

Kolanut pod husk as a biobase catalyst for fatty acid methyl ester production using *Thevetia peruviana* (Yellow oleander) seed oil

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Abstract. The potential of kolanut pod husk as a biobase catalyst for the conversion of *Thevetia peruviana* (yellow oleander) seed oil to fatty acid methyl ester (FAME) in transesterification reactions was investigated. Oil was extracted from *Thevetia peruviana* (yellow oleander) seeds and a yield of 60 % was obtained. Kolanut pod husk was ashed in a muffle furnace at 600 °C and characterized. In producing the FAME, three concentrations (0.5, 1.0 and 1.5 wt %) of kolanut pod husk ash (KPHA) were investigated in transesterification reactions. Methanol to oil ratio was kept constant at 6:1 while temperature and time were varied at 40-60 °C and 60-120 min respectively. The design of experiments was used in the transesterification step to determine the effects of process variables on the yield of *Thevetia peruviana* methyl esters (TPME). The result showed the TPME was consistent with ASTM specifications for biodiesel. The best yield of 84.50 % was obtained for 1.5 wt % KPHA at a temperature of 60 °C and a time of 90 min. XRD and elemental analysis indicated that the catalytic effect of KPHA resulted from the presence of potassium and the microstructural formation from calcination at 600 °C. The study highlights the possibility of reducing the cost of production for FAME by using non edible vegetable oil and kolanut pod husk, an agricultural waste as a biobase catalyst in transesterification reactions.

Key words: Kolanut pod, Fatty Acid Methyl Esters, Transesterification, Yellow Oleander

1. Introduction

Energy is an important tool needed for global development; the use of fossil fuel to meet energy demands has however brought with it prosperity as well as some negatives [1]. Energy sources from fossil fuel amount to about three quarters of the world's energy consumption [2] and this high reliance on it as a non renewable resource has led to its great depletion. The continuous and increasing need for energy resources and the desire to bridge the gap of insufficiencies has resulted in an obvious alternative: Biodiesel [3].

Biodiesel is attractive and a natural alternative to fossil fuel because it is a renewable fuel, it is environmental friendly; it is also biodegradable and non toxic [4]. Best of all it possess very similar characteristics with present day diesel fuel from fossils [5]. The very wide range of feedstock for biodiesel production is also an added advantage. Feedstock can be sourced from edible and non-edible vegetable oil, animal fats, waste cooking oil and more recently algae [5]. The production of biodiesel is achieved by the transesterification of triglyceride using alcohol with the aid of a catalyst [6]. Demand for biodiesel has greatly increased over the years; this has generated concern for its sustainability mainly because major industrial production of biodiesel is from food sources: starch and



sugar [7]. However Research into new generation bio-fuels from cellulose by enzymatic conversion and fermentation as well as non-edible plants and plant parts are currently on going. It is believed that in the near future, commercialization of biodiesel production from non-edible sources will take center stage.

Thevetia peruviana as a crop is one of such non-edible sources of feedstock for biodiesel production. It produces seeds which contain up to 65 % of non-edible vegetable oil [8]. It belongs to the order apocynales of apocyanaceae family [9]. It is a small tree believed to have its origin in tropical America: Mexico, Brazil and West Indies [10]. It also found in tropical parts of the world including Nigeria. It is a plant that grows well under varying climatic conditions; in arid zones as well as in areas with high rainfall. The evergreen plant starts to flower after 18months of planting and grows to a height of 3-4m. It flowers and fruits all year round producing about 400- 800 fruits per year [11]. The fruits are green in colour and become reddish black when fully mature and ripe; each mature fruit contains one to four seeds in its kernel.

In addition to using non edible oil in biodiesel production, another way to help reduce the cost of production is utilizing agricultural wastes as heterogeneous catalysts in place of homogenous ones [12]. The ashes of theses agricultural wastes are known to contain oxides of potassium and oxides of other elements [13] which have been reported to serve as effective bio-based catalysts for transesterification reactions [12].

In this paper, we investigate the use of kolanut pod husk ash as a bio-based catalyst for the transesterification of *Thevetia peruviana* seed oil. We also optimized the process variables (Temperature, reaction time and catalyst amount) for the transesterification reaction using response surface methodology (RSM).

2. Materials and methods

2.1. Materials

Thevetia peruviana seeds were handpicked at a residential premise in the Federal Capital Territory (F.C.T) Water Board Staff Quarters, Lower Usuma Dam Area, Abuja. Kolanut pods were sourced from Suleja market in Niger State, Nigeria. All chemicals and solvents used were of analytical grade, and were used without further treatment.

2.2. Methods

2.2.1. *Thevetia peruviana* seed oil extraction. The fleshy outer layers of the *Thevetia peruviana* seeds were peeled off and the inner part inner part sundried for 7 days then it was shelled and decorticated. The seeds were then sundried for another 14 days until a constant weight was reached. The seeds were ground to powder using a manual grinding machine and stored in an air tight plastic bag. The Soxhlet apparatus and petroleum ether as extraction solvent were used for this work. 250 ml of petroleum ether was delivered into the soxhlet extractor. 25 g of powered *Thevetia peruviana* seed on Whatman No1 filter paper was placed in the thimble of the soxhlet extractor. The heating mantle was set at a specified temperature and the extraction was carried out for a period of 3 h. The extraction solvent in the solvent-oil mixture was recovered by distillation.

2.2.2. Characterization of *Thevetia peruviana* seed oil. The *Thevetia peruviana* seed oil obtained was analyzed to determine its physical and chemical properties. Using ASTM standard methods (1983), density, specific gravity, viscosity, acid value, iodine value and saponification value were determined.

2.2.3. Preparation of kolanut pod husk catalyst. The Kolanut pods were manually peeled and the kolanut pod husks collected were washed with distilled water. They were then cut into smaller pieces to aid faster drying. The cut pieces were spread on a drying mat for continuous sun drying; which was carried out for 30 days until a constant weight was achieved. At the end of the drying period the

kolanut pod husks were placed in a furnace where it was combusted at a temperature of about 600°C for 3 h (until white ash was formed) and allowed to cool for another 2 h. The kolanut pod husk ashes (KPHA) formed were collected and stored in air tight plastic bags.

2.2.4. Characterization of KPHA. To determine the specific properties of the Kolanut Pod Husk Ash, various analyses were carried out. X-ray Diffraction (XRD) Analysis helped to show crystalline phases and x-ray diffraction patterns. To determine the surface area and pore size distribution, Brunauer, Emmett and Teller (BET) Analysis were performed. While elemental composition of the KPHA was determined using atomic absorption spectrophotometer.

2.2.5. Fatty acid methyl esters production. The biodiesel samples were prepared using transesterification reactions. KHPA Catalyst load of 0.5%, 1%, 1.5 % were utilized in the transesterification processes with methanol-to-oil ratio of 6:1 and reaction temperature of 40, 50 and 60°C. The reaction time used was varied from 60 to 120 min. A constant mixing speed of 400 rpm was utilized for all runs. The Thevetia peruviana methyl esters formed were then separated from the glycerol using a separating funnel after washing with distilled water. The washed Thevetia peruviana methyl esters were then allowed to air dry for 2 days. Air dried Biodiesel produced were characterized. Biodiesel yield was determined using equation 1.

$$\text{Biodiesel yield} = \frac{\text{Volume of biodiesel produced}}{\text{Volume of oil used}} \quad (1)$$

2.2.6. Experimental design for transesterification by Response surface methodology (RSM). The Thevetia peruviana methyl ester production was optimized using Response surface methodology, The Box-Behnken design with three factors and three coded levels having five centre points and 12 factorial points was used for a Quadratic, second order response surface.

Table 1 represents the optimization process variables and their code levels. It gives the three process variables used in the transesterification process, showing the symbols assigned to each variable and the three range and levels.

Table 1

Experimental range and levels of independent variables for Box-Behnken design

Variables	Symbols	Range and Levels		
		-1	0	1
Temperature (°C)	A	40	50	60
Time (min)	B	60	90	120
Catalyst (wt %)	C	0.5	1	1.5

The design expert version 7.0.0 (trial version) software was utilized in the regression analysis of actual experimental data.

2.2.7. Biodiesel Analysis. The biodiesel produced were analyzed for their density, viscosity, specific gravity and acid values according to ASTM standards. The biodiesel samples were also analyzed by Gas Chromatograph- Mass Spectrometer.

3. Results and discussion

3.1. Thevetia peruviana seed oil extraction and properties

The Thevetia peruviana seed oil produced was light gold in colour; it had a sweet smell and was liquid at room temperature. Analysis of the Thevetia peruviana oil produced determined some of its physical and chemical properties. Characteristics such as density, specific gravity, viscosity, acid value, iodine value and saponification value were determined, as shown in Table 2 below

Table 2

Physiochemical properties of *Thevetia peruviana* seed oil

Property	Value
Density @ 40 °C (g/cm ³)	0.895
Acid value (mg KOH/g)	1.089
Free fatty acid (mg KOH/g)	0.545
Saponification Value	341.599
Specific Gravity @ 40 °C	0.901
Viscosity @ 40 °C (Cp)	32.620
Oil Content (wt %)	59.66
Moisture content of seed cake (wt %)	2.797
Iodine Value (g I ₂ /100g)	70.600

The oil content of 60% obtained from the *Thevetia peruviana* seeds indicates that the seeds are rich in oil. This value is however lower than the value reported by Masime et al. [8] (66%) but can be considered to be ideal. It is ideal because for a seed to be seen as commercially viable with regards to large scale oil extraction it should possess at least 40% in oil content [14]. The low value for free fatty acid content of the extracted oil obtained in this research is an indication of its good resistance to hydrolysis. The acid value and free fatty acid values of 1.0893 and 0.5446 respectively were lower than the values reported by Yarkasuwa et al. [14] and Ogunneye et al. [15] but higher than that reported by Deka et al. [16]. The viscosity is also an important parameter in determining if an oil type would produce good biodiesel. The value obtained from this study shows a workable viscosity that would not prolong the time needed for complete transesterification of the oil.

3.2. Characterization of KPHA catalyst

The elemental compositions of KPHA are presented in Table 3. The major elements present were potassium, calcium, magnesium, silicon, phosphorous, sulphur, chlorine, aluminium and sodium with percent mass fraction 33.914, 25.382, 12.398, 7.335, 7.329, 4.921, 3.529, 1.959 and 1.740 respectively. The other elements were present in trace quantities.

X-ray diffraction analysis was used to identify the crystalline phase composition and crystallinity of KPHA as expressed in Fig 1. It showed the presence of Calcium Carbonate, 6-Aminopurine trihydrate, Calcium Hydroxide and Nitrogen. The KPHA surface area, pore size and pore volume were also determined. The specific surface area was found to be 398.547 m²/g, pore volume 0.203 cm³/g and the pore diameter 2.138 nm.

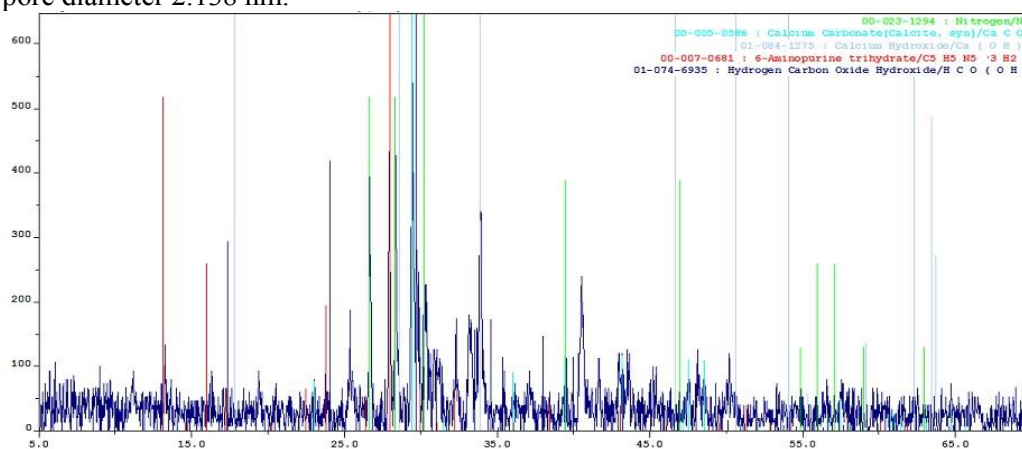


Figure 1. XRD chromograph of KPHA

From the pore diameter obtained the material is mesoporous. The high surface area and mesoporous nature attributes to the good performance of the catalyst.

Table 3
Elemental composition of KPHA

Element	% mass fraction
Potassium, K	33.914
Calcium, Ca	25.382
Magnesium, Mg	12.398
Silicon, Si	7.335
Phosphorous, P	7.329
Sulphur, S	4.921
Chlorine, Cl	3.529
Aluminum, Al	1.958
Sodium, Na	1.740
Iron, Fe	0.540
Manganese, Mn	0.407
Zinc, Zn	0.400
Others	0.148

3.3. Optimization of fatty acid methyl esters using RSM.

Table 4 below is a representation of the Ben-Behnken design showing the 17 standard runs randomly generated to minimize errors in the observed response. As shown in the table, the actual values obtained from the transesterification reactions and the predicted values generated are very similar which implies that the mathematical model generated (a quadratic regression model) best describes the process.

Table 4
Box-Behnken design for fatty acid methyl ester production

Standard run	A	B	C	Actual Value	Predicted Value	Residual
1	-1	-1	0	52	52.19	-0.19
2	1	1	0	72	72.56	-0.56
3	-1	1	0	57	56.44	0.56
4	1	1	0	79	78.81	0.19
5	-1	0	-1	55	55.50	-0.50
6	1	0	-1	73	73.13	-0.13
7	-1	0	1	59	58.88	0.13
8	1	0	1	84.5	84.00	0.50
9	0	-1	-1	65	64.31	0.69
10	0	1	-1	68	68.06	-0.063
11	0	-1	1	70	69.94	0.063
12	0	1	1	76	76.69	-0.69
13	0	0	0	69	68.94	0.060
14	0	0	0	68.7	68.94	-0.24
15	0	0	0	69.2	68.94	0.26
16	0	0	0	68.5	68.94	-0.44
17	0	0	0	69.3	68.94	0.36

A: Temperature; B: Time; C: Catalyst load

The Analysis of variance (ANOVA) test was used in the evaluation of the adequacy of the model. The results show that the quadratic regression model expressed using Equation 2 gives the best description of the process.

$$Yield = +68.94 + 10.69 * A + 2.62 * B + 3.56 * C + 0.50 * A * B + 1.88 * A * C + 0.75 * B * C - 2.91 * A^2 - 1.03 * B^2 + 1.84 * C^2 \quad (2)$$

where A is the reaction temperature, B is the reaction time and C is the catalyst load.

The Model F-value of 336.05 implies the model is significant. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, AB, AC, BC, A^2 , B^2 and C^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The standard deviation as obtained was 0.61 while the mean value was 67.95. The R-Squared value evaluated in experimental design is used to determine the amount of variation around the mean described by the model by adding factors to the model. The R^2 value evaluated for this work was 0.9977 meaning 99.77% of the variability can be accounted for. The Pred R-Squared value of 0.9688 is in reasonable agreement with the Adj R-Squared of 0.9947. Also the signal to noise ratio of 67.548 was obtained indicating adequate signal as a ratio greater than 4 is desirable.

Using the design expert software to solve the regression equation represented as equation 2, the optimum values for the process variables needed for the production of Thevetia peruviana methyl esters from Thevetia peruviana seed oil were obtained. They are reaction temperature 60 °C, reaction time 90 min and Catalyst load 1.5 wt %. The predicted yield of Thevetia peruviana methyl ester conversion under optimal condition was 84 %, this was however validated to be 84.12 % by redoing the experiment three times.

Table 5

Summary of the test of significance for regression coefficients and ANOVA

Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob>F	
Model	1140.44	9	126.72	336.05	< 0.0001	significant
A-Temperature	913.78	1	913.78	2423.36	< 0.0001	
B-Time	55.13	1	55.13	146.19	< 0.0001	
C-Catalyst	101.53	1	101.53	269.26	< 0.0001	
AB	1.00	1	1.00	2.65	0.1474	
AC	14.06	1	14.06	37.29	0.0005	
BC	2.25	1	2.25	5.97	0.0447	
A^2	35.59	1	35.59	94.40	< 0.0001	
B^2	4.49	1	4.49	11.90	0.0107	
C^2	14.29	1	14.29	37.91	0.0005	
Residual	2.64	7	0.38			Not significant
Lack of fit	2.19	3	0.73	6.45	0.0517	
Pure error	0.45	4	0.11			
Cor Total	1143.08	16	-			

Figure 2a illustrates the three dimensional plot of the relationship between temperature and time on the Thevetia peruviana seed oil conversion to biodiesel. The plot shows an increase in temperature significantly affects the conversion of oil to biodiesel. The three dimensional plot as a function of temperature and catalyst load is represented in Figure 2b. The significant influence of the variables of temperature and catalyst load on oil to biodiesel conversion is well defined in the plot. Figure 2c

represents the plot of reaction time and catalyst load, showing interactions between the reaction time and catalyst load.

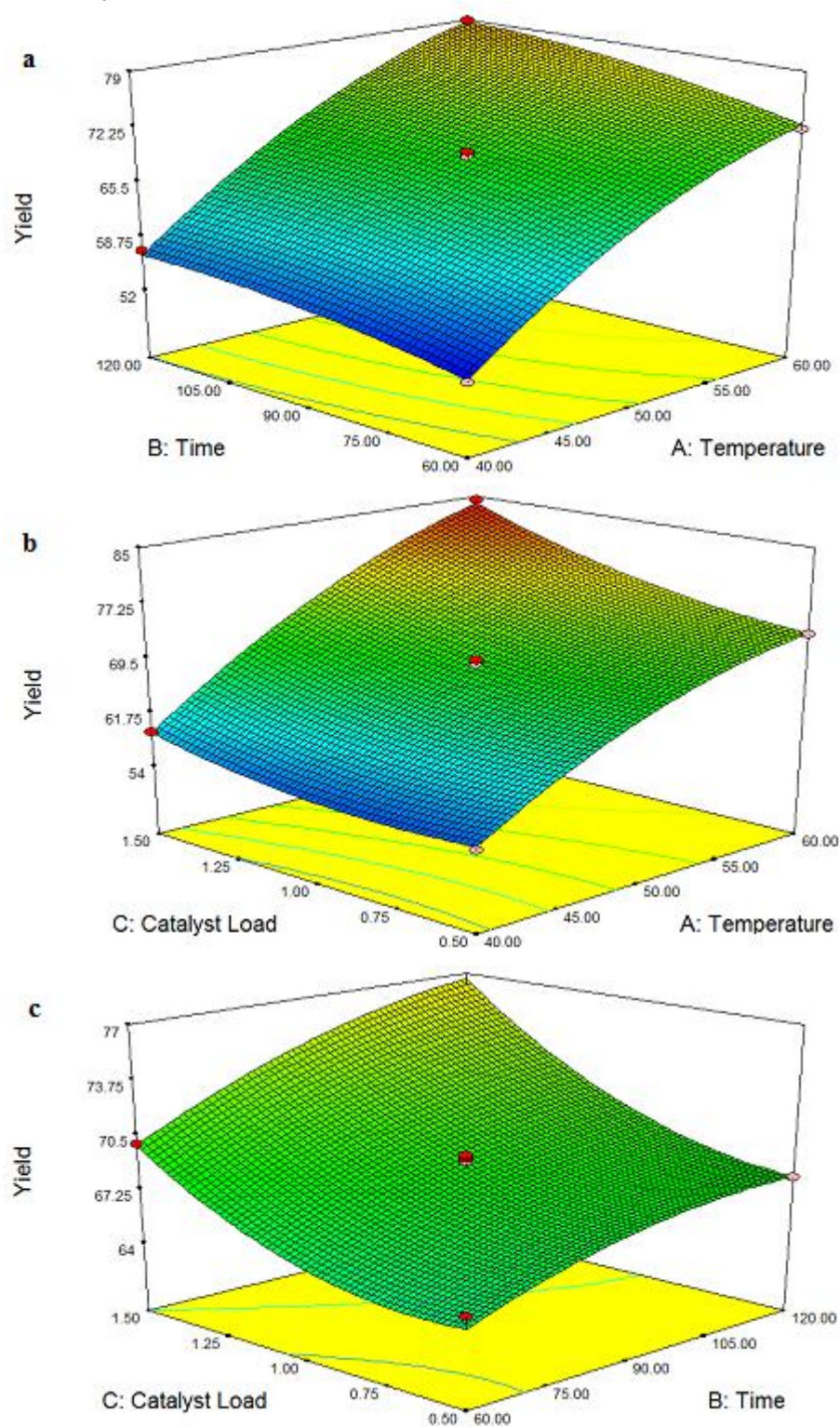


Figure 2. Three dimensional plot of Thevetia peruviana methyl ester yield

Figure 3 represents the plot of predicted values versus actual values obtained. The plot shows the similarity between the actual values obtained and the values predicted by the model, proving the accuracy of the model

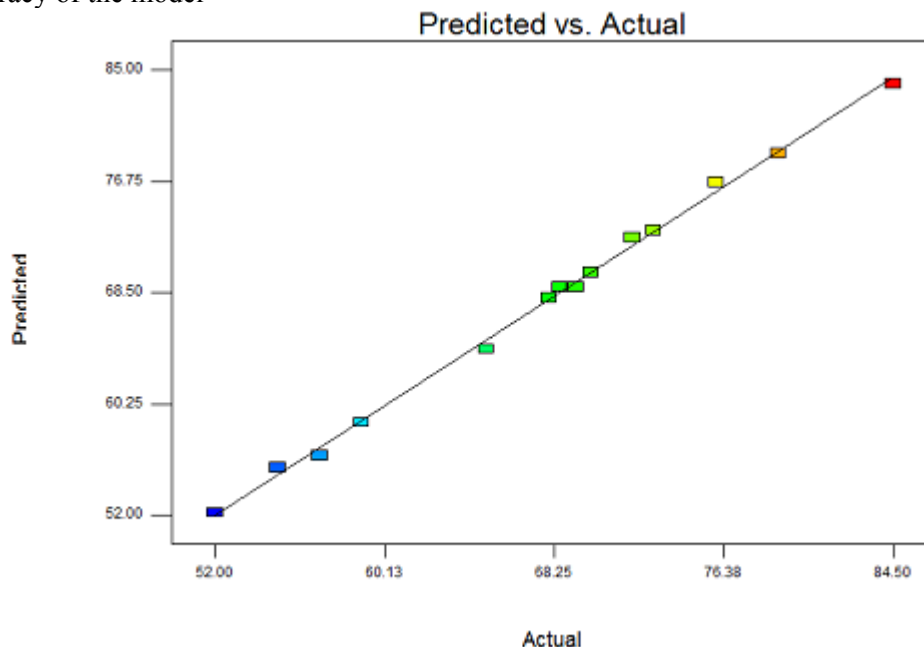


Figure 3. Plot of predicted values against actual values of biodiesel yield

3.4. Characterization of fatty acid methyl ester produced.

The summary of the fuel properties of the biodiesel produced from the KPHA catalysed transesterification reaction from *Thevetia peruviana* seed oil is shown in Table 6. The properties fell within the range of values specified by ASTM D6751 and ASTM D975 standards.

Table 6

Properties of biodiesel from *Thevetia peruviana* seed oil

Properties	Biodiesel from <i>Thevetia</i> <i>peruviana</i> seed oil	ASTM D6751 Standard for biodiesel	ASTM D975 Standard for Diesel fuel
Density (g/m ³)	0.872	0.88	0.85
Kinematic Viscosity 40 °C (mm ² /s)	5.4	1.9 - 6	1.3 - 4.1
Saponification Value (meq/kg)	170.8	-	-
Acid value (mgKOHg ⁻¹)	0.2	<0.8	-
Iodine Value (gI ₂ 100g ⁻¹)	84	-	-
Flash point (oC)	168	100-170	60-80
Cloud point (oC)	-5.6	-	-
Pour point (oC)	0.8	-15 to 10	(-35) to -15

4. Conclusion

The potential of the developed KPHA as an effective bio-base catalyst for biodiesel production has been demonstrated in this work. The availability of kolanut pod husk as an agricultural waste means the catalyst can be sourced with little or no cost. The successful optimization of process variables (reaction temperature, reaction time and catalyst load) in the transesterification reaction using response surface methodology to obtain a biodiesel yield of 84.5 % emphasizes the fact that *Thevetia peruviana* seed oil and kolanut pod husks can serve as cost effective feedstock for biodiesel production.

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