

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

3

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

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

19

Introduction

20 Human activities are largely dependent on energy and due to the increase in population, there has
21 been consistent demand in every arena for energy, all these resulted into high price of non-
22 renewable energy (45). Production of fossil fuel causes some many problems such as human
23 health problem, environmental degradation, global climate change, emission of greenhouse gases
24 etc. (7; 29) . Increase in growth of the economy, consumption rate of energy, depleting of fossil
25 fuel and negative effect of fossil fuel on the environment led to search for alternative fuel in
26 both developed and underdeveloped countries. Bio-diesel has been considered as one of the
27 alternative energy that can replace fossil fuel (29; 37 ; 41). Biodiesel, which is also called
28 mixture of fatty acid methyl esters (FAMES) or fatty acid ethyl ester (FAEE) has been designed
29 as one of the most renewable fuel and alternative fuel for diesel engine, it has many advantages

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

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

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86

87

MATERIAL AND METHODS

2.1 Sample collection and feedstock preparation

89 Palm oil sludge (POS) was collected from various locally palm oil processing place in
90 Ogbomosho, Oyo state, Nigeria. Methanol, sulphuric acid, propanol, potassium oxide and
91 phenolphthalein were obtained from a chemical store in Ibadan, Oyo state, Nigeria. A round

92 bottom flask was used as a reactor and magnetic stirrer with hot plate was used as a stirring and
93 heating medium. The palm oil sludge was heated at 70⁰C, thereafter the hot palm oil sludge was
94 filtered using filter paper in order remove its impurities, suspended particles and inorganic
95 materials present in the waste oil. The palm oil sludge was filtered to avoid impairment of oil
96 quality causing reduction in the productivity of the transesterification reaction and also to avoid
97 generation of undesirable by-products that will hurt the final product (12). The palm oil sludge
98 used for this research work are shown in plate 2.1



99
100 **Plate 2.1: Sample of palm oil sludge**

101 **2.2 Chemical characterization of the Palm Oil Sludge**

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

106 107 **2.2.1 Determination of density and dynamic of palm oil sludge and biodiesel**

108 Density of palm oil sludge and biodiesel at 15⁰C were determined by gravimetric
109 analysis, 25ml waste frying oil was measured with a glass cylinder and the mass of the oil was
110 determined by electronic scale. The density was calculated using equation (1).

$$111 \rho = \frac{m}{v}$$

1

112
113 m [g] is weight of the sample; v [cm³] volume of the sample.

114 **2.2.2 Determination of viscosity of palm oil sludge and biodiesel**

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

$$121 \quad \eta = k * t * (\rho_{ball} - \rho_{medium}) \quad 2a$$

$$122 \quad \nu = \frac{\eta}{\rho} \quad 2b$$

123 Where, η is the dynamic viscosity [g/cm. s], ν is the kinematic viscosity [g/cm, s],
124 k is the geometrical constant of the ball [m²], t is the fall time through the tube [s],
125 ρ_{ball} is the density of the ball [g/cm³] and ρ_{medium} is the density of the medium [g/cm³], ρ is the
126 density of the sample [g/cm³].

127 **2.2.3 Determination of refractive index of palm oil sludge and biodiesel**

129 The refractive index of a medium is a measure of how much the velocity of a wave is
130 reduced inside that medium. In this experiment the Abbe refractometer was used to measure the
131 refractive index. The light ray pitched on the interphase of phases then it was refracted. The
132 impact angles, rebound and the refraction were measured between a ray running perpendicular to
133 the phase interface. Ray break is a result of differences in the speed of light in both phases.
134 Refractive index is the ratio of the speed of light in phases, the light passes through. Its principle
135 is the detection of limit angle fracture (β_{max}), which is the maximum possible angle fracture
136 where the angle of impact is close to 90°.

137 **2.2.4 Determination of saponification value of palm oil sludge and biodiesel**

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

$$143 \quad SV = \frac{3 \times 56.1 \times 1000}{(MMW \times 3) + 92.09 - (3 \times 18)} \quad 3$$

144

145 Where:

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

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

148 56.1 is molecular mass of KOH (g/mol), 1000 is conversion of units (mg/g)

149 92.09 is molecular mass of glycerol (g/mol), 18 is molecular mass of water (g/mol)

150 **2.2.5 Determination of acid value of palm oil sludge and biodiesel**

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

$$159 \quad AV\left(\frac{mgKOH}{g}\right) = \frac{56.1 \times C_{KOH} \times V_{KOH}}{m} \quad 4$$

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

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

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

164 **2.2.6 Determination of iodine number of palm oil sludge and biodiesel**

165 This was determined according to the ASTM standard-5554. The iodine value was
166 obtained by weighing 0.5 g waste frying oil and pour into Erlenmeyer flask. 10 ml of chloroform
167 solution and 25 ml of Hanus solution (Iodine-Bromide Reagent) were added, shaken until all oil
168 were well blended and kept in a dark room for 30 minutes. 10 ml of 15% KI solution was added.
169 Titration was done with a solution of 0.1 N Na₂S₂O₃ and the indicator used was 1% starch. The
170 titration was stopped when a clear solution was obtained.

$$171 \quad \text{Iod Number} = \frac{(b-a) \times N \times Na_2S_2O_3 \times 12.69}{g} \quad 5$$

172 Where:

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

175 **2.2.7 Determination of free fatty acid of palm oil sludge**

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

$$183 \quad \%FFA = \frac{V \times M \times N}{m \times 10} \quad 6$$

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

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

186 **2.2.8 Determination of pour and flash points of biodiesel**

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

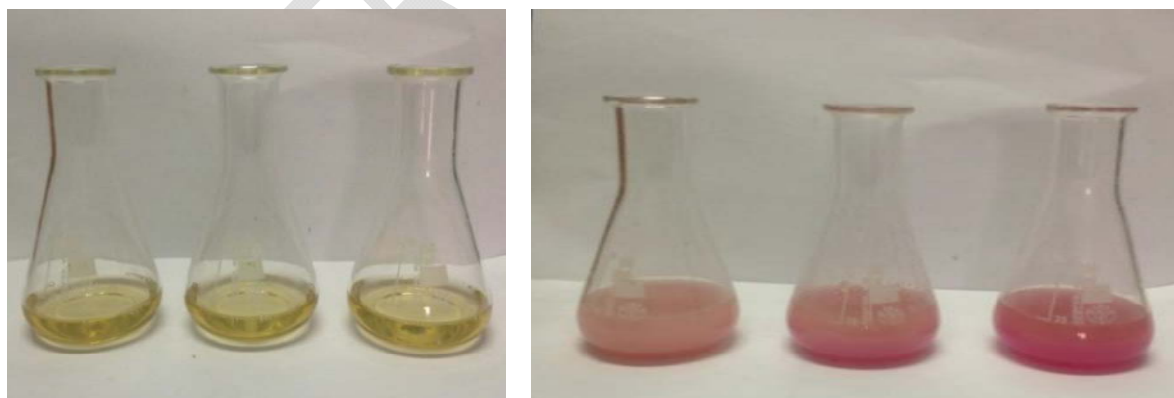


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190 **Plate 2.2: Free fatty acid titration**

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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.

198

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

200

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

202

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

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

205

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

207

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

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

210

2.3 Experimental Procedure

2.3.1 Desacidification of palm oil sludge by esterification reaction

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

2.3.2 Transesterification of treated palm oil sludge

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

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

$$235 \text{ Biodiesel yield}(\%) = \frac{MBP}{MWFO \text{ Used}} \times 100 \quad 9$$

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

237 **Table 2.1: Percentage of Catalyst used for each Run at Constant Reaction Time and Molar**
 238 **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

239

240

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

242

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

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

244

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 slugde



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255

256

257

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

259

260 2.6 Experimental Design

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

265

266

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

268

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

269

270

271

272 **RESULTS AND DISCUSSION**

273 **3.1 Physicochemical characterization of palm oil sludge used in biodiesel production.**

274 The result of the properties of palm oil sludge analyzed in this study is as presented in Table 3.1,
275 it was observed that the free fatty acid values of the sample was more than 2%, which justifies
276 pretreatment (esterification) of the samples in order to reduce the free fatty acids in the palm oil
277 sludge (1). The high free fatty acids content in the palm oil sludge (25.25%) can result into soap
278 formation in the presence of potassium hydroxide during transesterification reaction of the oil.
279 Studies also shown that high FFA reduces catalyst effectiveness and decreases the production
280 yield (50; 1). (21;56) reported the free fatty acid value of palm oil sludge to be 74.8% and 22.3%.
281 In this work the water content in the palm oil sludge was 0.03% which was less than 0.05%. The
282 results obtained are within the range reported in the literature (0.05%) (43). Presence of water
283 content in palm oil sludge is an important issue which also affect the biodiesel yield. Presence of
284 high water content in the oil during transesterification reaction has negative effect on free fatty
285 acid. High water content in the palm oil sludge lead to soap formation when it is reacted with
286 catalyst during transesterification reaction (39; 48; 55). Also hydrolysis is formed during
287 transesterification reaction, due to the presence of high water content in the palm oil sludge
288 samples and this increases the free fatty acid in the oil (58). These two properties (water content
289 and free fatty acid) in oil can reduce the effect of catalyst and lower the biodiesel yield (13;39).
290 To avoid the saponification reaction, hydrolysis and reduction in catalyst, the oil must be heated
291 at a particular temperature in order to remove the water, then pretreatment of this oil by the
292 esterification reaction with sulfuric acid in the presence of methanol was required to reduce the
293 free fatty acids (FFA) to the limit necessary to achieve the transesterification reaction. The
294 density of palm oil sludge used for the transesterification reaction was 976 kg/m^3 . The results
295 obtained are within the range reported in the literature (0.9625 g / ml and 0.9772 g / ml) (46).
296 Comparing this literature value with the density values of palm oil sludge in this research work,
297 we concluded that there is no significance difference with values reported in the literature. It was
298 observed from the result that the oil density decreased from 976 kg/m^3 to 857 kg/m^3 after
299 transesterification reaction and this has a significant impact on the viscosity value of the
300 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

301 value of the palm oil sludge used for the research work was 42.45 mm²/s (16) reported the
302 viscosity value of palm oil sludge to be 41mm²/s, which is in the range with the viscosity value
303 of palm oil sludge used in this research. Density, specific gravity and kinematic viscosities have
304 been described as one of the most basic and most important properties of fuel because some
305 important performance indicators such as cetane number and heating values are correlated with
306 the parameters (4; 6; 57).The saponification number of palm oil sludge used for this research
307 work was 191.6 mgKOH/g. The saponification number indicates the amount of potassium
308 hydroxide (KOH) needed to saponify (converted to soap) one gram of oil. (3) reported that the
309 saponification number of palm oil sludge ranges from 173.82 to 197 mg KOH / g oil. The
310 saponification number of palm oil sludge used in this work falls within the literature report. The
311 acid value of the palm oil sludge for this work was 50.50 mgKOH/g. The acid value is one of the
312 most important properties used to determine biodiesel quality and the percentage of free fatty
313 acids contained in each oil (28). It shows the amount of corrosive acid as well as oxidation
314 products present in the oil. From literature the acid value should be lower than 0.50 mgKOH/g
315 specified by ASTM standard (52). Comparing this result with the literature it shows that the
316 palm oil sludge used in this research work has a very high acid value. Therefore the oil must be
317 pretreated in order to reduce free fatty acids. The iodine value of palm oil sludge was
318 56.40gI₂/100g. The results obtained are within the range reported in the literature (40 – 55.7
319 gI₂/100g) (3). This indicate that the iodine value indicates the amount of this compound which
320 can absorb the palm oil sludge in unsaturated bonds, that is, the larger the index value the
321 greater adsorption on the double bonds present in the oil (5).

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

Parameters determined	Palm oil sludge
Viscosity at 40°C (mm ² /s)	42.45
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 gI ₂ /100g	56.40
Saponification value mgKOH/g	191.6
Water Content (%)	0.03

324

325 **3.3 Physical Property of Biodiesel Produced**

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

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

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

337 **Iodine value of biodiesel product**

338 The result of iodine number of methyl ester from palm oil sludge was 55.8gI₂/100g. The result of
 339 the analysis shows that iodine number in biodiesel from synthesis according to standard biodiesel
 340 value determined by SNI (31; 40). If the iodine value of biodiesel produced is higher than the
 341 standard of 115 gI₂/100 g it will lead to polymerization and formation of deposits in injector's
 342 nozzle and piston rings at the start of combustion.

343 **Density value of biodiesel product**

344 The result of density of transesterification process from palm oil sludge was 857 kg/m³. The
 345 results obtained meets the EN14214 and ASTM-D-6751 standard. Density provides information
 346 on how the fuel will work in diesel engines. High density value indicate some impurities in the

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

349 **Viscosity value of biodiesel product**

350 The result of viscosity value of biodiesel from palm oil sludge was 5.38 mm²/s. The result of the
351 analysis falls within the specification range of the ASTM D-6751 standard. Viscosity is defined
352 as fluid resistance to the flow rate of a mm-sized capillary. If the viscosity value is high it will
353 lead to formation of oxidized polymeric compounds and this can lead to the formation of gums
354 and sediments that clog the filters in the engine (10).

355 **Acid value of biodiesel product**

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

366 **Flash Point and Pour Point**

367 Flash point is the temperature at which biodiesel burns when in contact with ignition source. The
368 value of flash point of the biodiesel produced from palm oil sludge was 180 °C. This value fall
369 within the range of biodiesel flash point standard (ASTM D6751). Pour point has been described
370 as an important parameter for low temperature operation of a fuel also the lowest temperature at
371 which fuel can flow. It is the temperature at which wax becomes visible when the fuel is cooled
372 and it is sufficient to gel the fuel (6). The value of pour point of the biodiesel produced from
373 palm oil sludge was -5 °C. This value fall within the range of biodiesel pour point standard
374 (ASTM D6751). Lastly the appearances of the biodiesel produced was noticed, it was observed
375 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

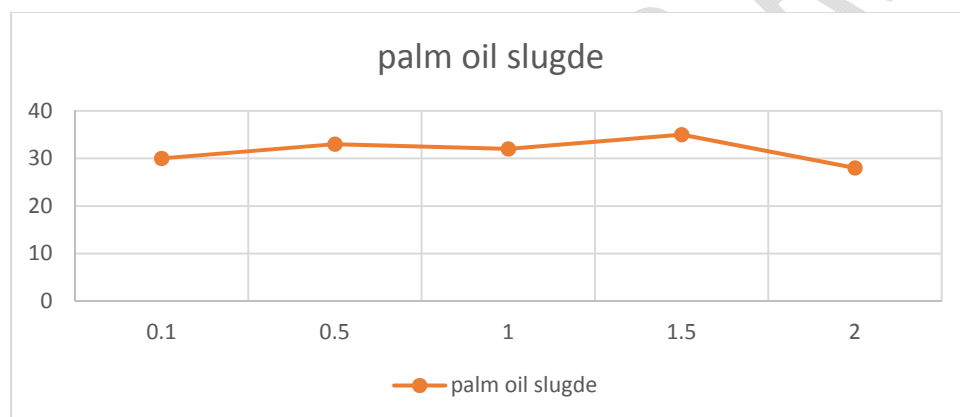
Properties	POS biodiesel	EN14214	ASTMD-6751
Acid value mgKOH/g	0.17	0.50	<0.8
Free fatty acid (%)	0.32		0.8
Density at 32°C (kg/m ³)	857	860-900	875-900
Kinematic viscosity at 40°C (mm ² /s)	5.38	3.5-5.0	1.9-6.0
Pour point(°C)	-5	-	-15 to 10
Flash point (°C)	180	120	>130
Iodine value gI ₂ /100g	55.8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

381

382 3.4 Effect of Catalyst Percentage on Biodiesel Yield

383 The result of the effect of catalyst loading on transesterification of palm oil sludge to
 384 biodiesel using 9:1 methanol to oil ratio, stirring rate of 300rpm and temperature of 60°C for 90
 385 min are shown in Figure 3. 1. It was observed from the graph that biodiesel yield increases with
 386 increase in catalyst loading up to 1.5 wt%. It was noticed that yield increases to 35% when the
 387 catalyst loading increases up to 1.5 wt% at 90 min, while it decreases to 28% above 1.5 wt%.
 388 The optimum catalyst that gives the highest biodiesel yield was 1.5wt%. It was noticed from the
 389 result that the yield of biodiesel increased slightly when the amount of catalyst increased from
 390 0.1%-1.5% and biodiesel yield reduced drastically when the catalyst was increased to 2%.

391 However, an increase in catalyst amount up to 1.5 wt% increases the total number of active sites,
392 resulting in an increase in biodiesel conversion (30;44), while an increase in catalyst loading
393 above 1.5 wt% makes the reactant and catalyst mixture too viscous which leads to problems with
394 mixing and poor diffusion of the reactants, resulting in a decrease in the biodiesel yield (9; 30;
395 34; 53) . Decrease in yield may also be attributed to the fact that the solubility of methanol in oil
396 is low and increasing catalyst loading provides more active sites to adsorb the products
397 consequently, the yield of biodiesel decreases (26). Also the low biodiesel yield at catalyst
398 loading above 1.5 wt% may be due to the attainment of mass transfer limitation (rate
399 determining step) between the reactant and catalyst (59). KOH concentration 1.5 % (in relation to
400 palm oil sludge mass) can therefore be taken as optimum for KOH-catalysed palm oil sludge
401 transesterification with methanol under reaction conditions of 60° C temperature, 90 minutes
402 duration.
403



404

405

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

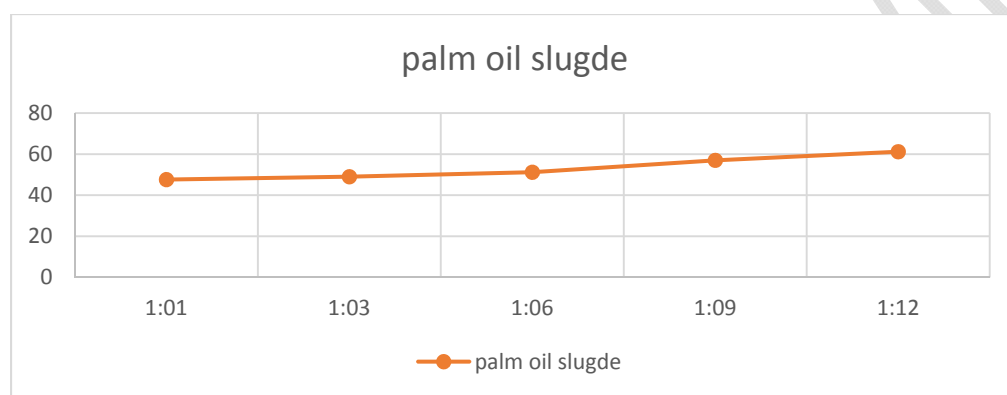
407 3.5 Effect of Methanol/Oil Molar Ratio on Biodiesel Yield

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

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

422

423



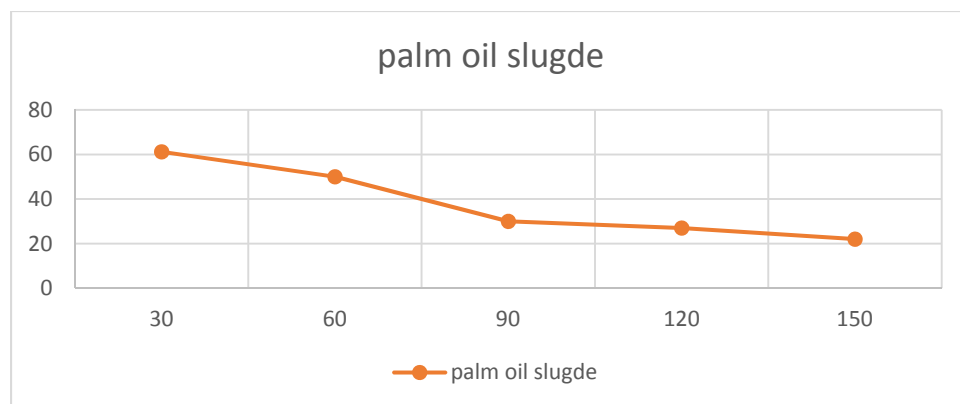
424

425

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

428 3.6 Effect of Reaction Time on Biodiesel Yield

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



439

440

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

442

Conclusion

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

456

457

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