



P2B-06: PRODUCTION OF RENEWABLE ENERGY FUEL FROM WASTE VEGETABLE OIL USING HETEROGENEOUS CATALYST DERIVED FROM TERMITE CLAY

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ABSTRACT

This paper reports the synthesis and characterization of heterogeneous catalyst from mixture of cow-bone and termite clay for the transesterification of waste vegetable oil (WVO) using simple 2^k factorial design method for the optimization of process parameters. Four factors Viz methanol to oil ratio, reaction temperature, catalyst loading and reaction time were investigated. It was found that the most significant factor on the biodiesel production was reaction time based on the factorial design method. The optimum FAME yield of 98.5% were achieved at methanol to oil ratio 6:1; catalyst loading of 2.0 wt%; reaction temperature of 65°C and reaction time of 1 h. The biodiesel produced with the optimized process parameters meets the global standard for biodiesel ASTM and thus could be considered as suitable substitute for conventional diesel in unmodified diesel engine application.

1.0 Introduction

The alarming global twin problems of fossil fuel depletion and environmental pollution has called for attention of researchers to seek an alternative fuel in which biodiesel, a renewable fuel is one of the key solution. Global economy majorly depends on transportation of goods and services while transportation depends on energy from petroleum product which results in high increase in fuel consumption. Energy is an important aspect and it plays a principal and irreplaceable role in the economy of all country of the world. Majority of these energy requirements are supplied by coal, petroleum resources, natural gas and nuclear energy (Zhang, Dube, McLean, and Kates, 2003). Among all the conventional fuels, petroleum is the most important in the growth of industries, transportation and agricultural sector to satisfy all the needs of human beings (Alvarez, Lopez, Amutio, Bilbao, and Olazar, 2014).

Biodiesel which is also known as fatty acid methyl ester (FAME) serve as an alternative to petrol-diesel due to several advantages (Erum *et al.*, 2014). Crude oil or petroleum fuels that the world solely depends on are non-renewable energy source which is highly degradable and poisonous and it greatly affects both the safety of humans and the environment. This negative impact led researchers to find an alternative energy source and one of the breakthroughs achieved was the invention of biofuels. According to Olutoye and Hameed, (2016) the introduction of an eco-friendly green technology is the current focus of the human society in the production of energy. Biodiesel has become more important because of its environmental benefits such as its biodegradability and nontoxicity, thereby making it environmentally beneficial due to its low emission profiles. Also, Yusuff *et al.* (2018) reported that biodiesel being the most promising substitute fuel to the fossil fuel is as a result of aforementioned benefits and advantages.

The FAME can be synthesized through a transesterification of vegetable oil or animal fat and alcohol in the presence of a catalyst. The catalyst which may either be homogenous or heterogeneous catalyst. Homogenous catalyst are mostly used for industrial production of

biodiesel but leads to high cost of production because of waste water generation and difficulty in separation (Yusuff *et al.*, 2018). The high cost of biodiesel is the major challenge in the commercialization of the process (Dhawane *et al.*, 2018) and the use of waste vegetable oil (WVO) instead of virgin oil is a way of reducing the cost, as WVO estimated to be about half the price of virgin oil (Ali *et al.*, 2018).

In this present study, heterogeneous catalyst was prepared from mixture of cow-bone and termite clay which was used for transesterification of WVO to produce biodiesel. Reaction parameters were optimized by varying the reaction time, methanol to oil molar ratio, catalyst loading and reaction temperature.

2.0 Materials and method

Termite clay was harvested from the locality of Tanke Iledu, Ilorin, Nigeria. Cow-bone was gathered from Ipata market, Ilorin. WVO used as feedstock for the production of the FAME was obtained from item 7 restaurant Oke-odo, Ilorin, Nigeria. Ethanol, KOH, distilled water, Petroleum ether, methanol (analytical grade, 99.5%) were obtained from Central Research Laboratory B, University of Ilorin Road, Ilorin Nigeria.

2.1 Catalyst preparation

The cow bone collected were thoroughly washed and cleaned with soap and water to remove dirt, sand and any unwanted materials on it. Thereafter, the bone was boiled at a temperature of 100°C and rinsed with distilled water to get rid of left over mucous inside the bone. Then, the washed bone was oven dried at 110°C for 48 h to remove moisture. The bone was later crushed into powder using mechanical grinding machine. The powdered bone was sieved with the use of 75 µm mesh which was kept in a desiccator to avoid moisture. Similarly, the harvested clay was initially washed using the distilled water to remove the impurities. It was further dried at 100 °C for 4 h. The clean clay was further crushed using ceramic mortar and pestle. The particles were sieved using 75 µm mesh. The cow-bone and fine clay were weighed and mixed in 50-50% proportion into a beaker. Adequate amount of distilled water was added to the mixture to form suspension and stirred for 4 h on a magnetic stirrer for proper mixing. The mixture was kept for 48 h for ageing and later dried in an oven at 110°C. Thereafter, calcined in a muffle furnace at 900°C for 4 h (Babatunde *et al.*, 2015), this synthesized catalyst is referred to as SC9 (that is silica/cowbone mixture calcined at 900 °C) catalyst in this paper.

2.2 Characterization of Catalyst

The catalyst was analyzed to know its morphology, elemental composition and crystallinity by Scanning Electron Microscopy, Energy Dispersive X-Ray Spectroscopy and X-Ray Diffraction respectively. Elemental analysis of the catalyst surface was done and all the elements present on the surface were quantified by using X-ray energy dispersive analysis (EDAX) using OXFORD Instrument INCAX-sight.

2.3 Transesterification of Waste Vegetable Oil

The transesterification reaction was carried out in a batch reactor (250 ml round bottom flask) with magnetic stirrers inserted. 40 ml of Waste vegetable oil measured into the flask. A calculated amount of methanol was added to a known amount of catalyst (2.0 wt% - 4.0 wt%) to ease miscibility and speed up the rate of the reaction. Afterwards, the mixture (with methanol to oil ratio of 6:1- 9:1) was stirred rigorously at constant agitation speed, temperature (50°C - 65 °C) and reaction time (1 h - 4h), the experimental matrix used was presented in Table 4. The effects

of methanol-oil ratio, reaction time, reaction temperature and catalyst loading, were investigated for a range of values. At the end of the transesterification reaction, 30 ml of distilled water was added to the products; biodiesel and glycerol, giving rise to two distinct phases which were separated from each other using a separating funnel, catalyst was separated through a filter paper which was aimed at preventing the catalyst from being lost in the mixture. The glycerol was drained out from the bottom of the funnel and left with only the biodiesel.

The yield was obtained using Equation 1 below:

$$\text{Yield}(\%) = \frac{\text{weight of biodiesel}}{\text{weight of oil}} \times 100 \quad (1)$$

2.4 Design of experiment

The biodiesel production was optimized using simple factorial design which was used to build the experimental design of four variables Viz methanol-oil ratio, reaction temperature, catalysts loading and reaction time were considered at two levels as shown in Table 1. Hence, it is important to analyze the parametric effects on biodiesel production process and their optimization to obtain the desired waste vegetable methyl ester (WVME) yield.

Table 1: The selected process parameters and their values at two levels for factorial design

Variables	Parameters	Low	High
A	Methanol/oil ratio	6:1	9:1
B	Temperature (°C)	50	65
C	Time (h)	1	3
D	Catalyst loading (wt%)	2.0	4.0

2.5 Determination of physicochemical properties of biodiesel produced

The density, viscosity, flash point, pour points, cetane number and iodine value of the WVME produced were determined and compared by the standard method of American Standard for Testing Materials (ASTM).

3.0 RESULTS AND DISCUSSION

3.1 Characterization of Waste Vegetable Oil

The WVO used as feedstock was characterized based on its physicochemical properties and the result obtained was presented in Table 2. From acid value and free fatty acid (FFA) content, the feedstock can be used directly since the FFA was below 2%.

Table 2: Physicochemical properties of Waste Vegetable Oil

S/N	Properties	Units	Value
1	Density	g/cm ³	0.873
2	Kinematic viscosity at 40°C	mm ² /s	34.65
3	Acid Value	Mg KOH/g	3.366
4	Iodine Value	g/100 g	125.32
5	Molecular Mass	g/mol	1380.02
6	FFA	%	1.683
7	Flash Point	°C	159

3.2 Characterization of Synthesized Catalyst

The results of SEM-EDX analysis for SC9 catalyst calcined at 900 °C can be seen in Figure 1 and 2. The various elemental compositions were presented in Table 3. Figure 1 revealed that the catalyst are rough in surface and contains large pores which is good enough for transesterification process to occur. The result is in agreement with Yusuff *et al* (2018). Figure 2 revealed the elemental composition and the major element present in the catalyst is calcium in form of oxide which is the major element for conversion of triglycerides into FAME. Elements like magnesium, silicon, iron, carbon, phosphorus were also found. The presence of calcium and silicon as the major constituent was an indication that the mixture of cow-bone and termite clay comprised of calcium carbonate and silica and upon calcination can be completely converted to calcium oxide and silicon oxide respectively. The XRD analysis was presented in Figure 3. The result shows that the sharp peaks at $2\theta = 23.6^\circ$ and 29.5° indicate the presence of calcium oxide and silica oxide respectively. The peaks are similar to those reported by Cheng *et al* (2016).

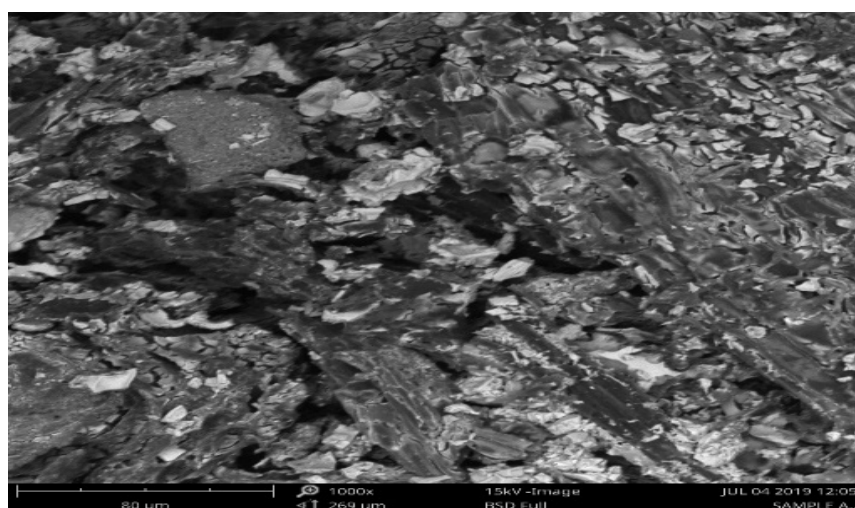


Figure1. SEM image of calcined SC9 catalyst

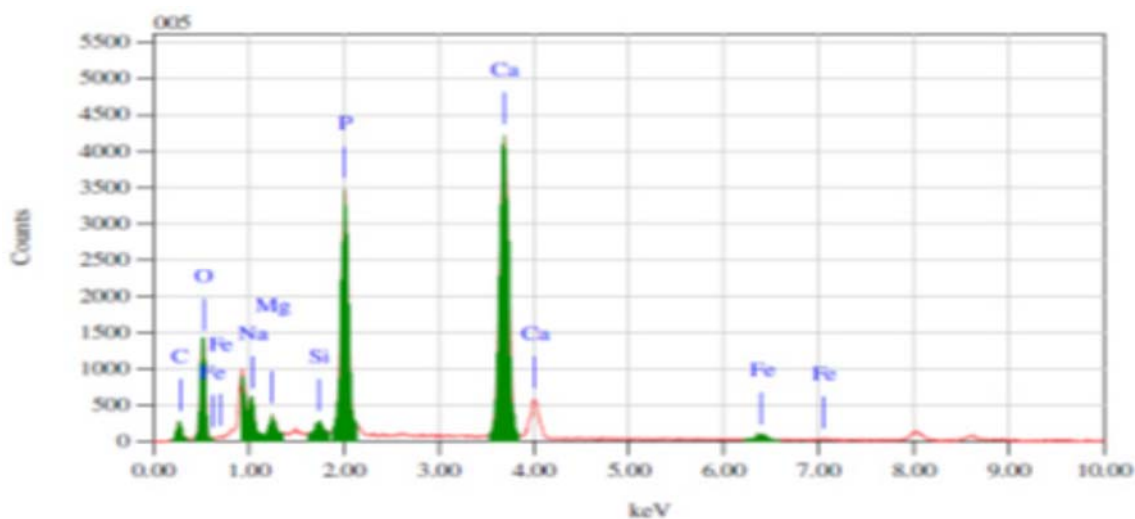


Figure2. EDX Analysis of calcined SC9 catalyst

Table 3. EDX analysis showing the elemental composition of SC9 catalyst

Element	Ca	P	Fe	S	Mg	Al	Si	O	Na	Cr	Ti	Total
Wt. %	46.06	26.83	6.80	0.03	2.07	0.85	3.61	11.59	0.29	1.17	0.69	100

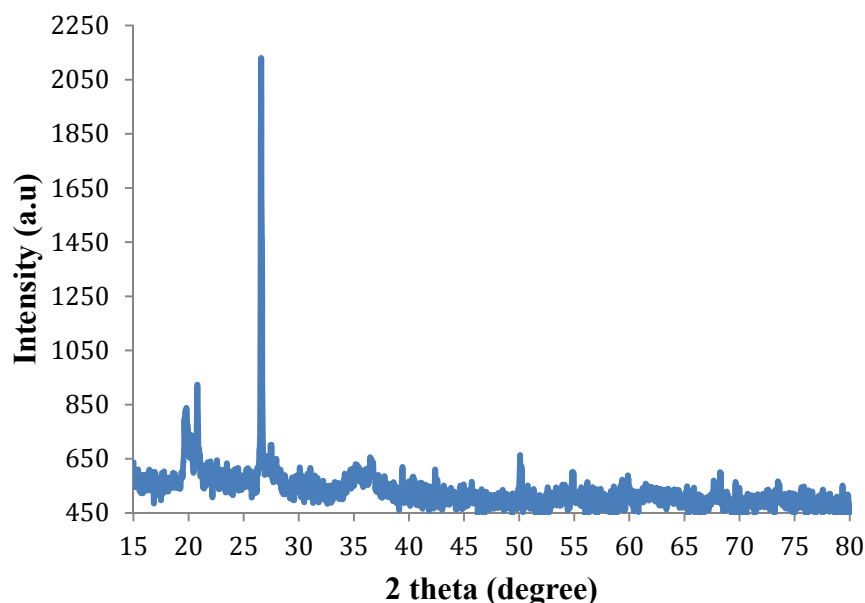


Figure 3.XRD Analysis of calcined SC9 catalyst

The result obtained on the influence of the operating parameters on the yield of biodiesel is summarized in Table 4. These effects are discussed in details below;

Table 4. Factorial design matrix for operating variables with biodiesel yield

Run	Temp (°C)	Time (h)	Catalyst (wt%)	MeOH/Oil	Biodiesel yield
1	65	1.00	2.00	12:1	96.8
2	45	1.00	2.00	6:1	85.5
3	45	1.00	4.00	6:1	84.3
4	45	3.00	2.00	12:1	84.6
5	65	1.00	4.00	6:1	94.6
6	65	1.00	4.00	12:1	95.6
7	45	1.00	2.00	12:1	87.5
8	65	1.00	2.00	6:1	98.5
9	45	3.00	2.00	12:1	83.7
10	65	1.00	4.00	12:1	97.9
11	65	1.00	2.00	6:1	94.8
12	45	3.00	4.00	6:1	82.3
13	65	3.00	4.00	6:1	97.2
14	65	1.00	2.00	6:1	98.4
15	45	3.00	4.00	12:1	88.6
16	45	1.00	4.00	12:1	85.9

3.3 Effect of Process Conditions on Biodiesel Yield

The effective production of biodiesel and energy efficient are affected by various operating parameters viz. Temperature, reaction time, catalyst loading and methanol to oil ratio.

3.3.1 Effect of methanol to oil ratio

Since the stoichiometric molar ratio of alcohol to oil for the transesterification is 3:1 and the reaction is reversible, higher molar ratios are required to increase the miscibility and to enhance contact between the alcohol molecule and the triglyceride. For this study, the molar ratio of methanol to WVO was varied from 6:1 and 12:1. Figure 4(a) shows increase in methanol to oil ratio results in slight decrease in biodiesel yield. Therefore, the yield of biodiesel increases with increase in the concentration of methanol up to certain concentration. However further increase of alcohol content (12:1) was found to result in excess unreacted methanol after separation of products which resulted into increase in the cost of methanol recovery. Ratio 6:1 relatively yields high at high temperature (run 8 and 14) and is recommended as the optimum for similar works of this kind (Taufiq-yap *et al.*, 2014).

3.3.2 Effect of reaction temperature

The temperature was varied from 45°C to 65°C. The result from Figure 4(b) shows that there was increase in the biodiesel yield with increase in temperature. This was because higher reaction temperatures increase the rate of reaction. Considering run 8 at 65°C the yield was 98.5% this is confirmed by the work of Ajala *et al* (2019). This result is expected as the rate of transesterification reaction depends on temperature (Ho, Ngo, and Guo, 2014).

3.3.3 Effect of catalyst loading

Catalyst loading is one of the most influential parameter affecting the yield of biodiesel. This parameter was varied at two levels viz. 2 and 4 wt% ,from Figure 4(c) it was observed that catalyst loading at 2 wt% gave highest yield compared to 4 wt% .Considering run 8 and 14 where highest biodiesel yield was obtained, catalyst loading of 2 wt% was used. Further increase in catalyst loading from 2 to 4 wt% slightly brought about decrease in the yield, which is in agreement with the work of Dhawane *et al* (2016). This decrease in yield can be attributed to leaching of the excess catalyst at higher concentration of catalyst and leading to saponification during the reaction.

3.3.4 Effect of reaction time

The dependence of the biodiesel yield on the reaction time was studied. As shown in Figure 4(d), the effect of reaction time on the yield was investigated in the range 1–3 h, the yield of biodiesel increased (98.5%) as the reaction time increased from 1 h to 3 h. This is because reaction time of 1-3 h was sufficient for completion of transesterification reaction with base catalyst (Nasim *et al.*, 2014). For higher reaction time leaching of catalyst may increase and thereby lower the catalyst active sites, this was in agreement with the report of Dhawane *et al* (2017).

3.4 Properties of WVME produced

The major properties of WVME produced were estimated and presented in Table 5. The reported properties namely density, viscosity, acid value, iodine value, flash point and cetane number were compared with ASTM standard for biodiesel. The results show that all the properties of WVME were found to meet the global standard; hence WVME could be a substitute to fossil diesel.

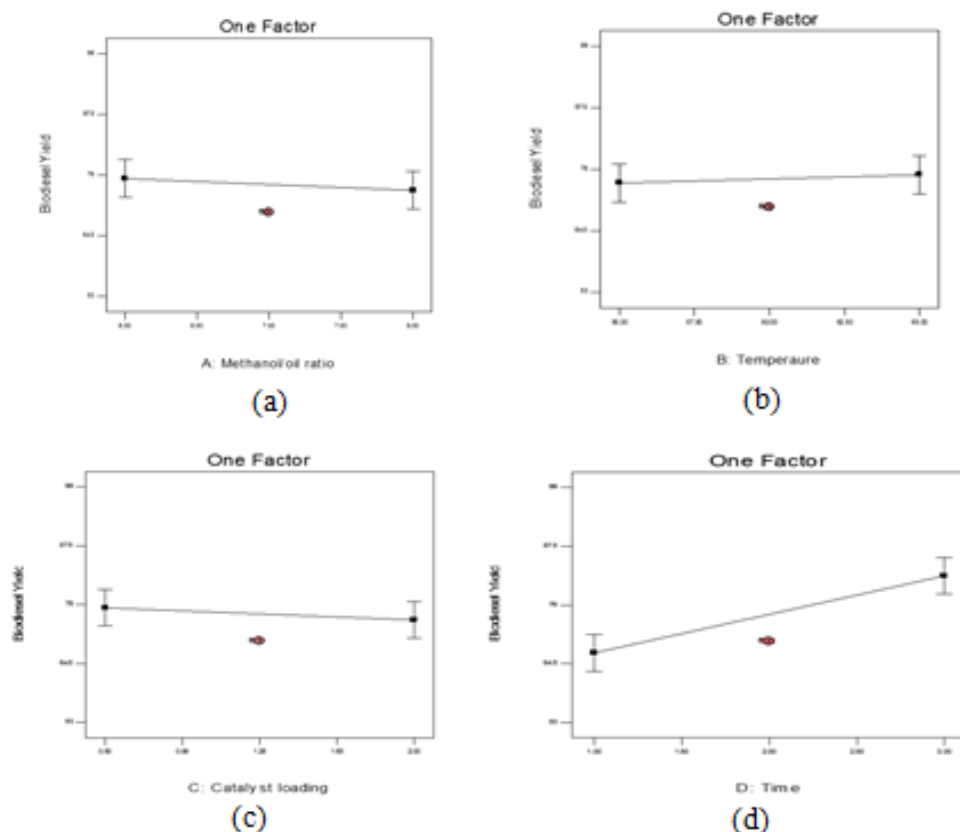


Figure 4. (a) Effect of methanol/oil ratio on WVME yield, (b) Effect of temperature on WVME yield, (c) Effect of catalyst loading on WVME yield (d) Effect of time on WVME yield

Table 5. Properties of waste vegetable methyl ester (WVME) in comparison with biodiesel standard (ASTM)

Properties	WVME	ASTM Limit	Testing procedure
Density at 15°C (g/cm ³)	0.875	0.875-0.900	ASTM D4052
Viscosity(mm ² /s)	4.56	5-6	ASTM D445
Acid value (mg KOH/g)	0.14	0.8	ASTM D974
Flash point(°C)	165	>130	ASTM D93
Pour point (°C)	-6	-	ASTM D97
Cetane number	52	>47	ASTM D975
Iodine value (g iodine/100 g)	63.5	<120	AOAC CD1-25

4.0 Conclusion

In this present study a composite of calcined cow-bone and termite clay obtained after calcination of mixture of cow-bone and termite clay (SC9) catalyst has shown excellent activity for transesterification of WVO with FAME yield of 98.5% under optimal conditions. This study has tackled environmental and economic aspects of FAME production by using waste materials as both feedstock and catalyst. The effects of various parameters have been studied in which the most significant parameter is time and FAME produced showed conformance with the ASTM

standard. Studies on leaching of catalyst and its reuse need to be carried out, the kinetics of the process also need to be analysed as well as detailed modeling and optimization.

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