodiesel produced from palm oil, palm kernel oil, refined soyabean oil, unrefined soyabean oil and jathropha curcas oil. Thesis, Master of Science, Department of Analytical Chemistry, Kwame Nkrumah University of Science and Technology, Kumasi. 2010;65.
23. Okta S, Ceria S, Risfidian M. Preparation of calcium oxide from cattle bones as catalyst for conversion of waste cooking oil to biodiesel. Science & Technology Indonesia. 2017;2:67-69.
24. Cheng J, Li Y, He S, Shen W, Liu Y, Song Y. Reaction kinetics of transesterification between vegetable oil and methanol under supercritical conditions. Energy Sourc. Part A, 2008;30:681-688.
25. Syviengkham Phimmasone. Pretreatment of high free fatty acid jatropha oil by esterification. Thesis, Master of Science, National University of Laos, Faculty of Science Techno Peace Corps, National Research Foundation of Korea. 2014;38-40.
26. Aworanti OA, Agarry SE, Ajani AO. Statistical optimization of process variables for biodiesel production from waste cooking oil using heterogeneous base catalyst. British Biotechnology Journal. 2013;3(2):116-132.
27. Abdullah, Rut Novalia Rahmawati Sianipar, Dahlena Ariyani, Iryanti Fatyasari. Nata Conversion of palm oil sludge to biodiesel using alum and KOH as catalysts Sustainable Environment Research. 2017;27:291-295.
28. Hayyan A, Alam Md Z, Mirghani MES, Kabbashia NA, Hakimi NINM, Siran YM, Tahiruddin S. Reduction of high content of free fatty acid in sludge palm oil via acid catalyst for biodiesel production. Fuel Processing Technology. 2011;92(5):920-924.
29. Sani J, Sokoto MA, Tambuwal AD, Garba NA. Effect of NiO/SiO2 on thermochemical conversion of waste cooking oil to hydrocarbons. Heliyon. 2017;3(5):e00304.
30. Usman T, Ariany L, Rahmalia W, Advant R. Esterification of fatty acid from palm oil waste (Sludge oil) by using alum catalyst. Indonesia Journal Chemical Engineering. 2009;9(3):474-478.
31. Renita Manurung, Debbie Aditia Ramadhani, Siti Maisarah. One step transesterification process of sludge palm oil (SPO) by using deep eutectic solvent (DES) in biodiesel production AIP Conference Proceedings. 2017;1855:070004-8.
32. Morad NA, Aziz MKA, Zim RBM. Process design in degumming and bleaching of palm oil. Centre of Lipids Engineering and Applied Research(Clear), Universiti Teknologi Malaysis; 2009.

33. Sanford SD, Sharmon D, White JM, Shah PS, Wee C, Valverde MA, Meier GR. Feedstock and biodiesel characteristics report. Renewable Energy Group Inc; 2009.
34. Tang Y, Meng M, Zhang J, Lu Y. Efficient preparation of biodiesel from rapeseed oil over modified Cao. Appl. Energy. 2011;88(8):2735–2739.
35. Vyas AP, Verna JL, Subrahmanyam NA. Review on FAME Production. Fuel. 2010;89:1-9.
36. Morad NA, Aziz MKA, Zim RBM. Process design in degumming and bleaching of palm oil. Centre of Lipids Engineering and Applied Research(Clear), Universiti Teknologi Malaysis; 2009.
37. Chesterfield DM, Rogers EO, Al-Zaini, Adesina AA. Production of biodiesel via ethanolysis of waste cooking oil using immobilised lipase. Chemical Engineering Journals. 2012;7(39):1-10.
38. Sánchez N, Encinar JM, Martínez G, González JF. Biodiesel production from castor oil under subcritical methanol conditions. International Journal of Environmental Science and Development. 2015a;6(1):61–66.
39. El-Araby R, Amin A, El Morsi AK, El-Ibiari NN, El-Diwani GI. Study on the characteristics of palm oil–biodiesel–diesel fuel blend. Egyptian Journal of Petroleum. 2018;27:187–194.
40. Ajav EA, Akingbehin AO. A study of some fuel properties of local ethanol blended with diesel fuel. Agricultural Engineering International: the CIGR Journal of Scientific Research and Development. Manuscript. 2002 EE 01 003;IV.
41. Alamu OJ, Waheed MA, Jekayinfa SO. Alkali-catalysed laboratory production and testing of biodiesel fuel from Nigerian Palm Kernel Oil. Agricultural Engineering International: The CIGR Ejournal. Manuscript Number EE 07 009. 2007;IX.
42. Van Gerpen J. Biodiesel processing and production. Fuel Processing Technology. 2004;20:1-11.
43. Ainie K, Siew WL, Tan YA, Ma AN. Characterization of a by-product of palm oil milling. Elaeis 1995;7(2):162–170.
44. Kapilan N, Ashok Babu TP, Reddy RP. Technical aspects of biodiesel and its oxidation stability. International Journal of Chem Tech Research. 2009;1(2):278–282.
45. Solomon WC, Kolade OA, Sa'ad A. Improving jatropha biodiesel yield through the box-behnken process variables optimization method. International Journal of Engineering Sciences and Research Technology. 2019;8:1 118-126.
46. Alam M, Akram D, Sharmin E, Zafar F, Ahmad S. Vegetable oil based eco-friendly coating materials: A review article. Arabian Journal of Chemistry. 2014;7(4):469–479.
47. Pinyaphong P, Sriburi P, Phutrakul S. Biodiesel fuel production by methanolysis of fish oil derived from the discarded parts of fish catalyzed by Carica Papaya Lipase. World Academy of Science, Engineering and Technology. 2011;76:466-472.
48. Lesbani A, Susi Y, Verawaty M, Mohadi R. Calcium oxide decomposed from chickens and goats bones as catalysts for converting discarded cooking oil to be biodiesel. Aceh International Journal of Science and Technology. 2015,;4:7-13.
49. Bouaid A, Martinez M, Jose A. Production of biodiesel from bioethanol and *Brassica carinata* oil: Oxidation stability study. Bioresource Technology. 2009;100(7): 2234-2239.
50. Lee SL, Wong YC, Tan YP, Yew SY. Transesterification of palm oil to biodiesel by using waste obtuse horn shell-derived Cao catalyst. Energy Convers. Manage. 2015;93:282–288.
51. Roschat W, T. Siritanon TT. Biodiesel production from palm oil using hydrated lime-derived CaO as a low-cost basic heterogeneous catalyst. Energy Conversion and Management. 2016; 108:459-67.
52. Birla A, Singh B, Upadhyay SN, Sharma YC. Kinetics studies of synthesis of biodiesel from waste frying oil using a heterogeneous catalyst derived from snail shell. Bioresour. Technol. 2012;106:95–100.
53. Maneerung T, Kawi S, Dai Y, Wang CH. Sustainable biodiesel production via transesterification of waste cooking oil by using Cao catalysts prepared from chicken manure. Energy Convers. Manage. 2016;123:487–497.
54. Syazwani ON, Teo SH, Islam A, Taufiq-Yap YH. Transesterification activity and characterization of natural Cao derived from waste venus clam (*Tapes belcheri* S.) material for enhancement of biodiesel production. Process Saf. Environ. Prot. 2017;105:303–315.
55. Israa M. Rashid, Mohammed A. Atiya, Hameed BH. Production of biodiesel from

waste cooking oil using Cao-Egg shell waste derived heterogeneous catalyst. International Journal of Science and Research. 2015;6:11,94-103.
56. Wei Z, Xu C, Li B. Application of waste Eggshell as low cost solid catalyst for biodiesel production. Bioresour. Technol. 2009;100:2883–2885.
57. Hossain ABMS, Mazen MA. Effects of catalyst types and concentrations on biodiesel production from waste soybean oil biomass as renewable energy and environmental recycling process. Australian Journal of Crop Science. 2010;550-555.
58. Girish N, Niju SP, Meera S, Begum KM, Anantharaman N. Utilization of a cost effective solid catalyst derived from natural white bivalve clam shell for transesterification of waste frying oil. Fuel. 2013;111:653–658.
59. Agarwala AK, Dhar A, Gupta JG, Woong KIl, Choi K, Lee CS, Park S. Effect of fuel injection pressure and injection timing of Karanja biodiesel blends on fuel spray, engine performance, emissions and combustion characteristics. Energy Convers. Manag. 2015;91:302–314.
60. Metaxas AC. Foundations of Electroheat; Wiley: New York, NY, USA; 1996.
61. Wong PK, Wong KI, Vong CM, Cheung CS. Modeling and optimization of biodiesel engine performance using kernel-based extreme learning machine and cuckoo search. Renew. Energy 2015;74:640–647.



*Peer-review history:*
*The peer review history for this paper can be accessed here:*
*http://www.sdiarticle3.com/review-history/48733*