

# 1 **Effect of process variables on the transesterification process of palm oil sludge** 2 **to biodiesel**

## 4 **Abstract**

5 In this research work, the optimum process variables (catalyst, methanol to oil ratio and reaction  
6 time) for transesterification of palm oil sludge (POS) to biodiesel were studied. The  
7 transesterification process was carried out by a mixture of palm oil sludge, methanol and catalyst  
8 with the help of magnetic stirrer at 300 rpm and at a temperature of 60°C. The catalyst used for  
9 the process was potassium hydroxide (KOH). One-Factor-at-A-Time was used to select the  
10 possible optimum levels of process variable that gives high biodiesel yield. The study was  
11 evaluated by five levels of oil-to-methanol molar ratio (1:1 – 2:1), catalyst (0.1- 2 %) and  
12 reaction time (30 – 150 min). The optimum process variables for transesterification of palm oil  
13 sludge (POS) to biodiesel were methanol to oil molar ratio of 2:1, catalyst loading of 1.5wt% and  
14 reaction time of 30 min. An optimum biodiesel yield of 61.2% was obtained with reaction  
15 parameters such as methanol to oil ratio of 12: 1, catalyst loading of 1.5 wt% and a reaction time  
16 of 30 min. The biodiesel produced from the transesterification of palm oil sludge meets the EN  
17 14214 and ASTM 6751 standard.

18  
19 **KEYWORDS:** Biodiesel, Palm Oil Sludge, Transesterification, Catalyst and Methanol  
20

## 21 **Introduction**

22 Human activities are largely dependent on energy and due to the increase in population, there has  
23 been consistent demand in every arena for energy, all these resulted into high price of non-  
24 renewable energy (45). Production of fossil fuel causes some many problems such as human  
25 health problem, environmental degradation, global climate change, emission of greenhouse gases  
26 etc. ( 7; 29) . Increase in growth of the economy, the consumption rate of energy, depleting of  
27 fossil fuel and negative effect of fossil fuel on the environment led to search for alternative fuel  
28 in both developed and underdeveloped countries. Bio-diesel has been considered as one of the

29 alternative energy that can replace fossil fuel (29; 37; 41). Biodiesel, which is also called a  
30 mixture of fatty acid methyl esters (FAMES) or fatty acid ethyl ester (FAEE) has been designed  
31 as one of the most renewable fuel and alternative fuel for diesel engine, it has many advantages  
32 over petroleum diesel, as it is a clean renewable fuel, biodegradable, nontoxic and produces less  
33 air pollutants with a lower smoke, airborne particle and carbon monoxide (17). Biodiesel can be  
34 used in diesel engines without requiring engine modification, its characteristics are similar to  
35 petroleum-based diesel fuels, it can be produced from edible and non-edible oil such as vegetable  
36 oils, palm oil, canola oil, soybean oil, sun flower oil and waste frying oil (14; 19). Biodiesel is  
37 obtained by esterification and transesterification of the edible and non-edible oil with alcohol in  
38 the presence of a catalyst (61). Esterification process involves reducing the free fatty acid in the  
39 oil by reacting the oil with methanol and sulfuric acid to obtain (excess water and oil) while,  
40 transesterification process involves the reaction between lipid (waste cooking oil) and in the  
41 presence of catalysts to form esters and by-product (glycerol) (18; 35). The most commonly use  
42 of alcohol is methanol because it's cheaper. Biodiesel has good fuel properties such as high  
43 flashing point, high cetane number and good lubrication. The main two types of catalysts use in  
44 transesterification process are homogeneous and heterogeneous catalyst, these catalysts are  
45 classified into two such as acid catalyst sulfuric acid or hydrochloric acid ( $H_2SO_4$  or  $HCl$ ) and  
46 alkali catalyst potassium hydroxide or sodium hydroxide( $KOH$  or  $NaOH$ ) (33).The reaction rate  
47 for homogeneous alkali catalyst is higher than heterogeneous catalyst and the reaction occur at  
48 reduced time ,for acid-catalyst it requires a high volume of methanol, longer reaction time and it  
49 is also corrosive(15). The preferable catalyst for transesterification is alkali catalyst because it is  
50 faster and cheaper and it does not require more time which will result in high energy  
51 consumption. The major barrier of commercialization of biodiesel is the cost of feedstock which  
52 led to the high cost of production. Generally, the feedstock used for biodiesel production is  
53 edible oil which makes its more expensive than petroleum diesel and not competitive, It is  
54 reported that approximately 70%-85% of the total cost of the raw material (51). Everywhere in  
55 the world, there are huge amount of waste oil generated from food canteen, food processing  
56 industries and fast food restaurants, if all these wastes are discharged into the environment it will  
57 result into environmental degradation and pollution (38). There is a need to explore a way to  
58 reduce the high cost of production and solve the major environmental pollution caused by the  
59 wastes. Therefore waste oil such as palm oil sludge was used as an alternative feedstock to

60 reduce the production cost of biodiesel and utilization of these wastes oil solve the major  
61 environmental degradation posed by the wastes. Many researchers have worked on biodiesel  
62 production from palm oil sludge using heterogeneous catalyst, an acid catalyst and also gives a  
63 report on the optimum condition of the process reaction. (22) worked on free fatty acid removal  
64 on the sludge of palm oil using heterogeneous solid catalyst derived from palm empty fruit  
65 bunch. The researcher investigated the activity of catalysts from biomass waste derived from  
66 palm empty fruit bunch. The main objectives of the research was to evaluate the effect of process  
67 variables on the esterification reaction by varying several parameters, i.e. the molar ratio of  
68 methanol to SPO catalyst to oil (8:1 - 14:1), the amounts of catalyst (0.5 - 5 wt. % SPO), and the  
69 reaction temperatures (40 - 60 °C). Hayyan et al. (23) Worked on the production of biodiesel  
70 from sludge palm oil by the esterification process using P-toluenesulfonic acid (PTSA) as an acid  
71 catalyst in different dosages in presence of methanol to convert free fatty acid (FFA) to fatty acid  
72 methyl ester (FAME). The researchers studied the influence of P-toluenesulfonic acid (PTSA)  
73 dosage (0.25-10% wt/wt), molar ratio of methanol to SPO (6:1-20:1), temperature (40-80 °C),  
74 reaction time (30-120 min) on batch esterification process of SPO. They monitored the effects of  
75 those parameters on the yield of crude biodiesel and conversion of FFA to FAME. While very  
76 few researchers working on homogeneous catalyst for the transesterification of biodiesel from  
77 palm oil sludge. 24. Hayyan et al. (24) worked on biodiesel production from sludge palm oil  
78 by two-step processes. The researcher worked on converting the free fatty acid to fatty acid  
79 methyl ester followed by a transesterification process using an alkaline catalyst. The aim was to  
80 determine the optimum conditions for the pretreatment process by esterification and the highest  
81 yield of biodiesel at optimum conditions of pretreatment by esterification. The aim of this  
82 research work was to determine the possible optimum levels of process variables use for  
83 biodiesel produced by transesterification of palm oil sludge mixed with homogeneous catalyst  
84 and alcohol for statistical optimization. The objectives of this study were to characterize the  
85 physicochemical properties of palm oil sludge and evaluate the possible optimum levels of  
86 process variables for statistical optimization that can be used for estimating maximum production  
87 of biodiesel.

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## MATERIAL AND METHODS

## 91 2.1 Sample collection and feedstock preparation

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



102  
103 **Plate 2.1: Sample of palm oil sludge**

## 104 2.2 Chemical characterization of the Palm Oil Sludge

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

### 109 110 2.2.1 Determination of density and dynamic of palm oil sludge and biodiesel

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

$$114 \quad \rho = \frac{m}{v} \quad 1$$

115  
116  $m$  [g] is weight of the sample;  $v$  [cm<sup>3</sup>] volume of the sample.

### 117 **2.2.2 Determination of viscosity of palm oil sludge and biodiesel**

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

$$124 \quad \eta = k * t * (\rho_{ball} - \rho_{medium}) \quad 2a$$

$$125 \quad \nu = \frac{\eta}{\rho} \quad 2b$$

126 Where,  $\eta$  is the dynamic viscosity [g/cm. s],  $\nu$  is the kinematic viscosity [g/cm, s],  
127  $k$  is the geometrical constant of the ball[m<sup>2</sup>],  $t$  is the fall time through the tube [s],  
128  $\rho_{ball}$  is the density of the ball [g/cm<sup>3</sup>] and  $\rho_{medium}$  is the density of the medium [g/cm<sup>3</sup>],  $\rho$  is the  
129 density of the sample [g/cm<sup>3</sup>].

### 130 131 **2.2.3 Determination of refractive index of palm oil sludge and biodiesel**

132 The refractive index of a medium is a measure of how much the velocity of a wave is  
133 reduced inside that medium. In this experiments the Abbe refractometer was used to measure the  
134 refractive index.

### 135 136 **2.2.4 Determination of saponification value of palm oil sludge and biodiesel**

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

$$SV = \frac{3 \times 56.1 \times 1000}{(MMW \times 3) + 92.09 - (3 \times 18)}$$

3

142

143 Where:

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

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

146 56.1 is molecular mass of KOH (g/mol), 1000 is conversion of units (mg/g)

147 92.09 is molecular mass of glycerol (g/mol), 18 is molecular mass of water (g/mol)

### 148 **2.2.5 Determination of acid value of palm oil sludge and biodiesel**

149 Acid value was determined according to ASTM-D 664. The acid value is the number of  
 150 milligrams of KOH required to neutralize all acid in 1g of the sample. The acid value was  
 151 determined by titration of the sample (oil or Biodiesel) dissolved in the mixture of ethanol-  
 152 toluene with a standardized titration solution of KOH. In this method, a weighed amount of the  
 153 sample (oil or Biodiesel) was added into a flask and it was dissolved in an ethanol-toluene  
 154 mixture; phenolphthalein was added as an indicator. KOH was used as titrant solution. The  
 155 titration process was stopped when the solution turned into pink color. The acid value (AV) was  
 156 calculated using the equation below:

$$157 \quad AV \left( \frac{mgKOH}{g} \right) = \frac{56.1 \times C_{KOH} \times V_{KOH}}{m}$$

4

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

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

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

### 162 **2.2.6 Determination of iodine number of palm oil sludge and biodiesel**

163 This was determined according to the ASTM standard- EN 14104. The iodine value was  
 164 obtained by weighing 0.5 g waste frying oil and pour into Erlenmeyer flask. 10 ml of chloroform  
 165 solution and 25 ml of Hanus solution (Iodine-Bromide Reagent) were added, shaken until all oil  
 166 were well blended and kept in a dark room for 30 minutes. 10 ml of 15% KI solution was added.  
 167 Titration was done with a solution of 0.1 N  $Na_2S_2O_3$  and the indicator used was 1% starch. The  
 168 titration was stopped when a clear solution was obtained.

169 Iod Number=
$$\frac{(b-a) \times N \times Na_2S_2O_3 \times 12.69}{g}$$

5

170 Where:

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

### 173 **2.2.7 Determination of free fatty acid of palm oil sludge**

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

181 
$$\%FFA = \frac{V \times M \times N}{m \times 10}$$

6

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

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

### 184 **2.2.8 Determination of pour and flash points of biodiesel**

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

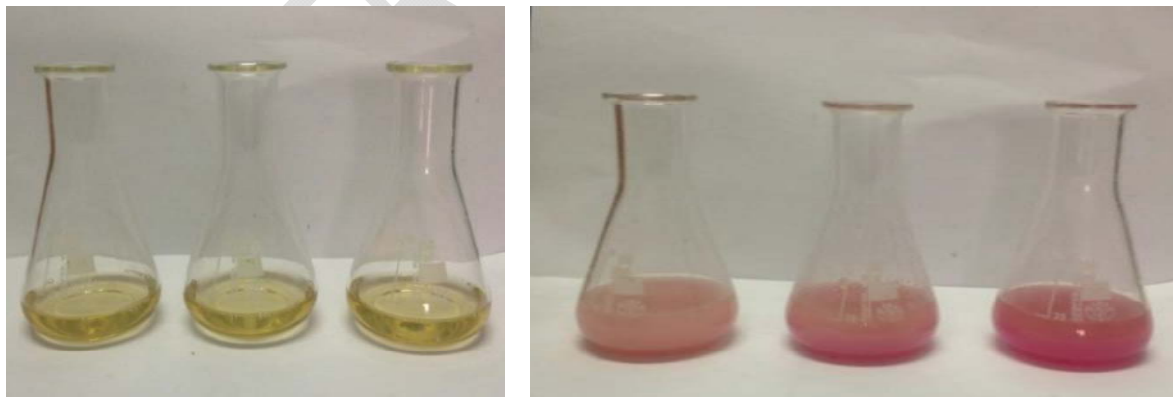


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188 **Plate 2.2: Free fatty acid titration**

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

### 195 **2.3.9 Determination of the amount of methanol to oil ratio used for the process.**

196

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

198

$$199 \quad M = \frac{56.1 \times 1000 \times 3}{SV - AV} \quad 7$$

200

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

202 Thereafter the amount of methanol was determined by using Equation (8)

203

$$204 \quad M = \frac{O \times b \times MWM}{a \times MWO} \quad 8$$

205

206 O=Amount of oil, M=Amount of methanol, MWO=Molecular weight of oil

207 MWM=Molecular weight of methanol, a=molar ratio of oil, b=molar ratio of methanol

208

## 209 **2.3 Experimental Procedure**

### 210 **2.3.1 Deacidification of palm oil sludge by esterification reaction**

211 The esterification reaction was done according to the procedure reported by (54).100ml  
212 of palm oil sludge (POS) was **measure and heated at 60°C by hot plate,** then sulphuric acid  
213 (0.14ml) and methanol (55ml) were added to the palm oil sludge, the mixture was poured into  
214 round bottom flasks and then stirred with magnetic stirrer at 800rpm for 60mins thereafter the  
215 mixture was allowed to settle in a separation funnel for 2hrs in order to achieve 2 distinct liquid  
216 phases (water at the top and preheated oil at the bottom).

### 217 **2.3.2 Transesterification of treated palm oil sludge**

218 The transesterification reaction was carried out in accordance with the procedure of  
219 Aworanti *et al.* ( 8). Different amount of methanol and catalyst which are shown in Table 2.1-  
220 2.2 were weighed and mixed vigorously with a magnetic stirrer in order for the catalyst to be  
221 dissolved and form potassium methoxide solution. Constant volume of pretreated palm oil sludge  
222 (100ml) was heated to 60°C, then potassium methoxide solution formed was poured gently into  
223 the heated palm oil sludge (POS) in a round bottom flask. The entire mixture was stirred with hot  
224 plate magnetic stirrer at 300 rpm and the temperature was maintained at 60°C. The reaction time  
225 for the process **were also varied and shown in Table** (2.3). After the process, the mixture was  
226 poured into a separating funnel and kept for 24hours so as to separate the glycerin from the  
227 biodiesel. The separation segment is glycerol layer at the bottom and biodiesel layer at the top.

228 Thereafter the physicochemical properties of biodiesel derived from the transesterification of  
 229 POS were determined and compared with European norms biodiesel. The apparatus set-up for  
 230 the biodiesel production is shown in plate 2.4. The samples of biodiesel produced are shown in  
 231 plate 2.6. The biodiesel yield of the transesterification process was calculated using Equation (9)

$$232 \text{ Biodiesel yield}(\%) = \frac{MBP}{MWFO \text{ Used}} \times 100 \quad 9$$

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

234 **Table 2.1: Percentage of Catalyst used for each Run at Constant Reaction Time and Molar**  
 235 **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

236  
 237

238 **Table 2.2: Oil to Methanol Molar Ratio used for each run at Constant Catalyst and Reaction Time**  
 239

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

240  
 241

**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

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



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



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

256

## 257 2.6 Experimental Design

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

262

263

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

265

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

266

267

268

## 269 RESULTS AND DISCUSSION

### 270 3.1 Physicochemical characterization of palm oil sludge used in biodiesel production.

271 The result of the properties of palm oil sludge analyzed in this study is as presented in Table 3.1,  
272 it was observed that the free fatty acid values of the sample were more than 2%, which justifies  
273 pretreatment (esterification) of the samples in order to reduce the free fatty acids in the palm oil  
274 sludge (1). The high free fatty acids content in the palm oil sludge (25.25%) can result in soap  
275 formation in the presence of potassium hydroxide during transesterification reaction of the oil.  
276 Studies also have shown that high FFA reduces catalyst effectiveness and decreases the  
277 production yield (50; 1). (21;56) reported the free fatty acid value of palm oil sludge to be 74.8%  
278 and 22.3%. In this work, the water content in the palm oil sludge was 0.03% which was less than  
279 0.05%. The results obtained are within the range reported in the literature (0.05%) (43). Presence  
280 of water content in palm oil sludge is an important issue which also affects the biodiesel yield.  
281 Presence of high water content in the oil during transesterification reaction has a negative effect  
282 on the free fatty acid. High water content in the palm oil sludge leads to soap formation when it  
283 is reacted with catalyst during transesterification reaction (39; 48; 55). **Hydrolysis is formed**  
284 **during transesterification reaction, due to the presence of high water content in the palm oil**  
285 **sludge samples and this increases the free fatty acid in the oil (58).** These two properties (water  
286 content and free fatty acid) in oil can reduce the effect of catalyst and lower the biodiesel yield  
287 (13;39). To avoid the saponification reaction, hydrolysis and reduction in catalyst, the oil must  
288 be heated at a particular temperature in order to remove the water, then pretreatment of this oil  
289 by the esterification reaction with sulfuric acid in the presence of methanol was required to  
290 reduce the free fatty acids (FFA) to the limit necessary to achieve the transesterification reaction.  
291 The density of palm oil sludge used for the transesterification reaction was  $976 \text{ kg/m}^3$ . The  
292 results obtained are within the range reported in the literature ( $0.9625 \text{ g / ml}$  and  $0.9772 \text{ g / ml}$ )  
293 (46). Comparing this literature value with **the specific gravity values of** palm oil sludge in this  
294 research work, we concluded that there is no significant difference with values reported in the  
295 literature. It was observed from the result that the oil density decreased from  $976 \text{ kg/m}^3$  to  $857$   
296  $\text{kg/m}^3$  after transesterification reaction and this has a significant impact on the viscosity value of  
297 the biodiesel i.e the viscosity decreased from  $42.45 \text{ mm}^2/\text{s}$  to  $5.35 \text{ mm}^2/\text{s}$ . The kinematic viscosity

298 value of the palm oil sludge used for the research work was 42.45 mm<sup>2</sup>/s (16) reported the  
 299 viscosity value of palm oil sludge to be 41mm<sup>2</sup>/s, which is in the range with the viscosity value  
 300 of palm oil sludge used in this research. Density, specific gravity and kinematic viscosities have  
 301 been described as one of the most basic and most important properties of fuel because some  
 302 important performance indicators such as cetane number and heating values are correlated with  
 303 the parameters ( 4; 6; 57). The saponification number of palm oil sludge used for this research  
 304 work was 191.6 mgKOH/g. The saponification number indicates the amount of potassium  
 305 hydroxide (KOH) needed to saponify (converted to soap) one gram of oil. (3) reported that the  
 306 saponification number of palm oil sludge ranges from 173.82 to 197 mg KOH / g oil. The  
 307 saponification number of palm oil sludge used in this work falls within the literature report. The  
 308 acid value of the palm oil sludge for this work was 50.50 mgKOH/g. The acid value is one of the  
 309 most important properties used to determine biodiesel quality and the percentage of free fatty  
 310 acids contained in each oil (28). It shows the amount of corrosive acid as well as oxidation  
 311 products present in the oil. From literature, the acid value should be lower than 0.50 mgKOH/g  
 312 specified by ASTM standard (52). Comparing this result with the literature it shows that the  
 313 palm oil sludge used in this research work has a very high acid value. Therefore the oil must be  
 314 pretreated in order to reduce free fatty acids. The iodine value of palm oil sludge was  
 315 56.40gI<sub>2</sub>/100g. The results obtained are within the range reported in the literature (40 – 55.7  
 316 gI<sub>2</sub>/100g) (3). This indicates that the iodine value indicates the amount of this compound which  
 317 can absorb the palm oil sludge in unsaturated bonds, that is, the larger the index value the greater  
 318 adsorption on the double bonds present in the oil (5).

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

Parameters determined	Palm oil sludge
Viscosity at 40°C (mm <sup>2</sup> /s)	42.45
Density (kg/m <sup>3</sup> )	976
Free fatty acid (%)	24.25
Specific gravity at 15°C g/cm <sup>3</sup>	0.976

Acid number mgKOH/g	50.50
Iodine value gI <sub>2</sub> /100g	56.40
Saponification value mgKOH/g	191.6
Water Content (%)	0.03

321

### 322 **3.3 Physical Property of Biodiesel Produced**

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

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

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

#### 334 **Iodine value of biodiesel product**

335 The result of iodine number of methyl ester from palm oil sludge was 55.8gI<sub>2</sub>/100g. The result of  
 336 the analysis shows that iodine number in biodiesel from synthesis according to standard biodiesel  
 337 value determined by SNI (31; 40). If the iodine value of biodiesel produced is higher than the  
 338 standard of 115 gI<sub>2</sub>/100 g it will lead to polymerization and formation of deposits in injector's  
 339 nozzle and piston rings at the start of combustion.

#### 340 **The density value of biodiesel product**

341 The result of density of the transesterification process from palm oil sludge was 857 kg/m<sup>3</sup>. The  
 342 results obtained meets the EN14214 and ASTM-D-6751 standard. Density provides information  
 343 on how the fuel will work in diesel engines. High-density value indicates some impurities in the

344 biodiesel (42).The use of high temperature during the transesterification reaction will increase  
345 the saponification reaction.

#### 346 **Viscosity value of biodiesel product**

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

#### 352 **Acid value of biodiesel product**

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

#### 363 **Flash Point and Pour Point**

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

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

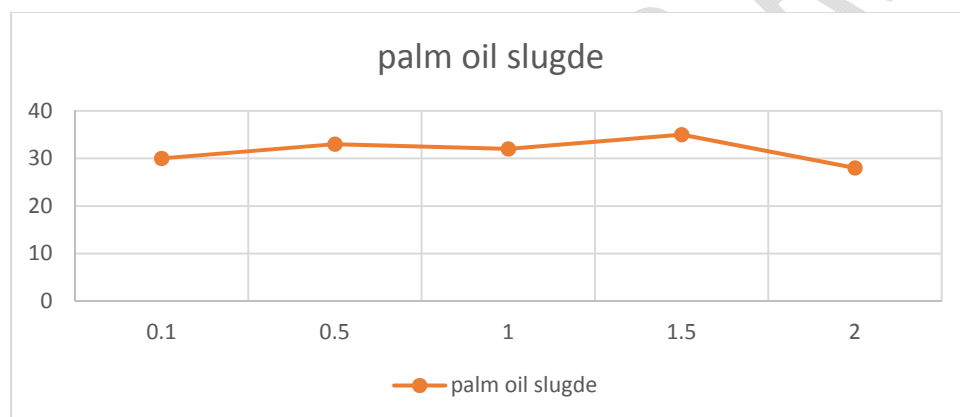
Properties	POS biodiesel	EN14214	ASTMD-6751
Acid value mgKOH/g	0.17	0.50	<0.8
Free fatty acid (%)	0.32		0.8
Density at 32°C (kg/m <sup>3</sup> )	857	860-900	875-900
Kinematic viscosity at 40°C (mm <sup>2</sup> /s)	5.38	3.5-5.0	1.9-6.0
Pour point(°C)	-5	-	-15 to 10
Flash point (°C)	180	120	>130
Iodine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

378

### 379 3.4 **Effect of Catalyst loading on Biodiesel Yield**

380 The result of the effect of catalyst loading on transesterification of palm oil sludge to  
 381 biodiesel using 9:1 methanol to oil ratio, stirring rate of 300rpm and temperature of 60°C for 90  
 382 min are shown in Figure 3. 1. It was observed from the graph that biodiesel yield increases with  
 383 an increase in catalyst loading up to 1.5 wt%. It was noticed that yield increases to 35% when the  
 384 catalyst loading increases by up to 1.5 wt% at 90 min, while it decreases to 28% above 1.5 wt%.  
 385 The optimum catalyst that gives the highest biodiesel yield was 1.5wt%. It was noticed from the  
 386 result that the yield of biodiesel increased slightly when the amount of catalyst increased from  
 387 0.1%-1.5% and biodiesel yield reduced drastically when the catalyst was increased to 2%.

388 However, an increase in catalyst amount up to 1.5 wt% increases the total number of active sites,  
389 resulting in an increase in biodiesel conversion (30;44), while an increase in catalyst loading  
390 above 1.5 wt% makes the reactant and catalyst mixture too viscous which leads to problems with  
391 mixing and poor diffusion of the reactants, resulting in a decrease in the biodiesel yield (9; 30;  
392 34; 53) . The decrease in yield may also be attributed to the fact that the solubility of methanol  
393 in oil is low and increasing catalyst loading provides more active sites to adsorb the products  
394 consequently, the yield of biodiesel decreases (26). Also the low biodiesel yield at catalyst  
395 loading above 1.5 wt% may be due to the attainment of mass transfer limitation (rate  
396 determining step) between the reactant and catalyst (59). KOH concentration 1.5 % (in relation to  
397 palm oil sludge mass) can, therefore, be taken as optimum for KOH-catalysed palm oil sludge  
398 transesterification with methanol under reaction conditions of 60° C temperature, 90 minutes  
399 duration.  
400



401

402

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

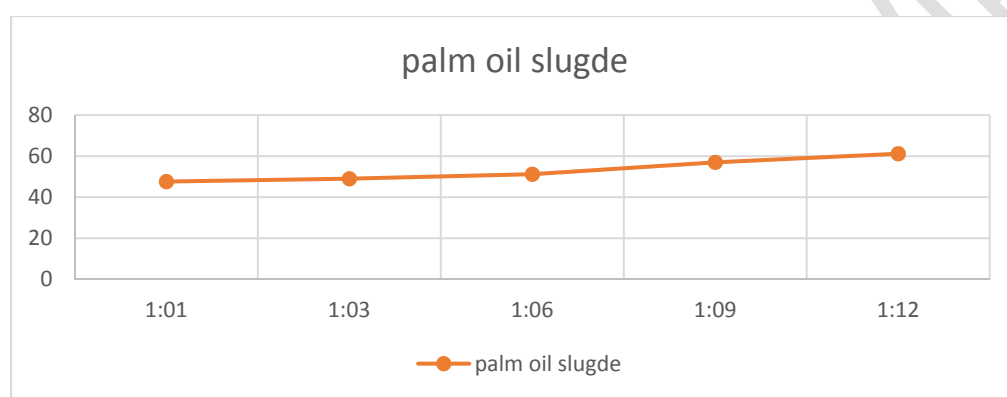
### 404 **3.5 Effect of Methanol/Oil Molar Ratio on Biodiesel Yield**

405 The effect of the varied molar ratio of palm oil sludge to methanol on the yield of biodiesel from  
406 transesterification of palm oil sludge are shown in Figure 3.2. Thus, this parameter was  
407 optimized by carrying out the transesterification reaction with various methanol to oil ratios (1 :  
408 1, 1 : 3, 1 : 6, 1:9 and 1 : 12) using a catalyst loading of 1.5% and at a time of 30min and  
409 temperature of 60°C. It was observed in Figure 3. 2, that methanol to oil ratio (12:1) gave the  
410 highest biodiesel yield of 61.2%. It was noticed that biodiesel yield increased as the methanol to  
411 oil ratio increased from 1:1 to 12:1 but it was a gradual increment. Thus, the optimum molar

412 ratio was 12:1 and this can be used for the production of biodiesel from palm oil sludge under a  
413 magnetic stirrer heating system, especially with the application of KOH catalyst and methanol.  
414 The methanol to oil ratio is another important factor which affects the biodiesel yield. In order to  
415 increase the biodiesel yield and to keep the equilibrium on the right side of the reaction, it is  
416 necessary to increase the methanol in the reaction (25). Hypothetically, every mole of biodiesel  
417 is a result of one mole of methanol and 1/3 of a triglyceride mole from the transesterification  
418 response. Stoichiometrically, 3 mol of methanol is required to one mol of glyceride (55).

419

420



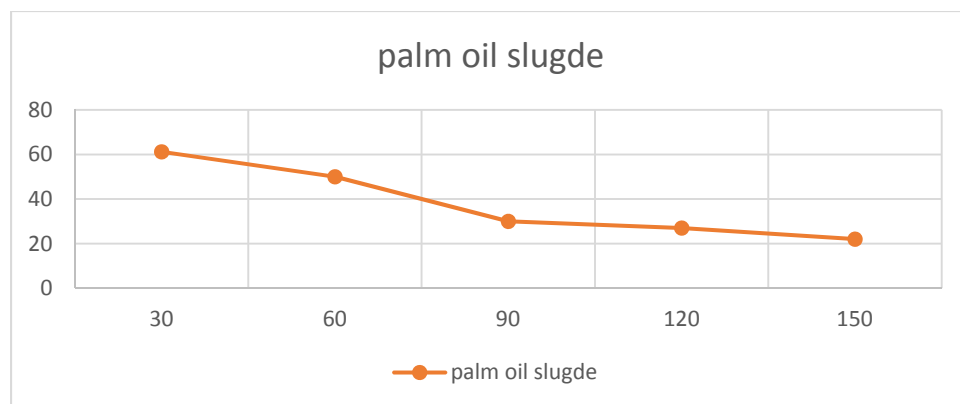
421

422

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

### 425 3.6 Effect of Reaction Time on Biodiesel Yield

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



436

437

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

439

## 440 **Conclusion**

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

454

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