Response Surface Modelling and Optimization Study of Transesterification of Castor Oil Using Calcined Anthill as Catalyst

Abstract

The source of catalyst and feedstock used for transesterification of oil play a significant role in cost, and starvation of consumers of oil especially for edible oil sources. This investigation aimed at the transesterification of castor oil with the aid of calcined anthill as the catalyst support. Box Behnken Design (BBD) of the Response Surface methodologywas employed to study the relationship among the variable of production such as time (1 – 3 h), temperature (40 – 60^{o}C), catalyst loading (1 – 9 g), methanol volume (10 – 60 ml) and agitation rate (100 – 400 rpm) on yield of biodiesel produced. The synthesized catalyst was characterized using X-Ray Fluorescence (XRF) while biodiesel produced was characterized through determination of physicochemical characterized and function group applicable to biodiesel.The calcined anthill was found to contain some mixed basic oxides. The physicochemical properties of produced biodiesel are within the American Standard Test Methods (ASTM) range (except density that is higher), and the functional groups found in biodiesel are typical of vibrations presence in biodiesel. The optimum condition for a volume of 11.73ml, agitation of 166.458rpm, reaction time of 2.34375hrs, temperature of 59.4552^{o}C, catalyst loading of 1.14g, and an optimal yield of 90.59 %.

Introduction

Biodiesel an alternative substitute for fossil fuel(Gomes et al., 2020) has several advantagesover its counterpart such as its biodegradability, low emission, low Sulphur and aromatic contents better lubricity and lots more(Babatunde et al., 2020). However, its high cost of production has been a limiting factor for its commercialization in developing countries(Babatunde et al., 2020). Biodiesel is a mixture of mono-alkyl esters derived from vegetable oils or animal fats (Kyari et al., 2017). Biodiesel is also referred to as Fatty Acid Methyl Esters (FAME)as is produced from the transesterification of triglycerides (lipids) with an alcohol in the presence of a catalyst(Yusuff, 2019; Yusuff & Adesina, 2020).Oil and fats in their untransesterified state has a high kinematic viscosity that disallows it from been used directly as biodiesel in most diesel engines and hence the need for the transesterification of fats and oil (L.C. Meher et al., 2006; Knothe et al., 2005). The sustainability of biodiesel has been proven to depend more on the feedstock and catalyst used in the transesterification reaction.The catalyst used in transesterification reaction can be grouped distinctly into the homogeneous and heterogeneous catalyst (Gomes et al., 2020).

The homogeneous catalyst may be acidic or basic in nature. The homogeneously based catalyzed transesterification process is the most widely used process to produce biodiesel (Yusuff, 2019). This is because the based catalyzed reaction has been proven to give a higher yield than the acid catalyzed reaction, also it is faster that the acid catalyzed reaction and its reaction conditions are relatively mild when compared to the acid catalyzed reaction(Gomes et al., 2020). However, despite its many advantages, some major drawbacks to the use of homogeneous catalyst in the production of biodiesel is that it leads to the generation of effluents,(Yusuff, 2019; Yusuff & Adesina, 2020), the FFA in the feedstock gets saponified by the homogeneous catalyst leading to excess soap formation and decrease in the biodiesel yield (Babatunde et al., 2020), difficulty in the reuse of catalyst and the high cost of production(Yusuff, 2019).

The identified limitations observed in the homogenously catalysed transesterification process were compensated for in the adoption of the use of heterogeneous catalyst for transesterification processes. Catalysts in this category are reusable, recoverable and ultimately reduce overall cost of production of biodiesel (Yusuff, 2019). A few examples of heterogenous catalyst that have been reportedly used in biodiesel production on a laboratory scale are chemical based alkali metal oxides and derivatives, mixed metal oxides and derivatives, alkaline earth metal oxides and derivatives, transition metal oxides and derivatives, synthesized catalysts from waste or residues, modified siliceous materials (clay and anthills)to mention but a few**.** (Chouhan & Sarma, 2011)**.**

Anthill as a catalyst in biodiesel production has been gaining attention due to its different metallic oxides' composition and other active compounds which could catalyze the transesterification reaction. Anthill is a naturally occurring siliceous or fire clay material formed by ants at the entrances of their colonies. Its capability as a catalyst(both in synthesized form or as a catalyst) to produce biodiesel is attributed to the presence of different metallic oxides Al_2O_3, CaO, and SiO_2. Several researchers have reported the transesterification of various feedstocks to biodiesel using either anthill or an anthill composites as catalyst. The various feedstock that was studies are edible oil such as Palm Olein, *Chrysopyllumalbidium* seed Oil, vegetable oil, and Waste frying oil(Babatunde et al., 2020; Yusuff, 2019; Yusuff & Adesina, 2020).

The use of edible feedstock for transesterification process create an imbalance in the food chain because human being depend of edible oil for sustainability. Other proven sources of feedstock is non-edible oil. Castor Oil is one of the acceptable non-edible oil suitable for transesterification process because it does not have a competing food values when compared with edible oil(Panhwar et al., 2019). Different catalysts such as sulphuric acid (Melo et al., 2008) ,Potassium hydroxide(Keera et al., 2018), sodium hydroxide (Dairo et al., 2013), derived heterogeneous catalyst (Ismail et al., 2016) and enzyme(Gomes et al., 2020) have been used with satisfactory result based on the use of optimum condition for transesterification process.

Response surface method (RSM) is a set of statistical and mathematical techniques used to study of relationships of several variables on a desired response (Morshedi and Akbarian, 2014). It is particularly useful in useful for developing, improving, and optimizing processes (Carley, Kamneva, and Reminga, 2004). Of the many RSM design, the Box-Behnken design (BBD) has been commonly used to optimize biodiesel production from several feedstock (Ansori, and Mahfud, 2021; Adejumo et al., 2019;Kyari et al., 2017; S. M. Sadrameli et al., 2016). This could be attributed to it having the least number of trials when compared to other design (Ansori, and Mahfud, , 2021).

There are limited reports on the use of derived heterogeneous catalyst from anthill on the transesterification of castor oil. This study was designed to provide more information on the transesterification of castor oil to biodiesel using an .In this study, the chemical properties of calcined anthill will be determined,and it will be used asa heterogeneous catalyst in the conversion of castor oil to biodiesel. The influence of reaction variables such as agitation, reaction temperature, methanol to oil volume, time and catalyst loading on biodiesel yield will be investigated and the optimum condition for the transesterification of castor oil to biodiesel using anthill as catalyst will be discovered. The produced biodiesel will be characterised and compared with biodiesel produced from other sources.

Materials and method

Sample Collection

The extracted Castor oil was purchased from a vendor store in Ogbomosho ($8^0$08´N$4^0$15´E), Oyo State Nigeria and used without further purification. Methanol (of 99% purity) was used as purchased with no further purification. The anthill used in the study was harvested from its mound located at LadokeAkintola University Farm, Ogbomosho, Oyo State Nigeria.

Materials Pre-processing

The procedure of (Yusuff, 2019) was modified and used for the processing of the anthill harvested from anthill heaps. The obtained anthill was pulverised to a size of 0.3 mm, oven dried at 110^{o}C for 4 hours. The dried anthill was calcinated in an electric furnace at a temperature of 800 °C for 2 h. The calcinated anthill was cooled and then ground, sieved, and kept in a desiccator(Babatunde et al., 2020). The chemical compositions of the calcined anthill were determined by X-ray fluorescence (XRF) analyser(ASTM D5381-93, 2021).

Biodiesel Production

A fixed volume of castor oil (9.61 g or 10 ml) was used for the transesterification process. Reaction time, temperature, catalyst loading, methanol volume and agitation rate are varied with the limit specified in Table 1 using BBD while the response was yield of production of biodiesel. A three neck round bottom flask was used as the reactor for the reaction. Castor oil and the mixture of methanol with catalyst are preheated to specified temperature according Table 1 before charging all to the 3-neck round bottom flask. The round bottom flask was connected to a reflux condenser; thermometer was introduced to the setup through another neck of the round bottom flask while the last neck was corked. The whole setup was mounted on a temperature and agitation controlled heater.(Afolabi, 2018; Mathiyazhagan & Ganapathi, 2011).

Table 1: Experimental range of independent variables and their limits

Independent variables	Lower limit	Upper limit
Reaction time (hrs.)	1	3
Reaction temperature (^oC)	40	60
Catalyst loading (g)	1	9
Methanol Volume (ml)	10	60
Agitation rate (rpm)	100	400

A total of 46 experimental run was generated using BBD using Design Expert 13.0. The optimum condition of the five variables that will give best yield will be established. Biodiesel produced at optimum condition was analysed using FTIR, density, pour point, flash point and viscosity according of respective standards(ASTM D1298-12b, 2017; ASTM D3828-16a, 2021; ASTM E1252-98, 2021; ASTMD8254-19, 2019; ASTMD97-17b, 2017).

Results and Discussion

Catalyst Characterization

The chemical compositions of calcinated anthill are presented in Table 2. The major metal oxides in raw anthill sample were found to be, silica (SiO_2), alumina (Al_2O_3), Calcium Oxide (CaO), iron oxide (Fe_2O_3) and Loss in ignition (LOI).Metal oxides such as SiO_2, ZrO_2, Al_2 O_3 and TiO_2 are in nature active for catalysis and have been employed in either their pure and or combined forms as catalysts in for biodiesel production from animal fat or plant oil(Yusuff & Adesina, 2020). The high values obtained for the loss on ignition (LOI) in the calcinated anthill was because of absorbed gases, organic matter, volatilecomponent, and moisture content leftover in the calcinatedanti hill.(Yusuff, 2019; Yusuff & Adesina, 2020)

Table 2.XRF Analysis Result

Sample	SiO_2	AI_2O_3	Fe_2O_3	CaO	TiO_2	Na_2O	MgO	Others	LOI
Wt%	9.4	21.35	7.6	50.4	1.02	1.3	1.44	2.61	4.88

Biodiesel Characterization

The fuel properties of produced biodiesel were determined and tabulated in Table 3 and was found to be compatible with ASTM D6751a and EN 14214 biodiesel standard except density which was greater than the specified value for biodiesel (870 kg/m^3). The high value of density was noticed in other published transterification of castor oil regardless of the catalyst used for this reaction(Amalia et al., 2019; Vázquez et al., 2020)

Table 3. Physio-chemical Characteristics of Castor oil

Property	Unit	Value
Density	Kg/m3	937
Viscosity	mm2/s	5.28
Pour point	^{o}C	-13
Flash point	^{o}C	172

FTIR is a mature technique used for characterization of biodiesel with a cheap, fast and accurate analysis of biodiesel(Mahamuni & Adewuyi, 2009). The obtained characterization of biodiesel produced from castor oil was presented in Figure 1. In this Figure, the identified peaks on this spectra are typical vibration found in biodiesel. Alcohol stretching vibration was observed at 3480.30 cm-1, Alkane stretching was observed at 2927.77 cm-1, ester was observed at 1743.42 cm-1. The other vibration presents are 1453.65, 1366.22 and 1166.11 cm-1 are bending alkane, bend stretching alkene and C-O stretch of ester. The vibration obtained was in line with published FTIR results of Biodiesel produced from other feedstock using anthill as catalyst (Yusuff & Adesina, 2020).

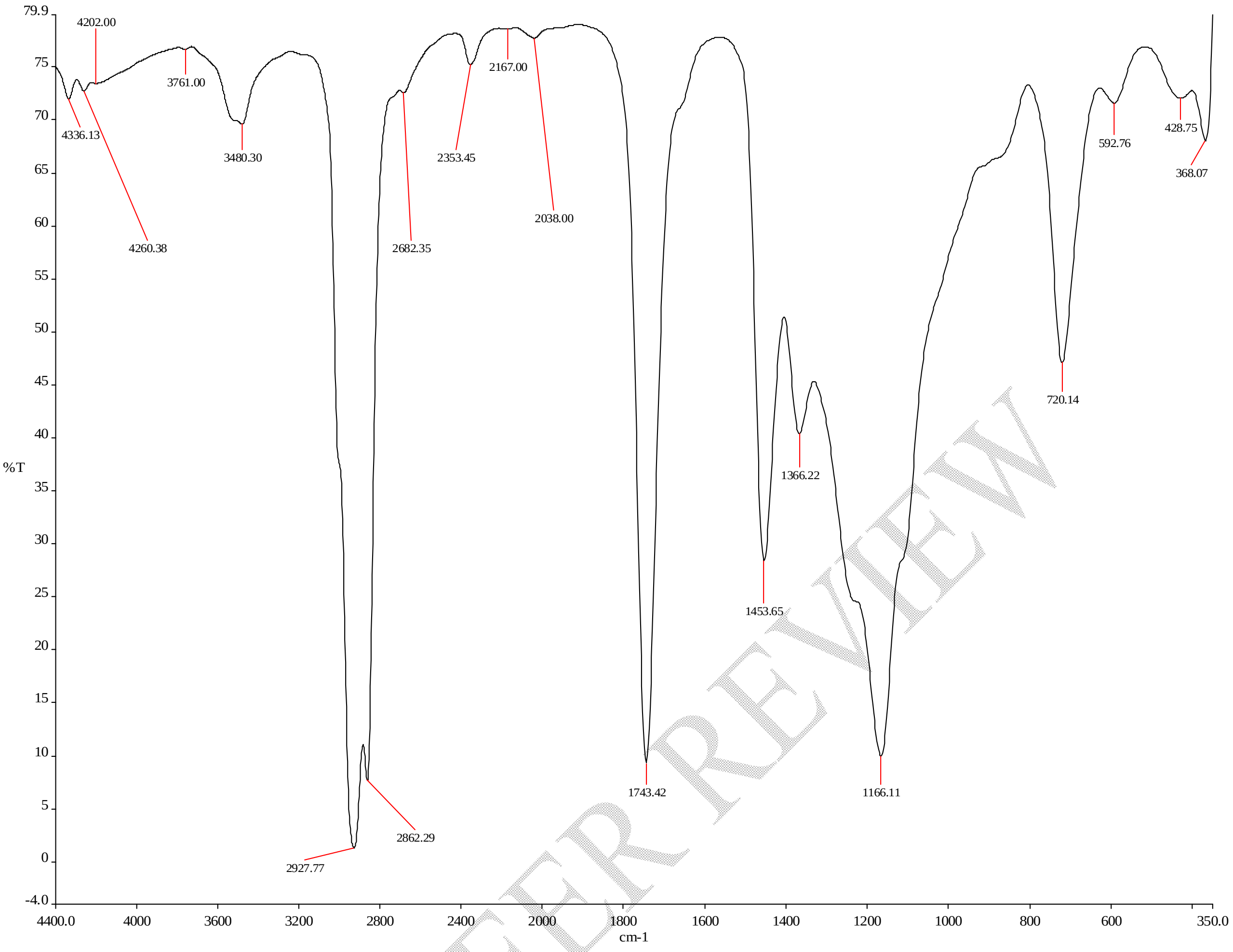

Figure 1. FTIR of biodiesel produced from castor oil.

Model Development

In this work, a mathematical model was developed based on the optimization of the five important operating variables to achieve the highest biodiesel yield. The variables are A: methanol to oil ratio B: Agitation (rpm), C: reaction time (hrs.), D: temperature (^{o}C) and E: catalyst loading (g). The experimental values of the variables and response are given in Table 3. Backward elimination regression method was used to remove terms with p-values >0.10 and tabulated in Table 4 below. The equation can be used to optimize the biodiesel synthesis process by performing the experiment at any set of condition. The yield in terms of the actual factors was presented in equation 1.

$$Yield = 112.98 - 0.044133A + 0.131B - 4.9875C - 2.49562D + 0.457135E + 0.027550AE - 0.003583BD + 0.2175CD - 0.096875DE - 0.001277A2 + 0.000071B2 - 1.25625C^{2} + 0.037271D^{2} + 0.447005E^{2} \qquad 1$$

From the equation the linear terms, quadratic terms and cross products showed both positive and negative coefficient values. The p-value of the model which was less than 0.0001 and the F-value of 34.70 implies that the model is significant. From the model B, C, D, E, AE, BD, CD, DE, B^2, C^2, D^2, E^2 are the significant terms.

Table 4. ANOVA for Reduced Quadratic model

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	
Model	1379.59	14	98.54	34.70	< 0.0001	significant
A-Methanol	0.2756	1	0.2756	0.0971	0.7575	
B-Agitation	58.52	1	58.52	20.61	< 0.0001	
C-Time	11.90	1	11.90	4.19	0.0492	
D-Temperature	131.10	1	131.10	46.17	< 0.0001	
E-Catalyst	284.77	1	284.77	100.28	< 0.0001	
AE	30.80	1	30.80	10.85	0.0025	
BD	115.56	1	115.56	40.70	< 0.0001	
CD	18.92	1	18.92	6.66	0.0148	
DE	60.06	1	60.06	21.15	< 0.0001	
A^2	5.56	1	5.56	1.96	0.1718	
B^2	22.17	1	22.17	7.81	0.0088	
C^2	13.77	1	13.77	4.85	0.0352	
D^2	121.23	1	121.23	42.69	< 0.0001	
E^2	446.42	1	446.42	157.21	< 0.0001	
Residual	88.03	31	2.84			
Cor Total	1467.62	45				

3.3 Perturbation Plot of Variables

The perturbation plot provided a one pass relationship between each of the five variables on yield of biodiesel production (Figure 2). Each of the five variables are considered while the remaining four not considered will be set to their respective mid-point value. For the relationship between increase in methanol volume and yield of biodiesel produced, the values of B, C, D, and E are fixed at their mid points such as 250 rpm, 2h, 50°C and 5g respectively. Increase in volume of methanol (10 to 35 ml) used for the transesterification process increased with yield of biodiesel produced from 70.5 to 71.5 %. Beyond 35 ml, the yield of biodiesel produced decreased to a final value of 70.8% at 60 ml of methanol. Agitation rate was increased from 100 to 400 rpm while the effect of this increase on yield of biodiesel produced was reported at fixed condition of A, C, D and E. B show a decline trend with increase agitation rate for this process. The effect of reaction time on the biodiesel yield during the transesterification of castor oil was studied at various time ranging from 1 to 3h using calcined anti hill as catalyst while keeping A, B, D and E constant at their mid-points. The biodiesel yield is directly proportional to the reaction times (Dhanasekaran & Dharmendirakumar, 2014). From the study, as C increased from 1 to 2.38 h, YB increase to 71.7% while further increase in C lead to reduction in YB produced.

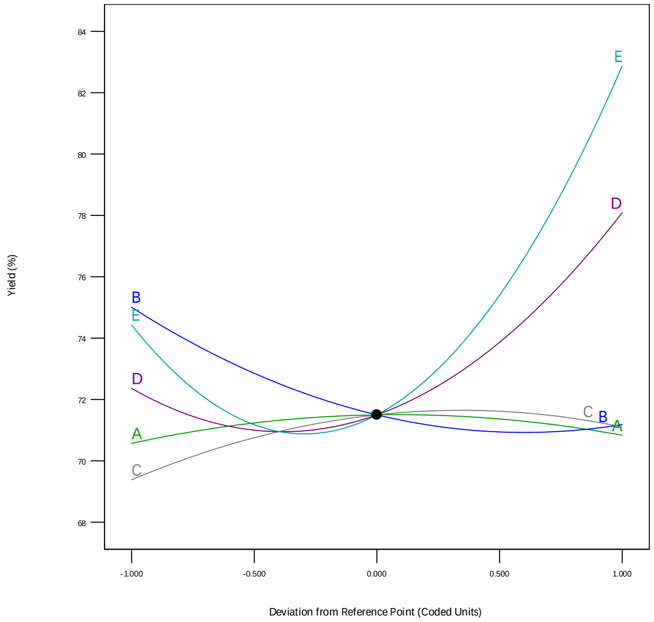

Figure 2. Perturbation plot of the effect of the five variables considered on yield of biodiesel.

The decrease in biodiesel yield could be because longer reaction time favours the saponification of soap and as such a decrease in biodiesel yield. This agrees with the work of Israa et al. (2015) where prolonged reaction time gave lower FAME yield due to saponification reaction and alsoadsorptive intake of reactants/products on the active sites of the catalyst used.

For the effect of D on YB while A,B,C and E are kept constant at their mid-points. A drop in yield was observed as the temperature increases from 40^{o}C to 45^{o}C while from 50^{o}C an increase in the yield was observed with a final YB of 78% at 60^{o}C. This agree with the report of Romano and Sorichetti 2011. Given the same reaction time, the conversion of oil to biodiesel is greater at higher temperatures. The boiling point of methanol is about68^{0}C, hence the temperature for transesterification at atmospheric pressure is usually in the range between 50 and 60^{o}C(Romano & Sorichetti, 2011).Increase in E on YB during the transesterification of castor oil was studied at various catalyst loading ranging from 1 to 9g while keeping other parameters constant as shown in in the perturbation plot. Two trends were noticed on the plot with respect of YB for the two trends. With increase in E from 1 to 3.5g, YB was less than 75% while further increase in E from 3.5 to 9g lead to a corresponding increase in YB to a final yield of 82%. Catalysts are expected to be dosed in right proportion because low dosage lead to incomplete conversion of oil(Bello et al., 2021) while high dosage lead to formation of soap especially for alkaline catalyst (Ayodeji et al., 2018).

3.4 3D Surface Plot of Variables

The 3D response surface graph is one of the most common ways to show the interaction of the different factors to the response variable. When two or more variables are to be considered in the model, two of the variables are plotted on a 3D graph, keeping the other variables at a constant value(Sánchez et al., 2015). In Figure 3-6, the 3-D surface plots of the interaction between two variables on the YB were presented. Figure 3 shows the surface plot of the interaction between variables AE (i.e. methanol volume vs catalyst). The interactive effect of increase in the methanol volume and increase in catalyst loading showed an increase in biodiesel yield as the highest biodiesel yield was gotten at themaximum methanol volume of 60ml and catalyst loading of 9g. This agrees with the work of previous researchers (Ayodele et al., 2017;Garba et al., 2017; N Sanchez et al., 2015; Ghadge and Raheman, 2006). Figure 4 shows the surface plot of the interaction between variables BD (i.e. temperature vs agitation). Biodiesel yield also increase significantly with an increase in the temperature and a moderate increase in biodiesel yield with an increase in agitation. This shows that agitation is strongly dependent on the reaction temperature. Figure 4.shows the surface plot of the interaction between variables CD (i.e. temperature vs time). The figure shows that higher values of reaction time with increase in temperature as no effect on the yield of biodiesel. However since most of the highest values for biodiesel yield was obtained within the limit of the range of the variables, there might be a need of designing a new experiment by increasing the limits of the some of the variables. The interaction between simultaneous increase in

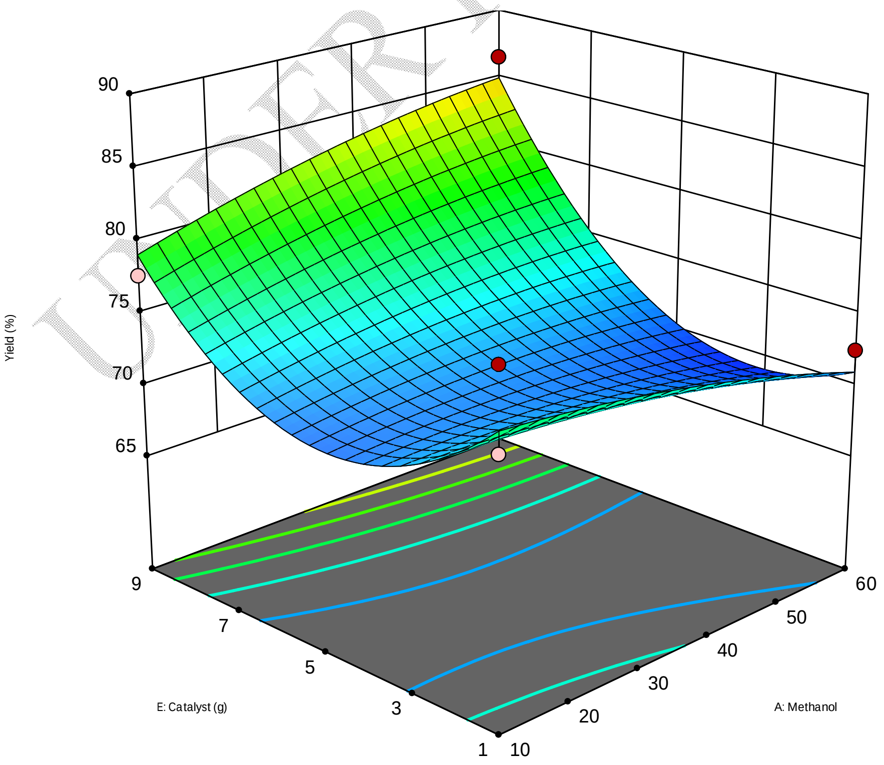

Fig 3. Interaction effect of Methanol volume and catalyst on YB.

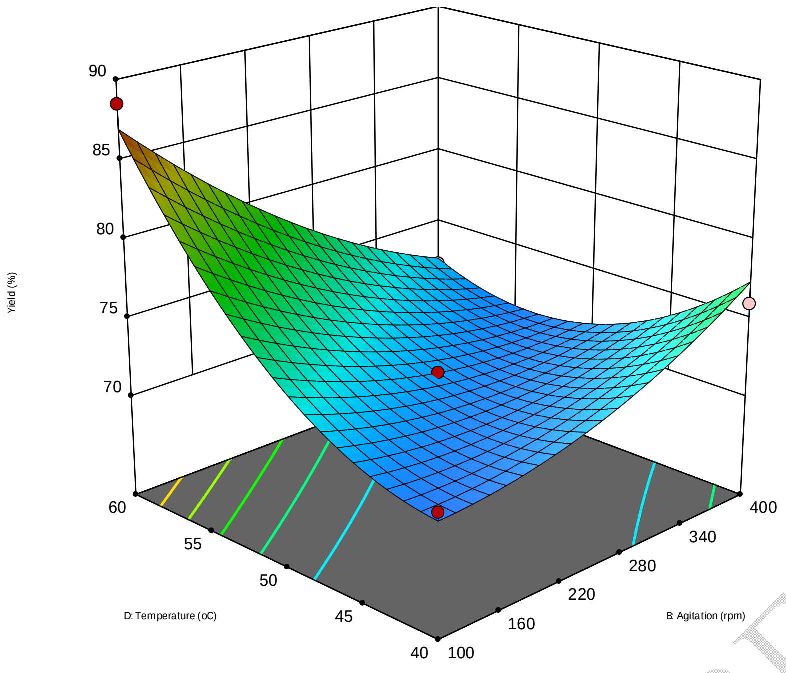

Fig 4. Interaction effect of Reaction Temperature and Agitation on YB.

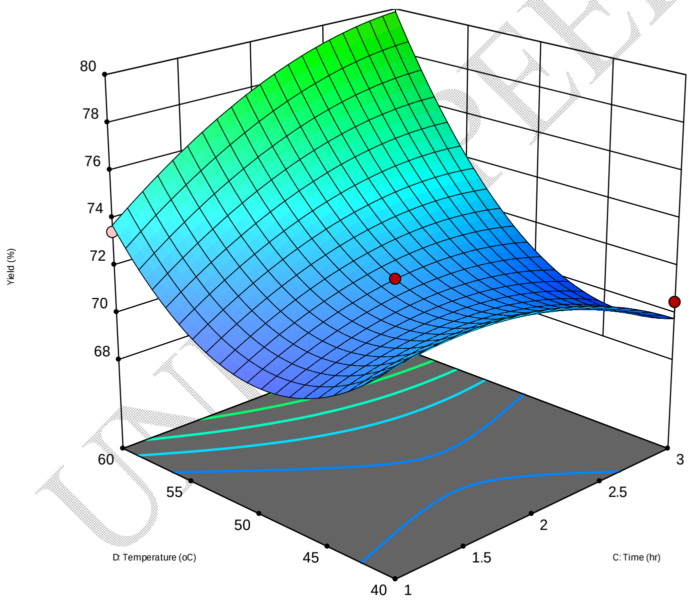

Figure 5. Interaction effect of Reaction Temperature and Time on YB.

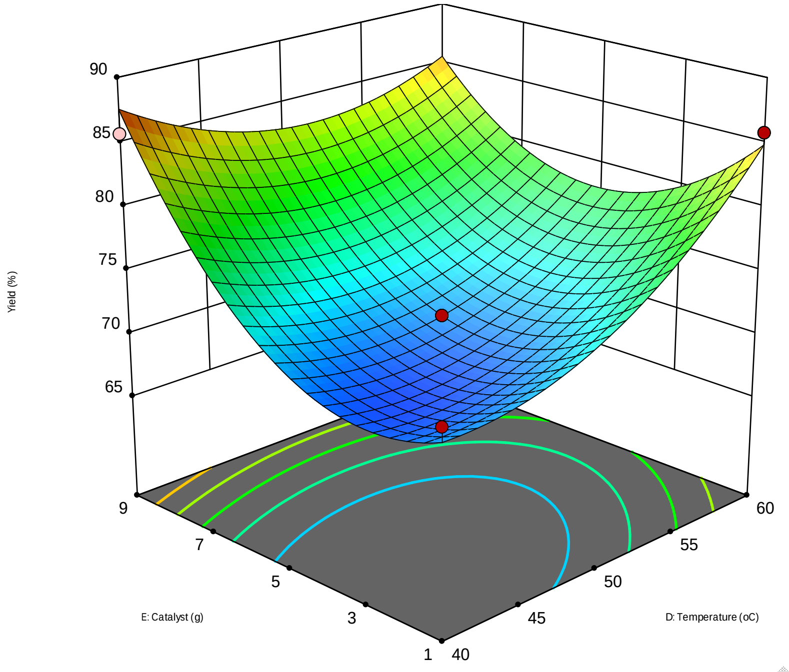

Figure 6. Interaction effect of Reaction Temperature and Catalyst on YB

3.5 Optimization of Process Variables

The optimization study was conducted using numerical optimization tool in the BBD design with the guidance of desirability function. The closer the desirability function to 1, the better the optimized condition. The ramp of optimization was presented in Figure 7. The optimization study gave an optimal value of volume of 11.73ml, agitation of 166.458rpm, reaction time of 2.34375hrs, temperature of 59.4552^{o}C, catalyst loading of 1.14g, and an optimal yield of 90.59 %. The optimized value was repeated in the laboratory and the experimental YB obtained was 91.3%. The percentage deviation was 0.7%

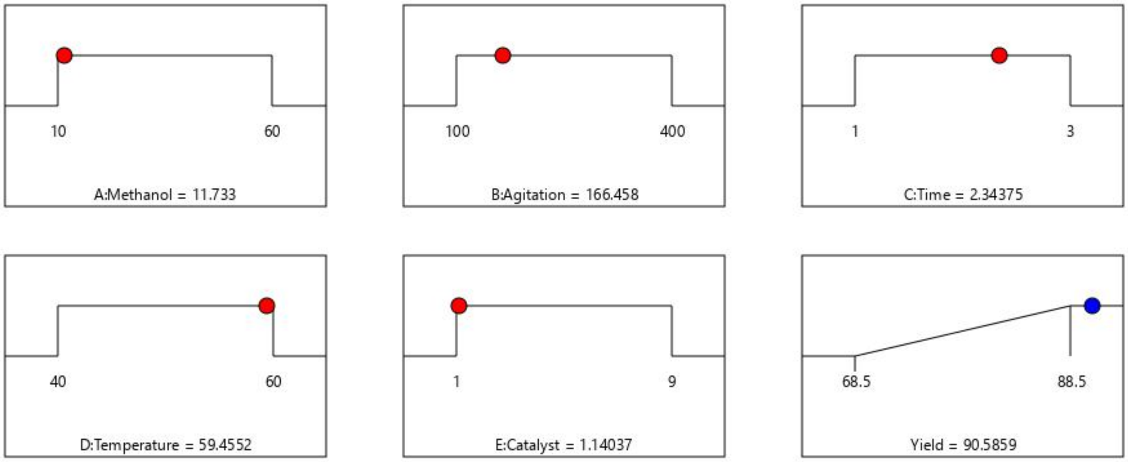

Fig 7. Optimum Variables for Biodiesel Production from Castor Oil using Anti-hill as Catalyst

Furthermore, the performance of the calcined Anthill catalyst was also compared with other catalysts studied by previous researchers as shown in Table 5

Table 5. Comparison of the Effect of Different catalyst on Biodiesel Production from different feedstock

Comparsion of the effect of different catalyst on biodiesel production from various feedstock							
Feedstock	**Catalyst**	**Temperature (^0C)**	**Reaction Time**	**Methanol:Oil**	**Catalyst Concentration**	**Yield**	**References**
Castor Oil	Calcined Anthill	59.46	2.344	11.73:1	1.14g	90.59%	Current Study
Waste Frying oil	anthill-eggshell-Ni-Co mixed oxides composite	70	2hrs	12:01	3 wt%	90.23%	A .S Yussuf et al., 2018a
Chrysophyllumalbidium seed oil	NaOH modified anthill (Na-MA) catalyst	64.82	2hrs	8:01	3 wt%	89%	A.SYusuff,2019
Chrysophyllumalbidium seed oil	Calcined Anthill	64.82	2hrs	8:01	3wt%	58.15%	A .S Yusuff,2019
Castor Oil	Mud Clam Shell based CaO	60	2hrs	14.0:1	3 wt%	96.70%	S Ismail et al., 2016
Jojoba Oil	Red seaCoraline Limestone based CaO	30	3hrs	12.0:1	5wt%	81.93%	Taiseer et al., 2019
Palm Olein	Calcined Anthill	70	3hrs	6:01	2wt%	78.20%	Yusuff and Adesina, 2020
Waste Frying oil	Composite Anthill-Chicken Eggshell	60	2hrs	6:01	5wt%	70.00%	A. S Yusuff et al., 2018b
Vegetable Oil	Activated Anthill	65	2hrs	9:01	1.5wt%	94.85%	E.O Babatunde et al., 2020
Orange Peel	Limestone based CaO	85	100 mins	16.5:1	2.7wt%	70%	Yenkwo et al., 2022

Conclusion and Recommendation

From the study, it was discovered that calcined anthill has a mixed alkaline compounds of CaO, Al_2O_3, SiO_2 and Fe_2O_3 which makes it suitable for use as a catalyst in the transesterification reaction. It was concluded that catalyst loading is the most influential variable while the interaction of agitation-temperature is most influential to biodiesel production. Presence of vibrations of alcohol (3480.3 cm^{-1}), alkane (2927.77 cm^{-1}) and esters (1743.42 cm^{-1}) confirmed the product to be biodiesel. The physicochemical properties of biodiesel produced are within the ASTM except viscosity that is greater than ASTM (870 kg/m^3). The optimum condition of a volume of 11.73ml, agitation of 166.458rpm, reaction time of 2.34375hrs, temperature of 59.4552°C, catalyst loading of 1.14g, gave a yield of 90.59% with a percentage deviation of 0.7% when validated with experimental value.

From the results of the study showed that the use of anthill as catalyst in the transesterification process is feasible and economical. However, it is recommended that further studies be carried out on the scaleup of the process for the industrial use of anthill as catalyst in the transesterification process as well as the economic analysis of the process to assists in the adoption of biodiesel in Nigeria.

References

Adejumo, B. A, Agboola, J. B, Orhevba, B. A, Obasa, P. A, Simeon, M. I (2019). Optimisation of the Production Parameters of DelonixRegia Methyl Ester Using Box- Behnken Design. *International Journal of Scientific & Technology Research* Volume 8, Issue 09. ISSN 2277-8616 2036.

Adeyinka S. Yusuff, Olalekan D. Adeniyi, Sarafa O. Azeez, Moses A. Olutoye, Uduak G. Akpan (2018a). Synthesis and Characterization of anthill-eggshell-Ni-Co mixed Oxides Composite Catalyst for Biodiesel production from Waste Frying oil | Biofuels, Bioprod. Bioref. DOI: 10.1002/bbb

Adeyinka S. Yusuff, Olalekan D. Adeniyi, Moses A. Olutoye, Uduak G. Akpan (2018b). Development And Characterization of a Composite Anthill-Chicken Eggshell Catalyst For Biodiesel Production From Waste Frying Oil. *International Journal of Technology* 1: 110-119 ISSN 2086-9614 © IJTech

Afolabi, D. I. (2018). Comparative Analysis of Production of Biodiesel via Homogeneous and Heterogeneous Transesterification. *International Journal of Academic and Applied Research (IJAAR)*, *2*(4), 1–5.

Afsaneh Morshedi and Mina Akbarian (2014). Application of Response Surface Methodology: Design of Experiments And Optimization: A Mini Review. *Centre for Info Bio Technology (CIBTech) 2434. Indian Journal of Fundamental and Applied Life Sciences* ISSN: 2231– 6345 (Online) An Open Access, Online International Journal Available at www.cibtech.org/sp.ed/jls/2014/04/jls.htm 2014 Vol. 4 (S4), pp. 2434-2439/

Amalia, S., Khalifah, S. N., Baroroh, H., & Muiz, A. (2019). Biodiesel production from castor oil using heterogeneous catalyst KOH / zeolite of natural zeolite Bandung Indonesia Biodiesel Production from Castor Oil Using Heterogeneous Catalyst KOH / Zeolite of Natural Zeolite Bandung Indonesia. *AIP Conference Proceedings 2120, 080016*(July), 3–10.

Ansori, A., Mahfud, M. (2021). "Box-Behnken Design for Optimization on Biodiesel Production from Palm Oil and Methyl Acetate using Ultrasound Assisted Interesterification Method", *Periodica Polytechnica Chemical Engineering*, https://doi.org/10.3311/PPch.17610

ASTM D1298-12b. (2017). *Standard Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method*. ASTM International. https://doi.org/10.1520/D1298-12BR17

ASTM D3828-16a. (2021). *Standard Test Methods for Flash Point by Small Scale Closed Cup Tester*.

ASTM D5381-93. (2021). *Standard Guide for X-Ray Fluorescence (XRF) Spectroscopy of Pigments and Extenders*.

ASTM E1252-98. (2021). *Standard Practice for General Techniques for Obtaining Infrared Spectra for Qualitative Analysis*.

ASTMD8254-19. (2019). *Standard Test Method for Flash and Fire Points of Asphalt by Cleveland Open Cup Tester*.

ASTMD97-17b. (2017). *Standard Test Method for Pour Point of Petroleum Products*.

Ayodeji, A. A., Ojewumi, M. E., Rasheed, B., & Ayodele, J. M. (2018). Data on CaO and eggshell catalysts used for biodiesel production. *Data in Brief*, *19*, 1466–1473. https://doi.org/10.1016/j.dib.2018.06.028

Babatunde, E. O., Saka, H. B., Olutoye, M. A., Akpan, U. G., & Auta, M. (2020). Synthesis of fatty acid methyl esters from used vegetable oil using activated anthill as catalyst. *Nigerian Journal of Technology*, *39*(1), 140–147. https://doi.org/10.4314/njt.v39i1.15

Bello, A. A., Igboro, S. B., Abubakar, U. A., & Nuhu, I. S. (2021). Production of Biodiesel from Waste Vegetable Oil Using Chicken Eggshell Waste as Heterogeneous Catalyst. *Journal of Science, Technology and Education*, *9*(2), 92–105.

Chouhan, A. P. S., & Sarma, A. K. (2011). Modern heterogeneous catalysts for biodiesel production: A comprehensive review. *Renewable and Sustainable Energy Reviews*, *15*(9), 4378–4399. https://doi.org/10.1016/j.rser.2011.07.112

Dairo, O. U., Olayanju, T. M., Ajisegiri, E. S., Alamu, O. J., & Adeleke, A. E. (2013). Optimization of in-situ Biodiesel Production from Raw Castor Oil-Bean Seed. *Journal of Energy Technologies and Policy*, *3*(13), 14–20.

Dhanasekaran, K., & Dharmendirakumar, M. (2014). Biodiesel characterization and optimization study of used frying palm oil. *International Journal of Current and Academic Review*, *2*(1), 105–120.

Gomes, E. D. S., De, T. L., Mattos, M. C. De, Filho, G., Victor, C., Pascoal, P., Carlos, J., & Monte, J. Q. (2020). Production of biodiesel by enzymatic catalysis from the castor oil : an analytical chemical study. *Journal of Analytical and Pharmaceutical Research*, *9*(3), 73–79. https://doi.org/10.15406/japlr.2020.09.00355

Ismail, S., Ahmed, A. S., Anr, R., & Hamdan, S. (2016). Biodiesel Production from Castor Oil by Using Calcium Oxide Derived from Mud Clam Shell. *Journal of Renewable Energy*, 1–8.

Kathleen M. Carley, Natalia Y. Kamneva, Jeff Reminga (2004).Response Surface Methodology *Carnegie Mellon University, School of Computer Science, Institute for Software Research International*, CASOS Technical Report CMU-ISRI -04-136

Keera, S. T., Sabagh, S. M. El, & Taman, A. R. (2018). Castor oil biodiesel production and optimization. *Egyptian Journal of Petroleum*, *27*(4), 979–984. https://doi.org/10.1016/j.ejpe.2018.02.007

Knothe, G., J. Krahl, and J. Van Gerpen. 2005. The Biodiesel Handbook. 1ST edition. AOCS Publishing, Urbana, IL.

L.C. Meher, D. Vidya Sagar, S.N. Naik (2006). Technical aspects of biodiesel production by transesterification—a review. *Renewable and Sustainable Energy Reviews* 10248–268

Mahamuni, N. N., & Adewuyi, Y. G. (2009). Fourier Transform Infrared Spectroscopy (FTIR) Method To Monitor Soy Biodiesel and Soybean Oil in Transesterification Reactions , Petrodiesel - Biodiesel Blends , and Blend Adulteration with Soy Oil. *Energy and Fuel*, *76*(11), 3773–3782.

Mathiyazhagan, M., & Ganapathi, A. (2011). *Factors Affecting Biodiesel Production*. *1*(2), 1–5.

Melo, W. C., dos Santos, A. S., Santa Anna, L. M. M., & Pereira, N. (2008). Acid and Enzymatic Hydrolysis of the Residue from Castor Bean (Ricinus communis L.) Oil Extraction for Ethanol Production: Detoxification and Biodiesel Process Integration. *Journal of Brazilian Chemical Society*, *19*(3), 418–425.

Mohammad Kord, Seyed Mojtaba Sadramelia, Barat Ghobadian (2006). Optimization of Biodiesel Production from Castor Oil Using a Microwave Via Response Surface Methodology (RSM). *JREE (Journal of Renewable Energy and Environment)*: Vol. 3, No. 4, pp 1□9

M. Z. Kyari, S. M. Danggoggo, B. B. Usman and A. B. Muhammad (2017). Optimization of Process Variables in the Biodiesel Production from Lophira lanceolata Seed Oil. *Nigerian Journal of Basic and Applied Science* 25(2): 75-86 DOI: http://dx.doi.org/10.4314/njbas.v25i2.9

Panhwar, T., Mahesar, S. A., Kandhro, A. A., Tufial, S., Sheerazi, H., Kori, A. H., Laghari, Z. H., & Memon, J. (2019). *Physicochemical composition and FTIR characterization of castor seed oil*. *8*(4), 778–787. https://doi.org/10.24263/2304-974X-2019-8-4-9

Romano, S. D., & Sorichetti, P. A. (2011). Dielectric Spectroscopy in Biodiesel Production and Characterization. *Green Energy and Technology*, 7–27. https://doi.org/10.1007/978-1-84996-519-4

Sánchez, N., Sánchez, R., Encinar, J. M., González, J. F., & Martínez, G. (2015). Complete analysis of castor oil methanolysis to obtain biodiesel Complete analysis of castor oil methanolysis to obtain biodiesel. *Fuel*, *147*, 95–99. https://doi.org/10.1016/j.fuel.2015.01.062

S. Ismail, A. S. Ahmed, Reddy Anr, and S (2016). Hamdan Biodiesel Production from Castor Oil by Using Calcium Oxide Derived from Mud Clam Shell. Hindawi Publishing Corporation, *Journal of Renewable Energy* Volume 2016, Article ID 5274917, 8 pages.

Taiseer Hassan M., Ahmed A. A. Youssif, Isameldeen Ibrahim H. A (2019). Optimization of Biodiesel Production from Jojoba Oil Using Red Sea Coralline limestone as a heterogeneous Catalyst. *International Journal of Engineering and Applied Sciences (IJEAS)* ISSN: 2394-3661, Volume-6, Issue-8.

Vázquez, V. Á., Aarón, R., Estrada, D., Mauricio, M., Flores, A., Alvarado, C. E., Christian, H., & Aguado, C. (2020). Transesterification of non-edible castor oil (Ricinus communis L .) from Mexico for biodiesel production : a physicochemical characterization

Transesterification of non-edible castor oil (Ricinus communis L .) from. *Biofuels*, *0*(0), 1–10. https://doi.org/10.1080/17597269.2020.1787700

Yenkwo K.C, Kovo A,S , Isa A.G and, Ogunjobi T.O (2020). Optimization of Biodiesel from Orange Peel Using calcium oxide Catalyst from Limestone via In-Situ Transesterification. SSAAR(JPAS); *Journal of pure and Applied Science*. Vol. 16(9) 79-102.

Yusuff, A. S. (2019). Characterization of alkaline modified anthill and investigation of its catalytic behaviour in transesterification of Chrysophyllum albidium seed oil. *South African Journal of Chemical Engineering*, *29*(May), 24–32. https://doi.org/10.1016/j.sajce.2019.05.001

Yusuff, A. S., & Adesina, O. A. (2020). Biodiesel Synthesis from Palm Olein Oil Using Anthill as Catalyst. *Journal of Chemical Technology and Metallurgy*, *55*(2), 300–306.