Cocoa pod ash as bio-based catalyst for biodiesel production from waste chicken fat

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Abstract: The growing interest in using sustainable raw materials coupled with the need to reduce the over- dependence on non-renewable petroleum resources has made agricultural residues attractive raw material for biofuel production. The potential utilization of cocoa pod ash (CPA) as a bio-based catalyst for the production of biodiesel from waste chicken fat was investigated. Bio-based catalyst was obtained from cocoa pods by ashing method. The catalyst was subjected to scanning electron microscope (SEM) analysis. The experimental design was based on a five level, two factor central composite design. CPA was used in the preparation of biodiesel from waste chicken fat (WCF) using a two-step esterification-transesterification process. The highest biodiesel yield of 75.4% was obtained at 3% wt catalyst concentration and 2 hours reaction time. The results obtained by GCMS analysis confirmed the fatty acid methyl ester production. The biodiesel properties such as density, viscosity, saponification value, iodine value, acid value and colour suggested CPA as a potential bio-based catalyst for transesterification of oil obtained from waste chicken fat.

Keywords: cocoa pod ash, agricultural residue, biofuel, bio-based catalyst, potash, Nigeria

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1 Introduction

Biodiesel has become a worldwide acceptable alternative fuel receiving much attention since it is believed to provide sustainable energy solution needed to mitigate the challenge of global warming. However, the higher production cost of biodiesel compared to the fossil fuel counterpart has been a bane in biodiesel production (Kirubakaran et al., 2018). The bid to reduce the production cost of biodiesel feedstock has led to more research towards using waste oils and animal fats as sources of biodiesel raw materials (Gameiro et al., 2015).

Cocoa pods are major agricultural wastes originating from cocoa plantations. The waste is worth considering because Nigeria is one of the major producers of cocoa in the world (ICCO, 2017). The use of agricultural residues such as cocoa pod for industrial purposes is ecologically friendly, cost effective and potentially sustainable. Cocoa pod ash is known to contain alkali metal carbonates mainly K_2CO_3 (Amos et al., 2016).

The feasibility of using ashes and solid carbon as catalyst or catalyst support for biodiesel production has been investigated by various workers (Narowska et al., 2019; Shan et al., 2018; Sharma et al., 2012; Dai et al., 2014; Zhao et al., 2018a; Zhao et al., 2018b). Some of the renewable resources include ashes obtained from plant/tree, bones, shells, *etc.* Beneficially, such catalysts that are prepared from renewable materials could make the biodiesel product more cost-effective, environmentally friendly and sustainable. Activated wood ash has been successfully used to catalyze the transesterification of jatropha oil with a range of 97%-99% conversion (Sharma et al., 2012). Ofori-Boateng and Lee (2013) investigated the use of cocoa pod husks (CPHs) potash in the transesterification of soybean oil into biodiesel. It was reported that CPH/MgO and CPH ash catalysts of potash used as green heterogeneous catalysts for biodiesel production gave

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98.7% and 91.4% yields for CPH/MgO and CPH ash catalysts respectively, with specifications falling within the limits of the European biodiesel quality standard (Ofori-Boateng and Lee, 2013). Pomelo peel biochar supported catalyst was reported as a potential biodiesel catalyst (Zhao et al., 2018a). The optimal performance of the catalyst was recorded with the sample loaded with 25 wt.% K_2CO_3 on the prepared biochar, calcined at 600°C. Rice husk biochar which was activated by KOH was used as a CaO-based catalysts carrier for biodiesel synthesis. A relatively high yield of 93.4% was also reported from pyrolytic rice husk biochar at 30% CaO loading and 700°C calcination temperature (Zhao et al., 2018b). KOH supported on activated carbon has been used for the transesterification of waste corn oil. The highest yield was 92% wt at 1h hour reaction time, 3:1 methanol-to-oil ratio, with increased glycerol purity (Narowska et al., 2019). Astar et al. (2017) reported the use of ash obtained from oil palm empty fruit bunches in biodiesel production as a bi-functional catalyst for esterification and transesterification processes for crude palm oil. Optimum conversion of methyl ester in the esterification reaction was found to occurs at 86.17% with the sample having 67.40% free fatty acid (FFA) content while transesterification conversion was 45.70% in the samples with 4.98% FFA content (Astar et al., 2017).

Waste chicken fats are animal fats that can be obtained from feather meal, offal and trims which are slaughter wastes generated after rendering process (Shi et al., 2013). Chicken fat are now avoided for human consumption due to recent health awareness (Shi et al., 2013). There is an accelerated increase in the world poultry production (Ferreira et al, 2018) which has led to the increase in waste generated from the poultry slaughter houses. Utilization of these wastes can add value to poultry slaughter house production, minimize the waste (Gameiro et al., 2015) and provide cheap source of biodiesel raw materials.

Oils for biodiesel production have been extracted using various methods which include the mechanical pressing, use of organic solvents, supercritical fluids, ultrasonic and microwave assisted extraction, however using solvent will add to the cost of biodiesel production (Pandit and Fulekar, 2017). Obtaining oil from waste chicken fat does not require the use of solvent.

Although, cocoa pod ash has mainly been used for production of black soap in some parts of Africa, recent findings indicate its potentials as biodiesel production catalyst in transesterification of parinari seed oil (Amos et al, 2016), transesterification of waste vegetable oil (Olugbenga et al, 2013) and waste cooking oil (Rachmat et al., 2018). However, to the best of our knowledge, no work has been reported on using cocoa pod ash catalyst for biodiesel production from oil obtained from waste chicken fat. Hence, this work is aimed at investigating the use cocoa pod ash as catalyst for the production of biodiesel from oil obtained from chicken slaughter waste.

2 Materials and methods

2.1 Materials collection

The cocoa pods were obtained from a farm in Abeokuta, Ogun State, Nigeria (Figure 1). The chicken fat trimmings were obtained from the chicken processing unit of a University's commercial farm in Omu-Aran, Kwara State, Nigeria, free of cost. All chemicals used such as methanol and H_2SO_4 acid were of analytical grade.

Figure 1 Sundried cocoa pods

2.2 Extraction of oil

The chicken fat was washed with distilled water to remove impurities. After which 500 g of chicken fat was then heated in 1000 mL of distilled water at 100°C for 2 hours in a 2000 mL beaker over the heating mantle. The melted fat mixture was filtered to further remove

impurities and poured in a 250 mL separating funnel and allowed to stand overnight to separate into water and oil layers. The aqueous portion was released from the funnel to leave the oil layer which was emptied into the beaker and dried at 95°C. The yield of the extraction was calculated thus:

$$Yield = \frac{Mass\ of\ oil\ extracted}{Mass\ of\ fat\ heated} \times 100 \quad (1)$$

2.3 Characterization of oil

The physico-chemical properties of the oil obtained were determined according to ASTM standards for acid value, iodine value, saponification value, pH value, viscosity, and density. The Gas Chromatography-Mass Spectrometry (GCMS) analysis of the oil was used for the determination of the composition of the oils with the Agilent Technologies GCMS Instrument Agilent 5975 Series MSD version. The fatty acid composition of the oils were analyzed under the following condition: Injection temperature 250^{o}C, interface temperature 300^{o}C. Helium carrier gas flow rate was 79.5.5 mL min^{-1}, split ratio 50:1, split flow 75 mL min^{-1}. MS zones set at MS Source 230^{o}C and MS Quad 150^{o}C. Column type 19091S-433HP-5MS, 325^{o}C (30 m x 250 μm; 0.25 μm film thickness), automatic injector with injection volume as 1 μL. The oven temperature program was 35^{o}C for 5 mins, then 4^{o}C min^{-1} to 150^{o}C for 2 mins, then 20^{o}C mins^{-1} to 250^{o}C for 5mins. Data processing was achieved by using the NIST library to identify the resulting peaks.

2.4 Pre-treatment of oil

The pre-treatment of the oil was necessary since the acid value of the chicken oil was higher than 1 mg KOH g^{-1}. The pre-treatment was done using methanol:oil molar ratio of 6:1 and 2% catalyst (H_2SO_4). The methanol-H_2SO_4 mixture heated to 40^{o}C was added to the oil and stirred for 30 minutes at 60^{o}C in a two-necked round bottom flask which was equipped with magnetic stirrer and reflux condenser. The mixture was left overnight to form two phases after esterification. The upper phase was a mixture of methanol, sulfuric acid and water while the lower phase consisted of chicken fat and esterified free fatty acid (Alptekin et al., 2011). After separation the acid value of the lower phase mixture was measured and recorded. The pretreatment was repeated twice until an acceptable acid value was obtained.

2.5 Catalyst preparation

The cocoa pod ash catalyst was prepared according to literature (Amos et al., 2016). The cocoa pods were sun dried for five days and ground to fine powder after which it was turned to ash in a Muffle furnace operating at 700^{o}C for 4 hours. Crystals were obtained from the ash by dissolution of 200 g cocoa pod ash in distilled water which was stirred for 1 hour and filtered. The filtrate was evaporated at 100^{o}C to obtain the potassium carbonate crystals which were subjected to SEM analysis to observe the structure of the catalyst surface.

2.6 Design of transesterification experiments

After the esterification pre-treatment step, the transesterification reaction proceeded. The methanol to oil molar ratio was 6:1 while the agitation speed the speed was kept constant at 250 rpm. A five–level-two factor Central Composite Design (CCD), requiring 13 experiments, was used to investigate the effect of catalyst weight and reaction time on the yield response of the transesterification reaction. The summary of the experimental design is as presented in Table 1. Multiple regression analysis of the experimental data was done using Design Expert software 6.0.8. The independent and the dependent variables were fitted to the second-order model equation.

Table 1 Experimental design summary for biodiesel production

Factor	Name	Units	Type		Level				
					$-\alpha$	–1	0	+1	$+\alpha$
A	Catalyst weight	%	Numeric	374	0.585786	1	2	3	3.41421
B	Reaction Time	h	Numeric	1909	0.585786	1	2	3	3.41421

Note: α = 1.41421.

2.7 Preparation of biodiesel

The biodiesel was prepared according to the methods described in literature (Amos et al., 2016), as shown in Figure 2. Preliminary study indicated the use of oil to methanol ratio of 1:6, temperature of 65^{o}C and agitation speed of 250 rpm. The transesterification was carried out

in a two-necked round bottom flask equipped with a reflux condenser and a magnetic stirrer. After the transesterification reaction the mixture was separated with a centrifuge at 5000 rpm for 10 minutes. The biodiesel at the upper phase was carefully decanted from the glycerol, measured and the yield of biodiesel from oil was obtained. The biodiesel with the highest yield was then characterized according to ASTM D6751 standards (1998). The GCMS analyses of the biodiesel were done to confirm the production of fatty acid methyl esters (FAME).

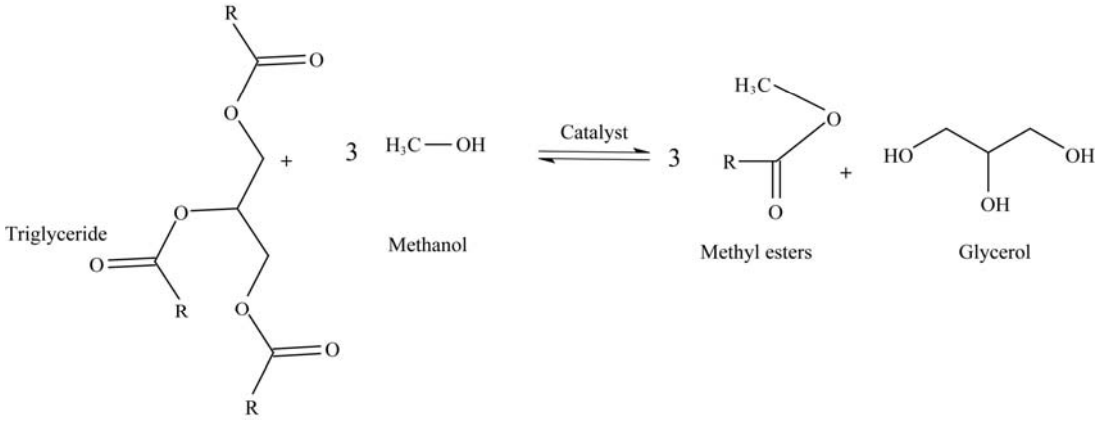


Figure 2 Production of fatty acid methyl esters (Amos et al., 2016)

3 Results and discussions

3.1 Characterization of oil

The yield of the oil from waste chicken fat was 76.5%. The oil was yellowish in colour (Figure 3). The physicochemical properties of the oil obtained were as summarized in Table 2. The result of the GCMS analysis of chicken oil indicated the main fatty acids as Hexadecanoic acid (22.3%), Octadecenoic acid (36.2%) and 10,13-Octadecadienoic acid 17.5%), 9-Hexadecenoic acid methyl ester (12.21%) and Octadecanoic acid 6.9%. The fatty acid content was similar to the profile of chicken fat obtained by Almeida et al. (2016).

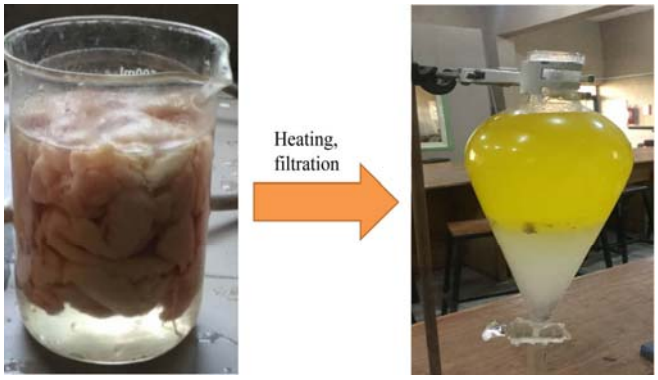


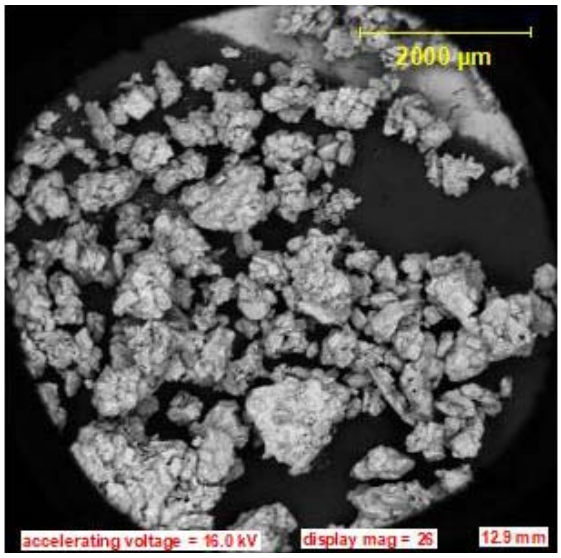
Figure 3 Extraction of oil from waste chicken fat using separating funnel

Table 2 Physico chemical properties of oil obtained from waste chicken fat

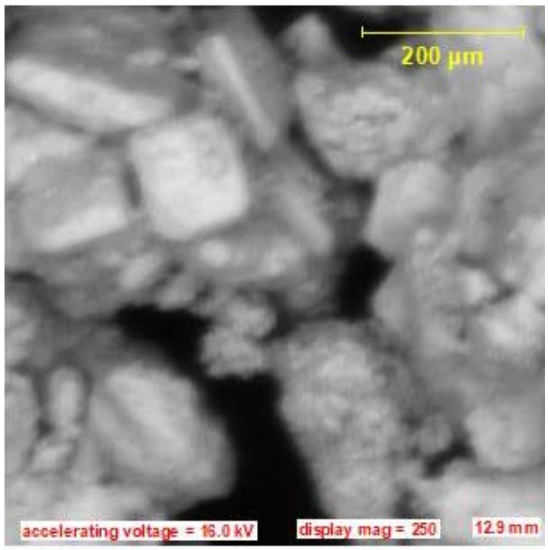
Properties	Unit	Chicken Oil (This work)	Chicken Oil (Olutoye et al., 2016)
Acid value	mg KOH g^{-1}	5.33	5.61
Free fatty acid	%	2.67	2.805
Iodine value	mg I_2 100 g^{-1}	55.64	42.58
Saponification value	mg g^{-1}	103.95	103.785
Viscosity at 40 °C	mPa.s	13.2	21.50
Density	g mL^{-1}	1.47	0.919
pH value		3.95	-

3.2 Catalyst characterization

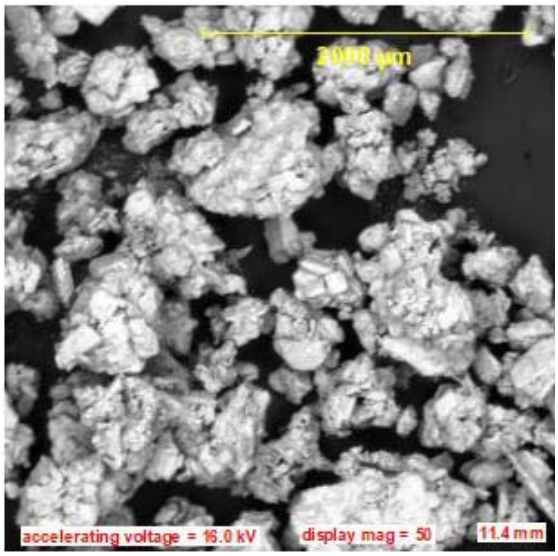
Potassium carbonate (K_2CO_3) was effectively filtered out of CPA with an average recovery of 50 g L^{-1} filtrate based on the potash content. The yield of K_2CO_3 was relatively lower than 57.6 g L^{-1} obtained by Ofori-Boateng et al. (2013). The scanning electron microscope images of the Potassium carbonate catalyst were as shown in Figure 4. The morphology and particle size were indicated. The individual particles mostly had irregular sizes ranging from 50-150 μm. Some square-like aggregated particles were also observed. This aggregated distribution usually occurs due to interparticle interactions (Alhawi, 2015). The agglomerate of flat square-like shape plates was indicative of available surface area for reaction.



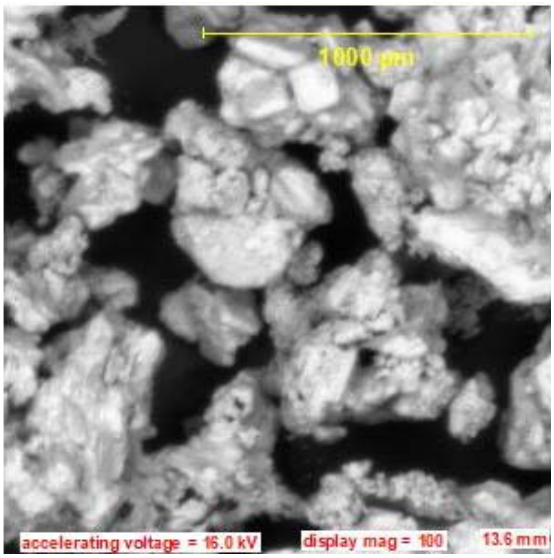
(a) 2000 µm and display mag 26



(b) at 200 µm and display mag 250



(c) 2000 µm and display mag 50



(d) at 1000 µm and display mag 100

Figure 4 SEM images of CPA K_2CO_3

3.3 Model fitting and analysis

The CCD Experimental design values and the corresponding experimental yields of the biodiesel prepared were as indicated in Table 3. Regression analysis of the data gave the following second order polynomial equation. The model for the biodiesel yield in term of coded factors was given by:

$$Yield = 72.03 + 5.35A + 2B - 2.39A^2 - 1.15B^2 + 1.64AB \quad (2)$$

where, A and B were catalyst weight (%) and reaction time (h) respectively.

Table 3 CCD Experimental design values and biodiesel yields

Run order	Catalyst weight (%)	Reaction time (h)	Biodiesel yield % (Experimental)	Biodiesel yield % (Predicted)
1	2.00	2.00	72.1	72.03
2	3.00	3.00	74.2	74.2
3	3.00	2.00	75.4	75.00
4	2.00	2.00	71.6	72.03
5	2.00	2.00	72.1	72.03
6	2.00	0.59	66.9	66.91
7	2.00	2.00	72.3	72.03
8	2.00	3.41	72.6	72.55
9	3.41	2.00	74.6	74.82
10	2.00	2.00	71.8	72.03
11	2.00	3.00	72.8	72.03
12	1.00	2.00	64.5	64.29
13	0.59	2.00	59.6	59.68

The result of the statistical testing of the model by the analysis of variance (ANOVA) showed that the quadratic regression model was adequate because it had a relatively low *p* value of less than 0.0001. The determination coefficient (R^2) and adjusted coefficients (R^2_{adj}) obtained as 99.75 and 99.58, respectively indicated that the model's adequacy was high. The p value for lack of fit of the model, which was found as 0.406, was acceptable as it was not significant.

The model terms A, B, A^2, B^2 and AB were all significant as A, B, A^2, B^2 were found to have p values of less than 0.0001 while AB had p value of 0.0027 which was also acceptable. Catalyst weight was found to have a higher linear effect than the reaction time. The interaction of catalyst weight and reaction time on the yield of biodiesel produced is as shown in Figure 5.

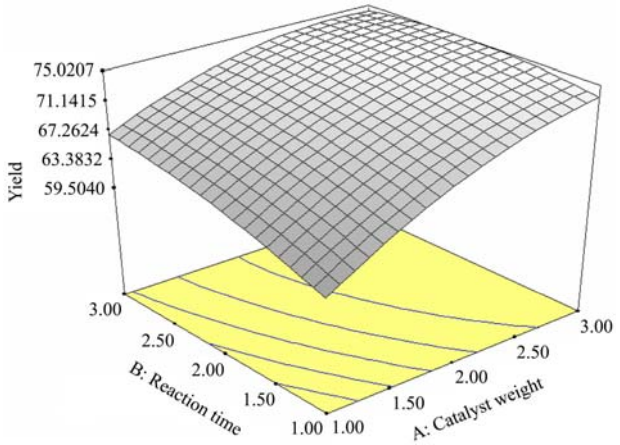


Figure 5 Surface plot showing the effect of catalyst weight (%) and reaction time (h) on yield

The yield at the optimum condition (catalyst weight of 3.00 g and reaction time of 2.15 hours) was predicted to be 75.02%.

3.4 Biodiesel characterization

The properties of the biodiesel with the highest yield were determined and the results were as stated in Table 4.

Table 4 Fuel properties of biodiesel produced compared with the ASTM standard

Parameters	Unit	Biodiesel	ASTM(2010)
Density	g mL^{-1}	0.90	0.87 - 0.89
Viscosity	mpa.s	5.73	1.9 - 6.0
Saponification value	mg KOH g^{-1}	218.74	–
Iodine value	mg I_2 100 g^{-1}	45.56	–
Acid value	mg KOH g^{-1}	2.37	0.50 max
Colour		Golden yellow	

The viscosity of the biodiesel produced was within the range of the ASTM standard. Saponification value of the biodiesel of 218.74 mg KOH g^{-1} was higher than the saponification value of the chicken oil thereby indicating a reduction in molecular weight after transesterification (Olutoye et al., 2016). The density of the biodiesel produced was nearly at the higher range of the ASTM standard. Figure 6 shows the gas chromatogram of the biodiesel obtained from chicken oil. The result shows the presence of the main fatty acid methyl esters as indicated in Table 5.

Table 5 Main fatty acid methyl esters (FAME) in waste chicken fat biodiesel

Peak	Area %	FAME	Common name	Cn:m
37.096	5.77	9-Hexadecenoic acid methyl ester	Palmitoleic acid	C16:1
37.552	22.30	Hexadecanoic acid methyl ester	Palmitic	C16:0
40.761	17.50	10,13-Octadecadienoic acid methyl ester	Linoleic acid	C18:2
40.928	36.20	9-Octadecenoic acid, methyl ester	Oleic acid	C18:1
41.295	6.44	9-Hexadecenoic acid methyl ester	Palmitoleic acid isomer	C16:1
47.096	1.83	9,12-Octadecadienoic acid (Z,Z) methyl ester	Linoleic acid (isomer)	C18:2
47.185	6.89	Octadecanoic acid	Stearic acid	C18:0

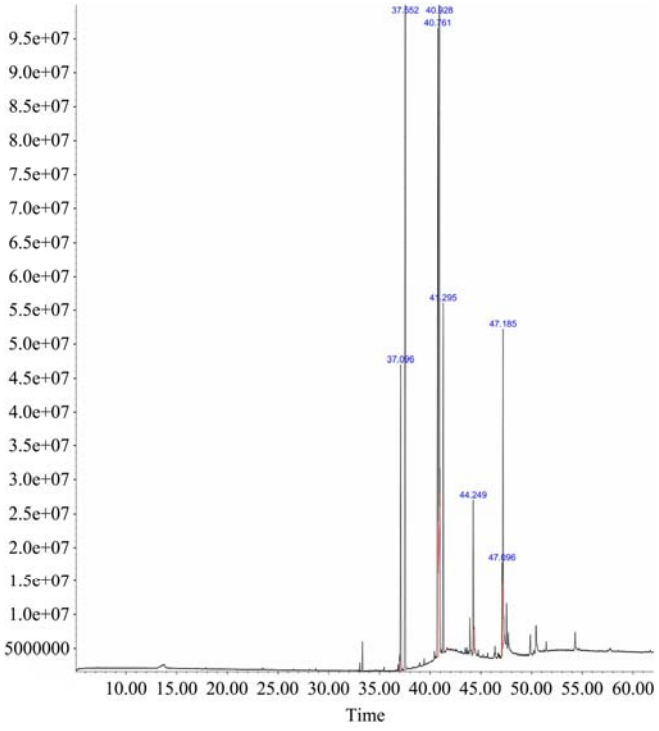


Figure 6 The fatty acid methyl ester of biodiesel from waste chicken fat

4 Conclusion

Cocoa pod ash was found to be suitable as a potential catalyst for transesterification of oil obtained from waste chicken fat. The biodiesel of the highest yield of 75.4% was obtained at 2 hours reaction time and 3% wt catalyst.

Catalyst weight was found to have a higher linear effect on transesterification than the reaction time. The interaction of catalyst weight and reaction time on the yield of biodiesel produced was also significant. The determination coefficient (R^2) and adjusted coefficients (R^2_{adj}) obtained as 99.75 and 99.58, respectively indicated that the model's adequacy was high. Cocoa pod ash can be considered as a biobased catalyst material for sustainable biodiesel production. However, more work is to be done to improve the biodiesel yield to harness the promising cost effective bio-based catalyst.

References

Alhawi, T., M. Rehan, D. York, and X. Lai. 2015. Hydrothermal synthesis of zinc carbonate hydroxide nanoparticles. *Procedia Engineering*, 102: 356–361.

Almeida, T. A., I. A. Rodrigues, T. S. Estrela, C. N. Nunes, L. L. Machado, K. V. Le~ao, I. C. Barros, F. A. Amorim, and V. S. Braga. 2016. Synthesis of ethyl biodiesel from soybean oil, frying oil and chicken fat, using catalysts based on vanadium pentoxide. *Energy,* 97 528–533.

Alptekin, E., M. Canakei, and H., Sanli. 2011. Methyl ester production from chicken fat with high FFA *Bioenergy Technology,* 319–326. *Proceeding of World Renewable Energy Congress, Likoping, Sweden* 2011.

American Society for Testing and Materials (ASTM). 1998. Designation ASTM D 6751. Standard specification for biodiesel fuel (b100) blend stock for distillate fuels. PA. West Conshohocken: ASTM International.

American Society for Testing and Materials (ASTM). 2010. Designation D6751-10. Standard specification for biodiesel fuel (b100) blend stock for distillate fuels. PA. West Conshohocken: ASTM International.

Amos, O., D. Ogunniyi, and T. Odetoye. 2016. Production of biodiesel from *parinari polyandra* b. seed oil using bio-based catalysts. *Nigerian Journal of Technological Development,* 13(1): 26–30.

Astar, I., T. Usman, N. Wahyuni and A.H. Alimuddin. 2017. Bifunctional heterogeneous catalysts from oil palm empty fruit bunches ash and alum for biodiesel synthesis simultaneously. In *AIP Conference Proceedings,* 1823(1): 020104. Chongqing City, China., May.

Dai, M., K. Chen, J. Wang, and C. Chen. 2014. Application of peanut husk ash as a low-cost solid catalyst for biodiesel production. *International Journal of Chemical Engineering and Applications*, 5(3): 276.

Ferreira, A., S. S. Kunh, P. A. Cremonez, J. Dieter, J. G. Teleken, S. C. Sampaio, and P. D. Kunh. 2018. Brazilian poultry activity waste: Destinations and energetic potential. *Renewable and Sustainable Energy Reviews,* 81(2): 3081–3091.

Gameiro, M., P. Lisboa, A. Paiva, S. Barreiros, and P. Simões. 2015. Supercritical carbon dioxide-based integrated continuous extraction of oil from chicken feather meal, and its conversion to biodiesel in a packed-bed enzymatic reactor, at pilot scale. *Fuel,* 153: 135–142.

ICCO. 2017. International Cocoa Organization Quarterly Bulletin of Cocoa Statistics. Available at: http://andersonlid.com/wp-content/uploads/2017/04/Cocoa-Statistics.pdf. Assessed 25 July 2018.

Kirubakaran, M., V. Arul, and M. Selvan. 2018. A comprehensive review of low cost biodiesel production from waste chicken fat. *Renewable and Sustainable Energy Reviews*, 82(1): 390–401.

Narowska, B., M. Kułażyński, M. Lukaszewicz, and E. Burchacka, 2019. Use of activated carbons as catalyst supports for biodiesel production. *Renewable Energy*, 135: 176–185.

Ofori-Boateng, C., and K. T. Lee. 2013. The potential of using cocoa pod husks as green solid base catalysts for the transesterification of soybean oil into biodiesel: Effects of biodiesel on engine performance. *Chemical Engineering Journal,* 220: 395–401.

Olugbenga, A. G., A. Mohammed, and O. N. Ajakaye. 2013. Biodiesel production in nigeria using cocoa pod ash as a catalyst base. *International Journal of Science and Engineering Investigation,* 2(15): 144–147.

Olutoye, M. A., U. G. Akpan, and M. A. Salihu. 2016. Synthesis of fatty acid ethyl ester from chicken fat using ZnO/SiO2 heterogeneous catalyst. *Nigerian Journal of Technology*, 35(1): 97–106.

Pandit, P. R., and M. H. Fulekar. 2017. Egg shell waste as heterogeneous nanocatalyst for biodiesel production: Optimized by response surface methodology. *Journal of Environmental Management,* 198(1): 319–329.

Rachmat, D., L. J. Mawarani, and D. D. Risanti. 2018. Utilization of cocoa pod husk (*Theobroma cacao* l.) as activated carbon and catalyst in biodiesel production process from waste cooking oil. In *IOP Conf. Series: Materials Science and Engineering*, pp. 299: 012093. Malang, 4-5th November, 2017.

Sharma, M., A. Khan, S. K. Puri, and D. K. Tuli. 2012. Wood ash as a potential heterogeneous catalyst for biodiesel synthesis. *Biomass and Bioenergy,* 41: 94–106.

Shi, W., J. Li, B. He, F. Yan, Z. Cui, K. Wu, L. Lin, X. Qian, and Y. Cheng. 2013. Biodiesel production from waste chicken fat with low free fatty acids by an integrated catalytic process of composite membrane and sodium methoxide. *Bioresource Technology*, 139(13): 316–322.

Shan, R., L. Lu, Shi. Y, and Yuan. H. 2018 Catalysts from

renewable resources for biodiesel production. *Energy Conversion and Management*, 178: 277–289.

Zhao, C., P. Lv, L. Yang, S. Xing, W. Luo, and Z. Wang. 2018a. Biodiesel synthesis over biochar-based catalyst from biomass waste pomelo peel. *Energy Conversion Management*, 160 477–485.

Zhao, C., L. Yang, S. Xing, W. Luo, Z. Wang, and P. Lv. 2018b Biodiesel production by a highly effective renewable catalyst from pyrolytic rice husk. *Journal of Cleaner Production*, 199: 772–780.