

Adeyinka S. Yusuff*, Temitayo M. Azeez and Esther O. Babatunde

Titania-termite hill composite as a heterogeneous catalyst: preparation, characterization, and performance in transesterification of waste frying oil

<https://doi.org/10.1515/ijcre-2020-0087>

Received June 6, 2020; accepted October 3, 2020;

published online October 21, 2020

Abstract: To reveal the catalytic potential of abandoned naturally occurring material, we synthesized titania-termite hill composite (Ti-THC) via an incipient wetness impregnation route, characterized by various techniques and tested as a catalyst for transesterification of waste frying oil (WFO). The reusability of the prepared catalyst was also studied to evaluate its stability. The effects of reaction process parameters, such as temperature, time, catalyst loading and methanol/WFO molar ratio on fatty acid methyl ester (FAME) yield, were investigated using a central composite design approach. SEM result revealed pores formation on the catalyst surface, while XRD and EDX analyses confirmed successful insertion of titania into the aluminosilicate layer of the termite hill. The maximum FAME yield of 90.78% was obtained at optimum experimental conditions of 71.16 °C reaction temperature, 2.12 h reaction time, 1.03 wt.% catalyst loading and 9.96:1 methanol/WFO molar ratio. The catalyst still maintained its better stability after being reused for three reaction cycles.

Keywords: catalyst; characterization; FAME; optimization; titania; termite hill.

1 Introduction

It is no longer news that the opportunities and challenges available in this 21st century as the industry and

population increase are so many and valuable. Energy, which is one of the available opportunities and challenges, plays a significant role in people's lives, and the use of energy is regarded as an essential factor that measures the economic growth of a nation (Endalew, Kiros, and Zanzi 2011).

In the last decades, fossil hydrocarbon fuels such as petroleum, coal and natural gas have been the significant sources of energy used all over the world for transportation, industrial and domestic purposes (Endalew, Kiros, and Zanzi 2011; Kiss, Dimian, and Rothenberg 2006). However, these energy sources are associated with some demerits such as depletion tendency, non-renewable, generation of large volumes of greenhouse gases, environmental degradation and oil crisis (Bugaje, Mohammed 2008). Greenhouse gas emission has been identified as one of the significant contributors to global warming and climate change (Hassani et al. 2014; Yusuff et al. 2019). All these problems, as mentioned earlier, necessitate the need to identify an alternative source of energy that is non-toxic, biodegradable, environmentally friendly, available in abundance and relatively cheap. These unique features can be attributed to biofuels such as biohydrogen, bioethanol, biogas and biodiesel (Demirbas 2009).

Biodiesel, which is receiving tremendous attention and known with those features mentioned above, is usually produced from plant oils (edible and non-edible), animal fat and greases via a transesterification reaction (Patil et al. 2018; Yusuff and Owolabi 2019; Yusuff and Popoola 2019). The chemical process involves the reaction between one mole of triglyceride present in oil/fat and three moles of primary alcohol (methanol or ethanol) to produce three moles of (m)ethyl esters and one mole of glycerol. This reaction occurs in three consecutive reversible stages, namely triglyceride to diglyceride, diglyceride to monoglyceride, and finally monoglyceride to fatty acid alkyl ester and glycerol, and it occurs in the presence of a suitable catalyst. The fatty acid alkyl ester is referred to as biodiesel, which can be used to power vehicular and diesel engines in pure form or mixed with fossil fuel in appropriate proportion (Patil et al. 2019a; Yusuff et al. 2018).

*Corresponding author: Adeyinka S. Yusuff, Laboratory of Chemical Reaction Engineering and Catalysis, Department of Chemical and Petroleum Engineering, College of Engineering, Afe Babalola University, Ado-Ekiti, Nigeria, E-mail: yusuffas@abuar.edu.ng, <https://orcid.org/0000-0002-6630-6411>

Temitayo M. Azeez, Laboratory of Material Science and Renewable Energy, Department of Mechanical and Mechatronic Engineering, College of Engineering, Afe Babalola University, Ado-Ekiti, Nigeria
Esther O. Babatunde, Department of Chemical Engineering, Faculty of Engineering, University of Ilorin, Ilorin, Nigeria

For large scale production of biodiesel, a homogeneous catalyzed reaction process remains till today, the viable option. However, the biodiesel from this process is about 1.5–3.0 times higher in cost than the cost of fossil diesel (Endalew, Kiros, and Zanzi 2011). According to some researchers, the high cost of biodiesel production can be minimized by adopting the use of feedstock from non-edible and waste oils (Hassani et al. 2014; Tan et al. 2015). Most of these second-generation feedstocks are associated with high free fatty acid (FFA) content, which reacts with base catalyst, thereby resulting in soap formation and low biodiesel yield. While the reaction is relatively slow with a homogeneous acid catalyst, it is also known to be corrosive, toxic and requires product washing with water, which leads to wastewater generation (Calgaroto et al. 2013; Yusuff et al. 2019). The purity of glycerol produced via a homogeneous catalyzed reaction process is guaranteed if it is distilled, which together, unfortunately, will increase the cost of production of biodiesel and glycerol (Olutoye et al. 2016). Because of these, the application of heterogeneous catalysts to catalyze the transesterification of triglyceride with methanol to produce biodiesel and glycerol has been a subject of an investigation by many researchers (Betiku et al. 2019; Olutoye and Hameed 2013).

The choice of solid catalyst for the catalytic reaction process depends on the FFA content in the feedstock. Hence heterogeneous catalyst tends to exhibit excellent activity towards oil conversion to biodiesel and tolerance to water (Hassani et al. 2014; Yusuff and Bello 2019). The solid acid catalyst is known to be less corrosive, non-toxic and eco-friendly. Still, it requires a high reaction temperature, prolonged reaction time, high alcohol/oil molar ratio and high pressure. While the solid base catalyst is recyclable, it reduces wastewater generation and simplifies biodiesel production and purification. It also guarantees product quality (Chouhan and Sarma 2011).

Naturally occurring materials such as clay, rocks and others had been identified among the fascinating catalyst sources due to their efficiency, durability, availability and effectiveness. Clay is a mesoporous aluminosilicate material, characterized by better surface area, high porosity, nontoxicity and amphoteric sites (Olutoye and Hameed 2013; Olutoye et al. 2016). Besides, it can be a cheap source of silica, alumina and iron oxide, which have been reported as suitable catalyst supports (Taufiq-Yap, Abdullah, and Basri 2011). Moreover, readily available termite hill can serve as a good source of catalyst ingredient.

Termite hill is a pile of sand, clay or composite of clay and other materials that build up at the entrances of the

subterranean dwellings of ant colonies (Henne, 2013). It is an aluminosilicate material exhibiting a wide variability in chemical composition and physical properties. While the most common elements in termite hill include Si, Al, Ca, Mg, K, Ti and Na, the chemical and the mineralogical composition of the termite hill varies from location to location. It contains different crystalline and amorphous phases and amongst the common minerals present in anthill are quartz, kaolinite, cristobalite and tridymite in larger quantity, while alumina, calcite and hematite are present as minor phases (Yusuff et al. 2020). In particular, aluminosilicate-based catalysts, i.e. metal oxide immobilized on clays, zeolite, fly ash and pumice stone, have been successfully used in heterogeneous catalytic transesterification process (Olutoye et al. 2016; Yusuff and Bello 2019; Lawan et al. 2020). For example, Wu and co-authors reported the preparation of a zeolite supported CaO as a strong base catalyst for transesterification of soybean oil with methanol to produce biodiesel. The obtained results showed that at reaction temperature of 65 °C, methanol/oil molar ratio of 9:1 and reaction time of 3 h, the biodiesel yield from the process was 95% (Wu et al. 2013). In another study, fly ash supported CaO catalyst was tested for biodiesel synthesis from crude palm oil and was found to be efficient (Ho et al. 2014).

Conversion of oil/fat to biodiesel via a transesterification process is influenced by different operational parameters, such as reaction temperature, reaction time, catalyst concentration, methanol/oil molar ratio, FFA content in the feedstock and stirring rate. Thus, optimization of biodiesel production process parameters using a statistical experimental design approach is highly important as the interaction effects between independent variables and output variable(s) are revealed. In the present study, a central composite design (CCD), which is a commonly used form of response surface methodology (RSM), has been chosen to optimize the biodiesel production process and to evaluate the effects of process variables on the biodiesel yield. So far, to the best of our knowledge and based on literature research, optimization of process parameters for transesterification of WFO over titania supported termite hill catalyst has not been considered.

This current study was therefore focused on the utilization of titania modified termite hill composite (Ti-THC) as a heterogeneous catalyst to produce FAME from WFO via the transesterification process. The factors affecting the process, such as reaction temperature, reaction time, catalyst loading and methanol/WFO molar ratio, were optimized using the central composite design. Moreover, the catalyst regeneration and reusability were studied to examine its stability.

2 Materials and method

2.1 Materials

Waste frying oil used in this study was collected from Afe Babalola University's cafeteria, Ado-Ekiti, Nigeria. The main fatty acid contained in the WFO sample, according to gas chromatography analysis, were stearic (8.20%), oleic (45.17%), palmitic (38.64%), linoleic (5.43%) and myristic (2.56%) acids. The catalytic material used in this study was harvested from the termite mound located at Afe Babalola University, Ado-Ekiti, Nigeria. The chemical reagents used, such as methanol (99.5%), titanium (IV) isopropoxide (TTIP 97%, source of titanium) and n-hexane (98%), were of analytical grades, and they were all purchased from Topjay Scientific Limited, Ado-Ekiti, Nigeria.

2.2 Preparation of catalyst

The harvested termite hill material was gently crushed with the aid of mortar and pestle and screened to obtain the required particle size (below 63 μm). Titania modified termite hill composite catalyst was synthesized by the impregnation method. In preparing the catalyst, 15 g of fine termite hill powder was added into the 100 mL of TTIP solution and then stirred by magnetic stirrer at 150 °C for 4 h for complete deposition of titania on the termite hill. The slurry was then dried in an oven at 125 °C until the excess water completely removed. Finally, the dried sample was calcined at 500 °C for 4 h in a muffle furnace. A heating rate of 10 °C/min was adopted during calcination.

2.3 Characterization of the prepared catalyst

The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out to evaluate the decomposition trend of the titania modified termite hill catalyst using a TGA/DTA analyzer (Shimadzu DTG 60, Japan). The catalyst sample was treated under nitrogen gas at a flow rate of 100 mL/min and a heating rate of 15 °C/min from ambient temperature to 900 °C. The morphologies and elemental compositions of both raw termite hill (TH) and Ti-THC catalyst were evaluated simultaneously using a scanning electron microscopy-energy dispersive X-ray (SEM-EDX) analyzer (JEOL-JSM 7600F). The functional groups present on the two samples were determined using Fourier transform infrared spectrophotometer (IR Affinity-1S, Shimadzu, Japan), and the spectra were recorded from 4000 to 400 cm^{-1} . The phases and crystal structures of the TH and Ti-THC were analyzed using an X-ray diffractometer (Rigaku D/Max-III, Tokyo, Japan) with Cu K α radiation at 1.5405 Å in the 2 θ range from 8 to 80° with a step size of 0.02°/s. The N₂ adsorption/desorption isotherms of the raw TH and Ti-THC catalyst were measured at 77 K using a BELSORP Max analyzer (BEL, Japan). The studied samples were degassed before analysis at 250 °C for 3 h to remove the adsorbed gases that filled up the pores available on them, and their surface areas were computed using the Brunauer-Emmett-Teller (BET) model. The total pore volume and pore size were determined by the Barrett-Joyner-Halenda (BJH) method and studied near the saturation pressure of N₂ (P/P_o = 0.99). The composition of the TH and Ti-THC samples were determined using X-ray fluorescence (XRF) analyzer. The basic catalytic sites of the prepared catalyst were measured by the colorimetric titration technique by

dissolving 20 mg of Ti-THC catalyst sample in 5 mL of deionized water and stirred for 20 min. The catalyst solution was then titrated against HCl with phenolphthalein as an indicator.

2.4 Transesterification reaction process

Synthesis of FAME from WFO was carried out in a three-necked round bottom flask (250 mL) equipped with a condenser and a magnetic stirrer. The required amounts of WFO, catalyst and methanol were charged into the reaction vessel, and the mixtures were stirred at 300 rpm. Each reaction run was conducted according to the experimental values of the independent test variables (Table 1). After the completion of the reaction, product mixtures were centrifuged to separate the catalyst and allowed the liquid mixture to settle for further separation. The unreacted methanol was removed by heating the mixture on a hot plate at 70 °C. The FAME content in the biodiesel was analyzed using gas chromatography-mass spectroscopy (GC-MS) equipped with flame ionization detection (FID) and a capillary column (60 mm $\times$ 0.320 mm $\times$ 1.8 μm). Helium, methyl octanoate and hexane were used as the carrier gas, internal standard and solvent, respectively. The FAME content was determined using Eq. (1).

$$\text{FAME content (\%)} = \frac{m_i a_b}{m_b a_i} \times 100\% \quad (1)$$

m_i , m_b are masses of internal standard and biodiesel sample, respectively, while a_i , a_b are peak areas of internal standard and biodiesel sample, respectively.

$$\alpha = \pm 1.682$$

2.5 Experimental design

In this study, the influence of independent variables on FAME yield (response) was evaluated by applying a central composite design. The independent variables studied were reaction temperature, reaction time, catalyst loading and methanol/oil molar ratio. A total of twenty-one (21) experimental runs were conducted, and the obtained data were analyzed using Design Expert software version 7.0.0. Table 1 shows the design for the experiment using the CCD approach.

2.6 Stability and leaching tests

Catalyst stability study helps in evaluating the efficiency of a catalyst. After the reaction process, the solid catalyst was recovered from the

Table 1: Variables for transesterification of WFO in two (2) levels for CCD.

Item	Temperature, T °C	Time, t h	Catalyst loading, C wt. %	Methanol/oil molar ratio, M
Lower level (−1)	50	2	1	6:1
Upper level (+1)	80	4	2	10:1
Lower axial (− α)	39.8	1.3	0.7	4.6
Upper axial (+ α)	90.2	4.7	2.3	11.4
Centre point (0)	65	3	1.5	8:1

product mixture by centrifuge at 7500 rpm for 10 min. The liquid mixture was thereafter decanted and the spent solid catalyst was washed severally with hexane to remove adsorbed oil. The solution was then filtered to remove hexane, and the recovered Ti-THC catalyst was dried in an oven at 110 °C for 24 h. The regenerated catalyst was weighed and used immediately for the subsequent reactions. For the leaching test, the Ti-THC catalyst was placed in contact with methanol at 60 °C for 3 h. The methanol was then recovered by filtration and used for transesterification of WFO under optimum reaction conditions. Also, a control experiment in the absence of catalyst was conducted with pure methanol and oil under the same reaction conditions.

3 Results and discussion

3.1 Catalyst characterization

3.1.1 TGA/DTA analysis of titania-termite hill composite

Figure 1 shows the plot of TGA/DTA analysis of the titania modified termite hill catalyst before calcination. As shown in the figure, the first weight loss of the studied sample occurs at a temperature of 100 °C, which can be ascribed to the loss of moisture content present on the sample. Also, further weight loss is noticed between 200 and 400 °C, which corresponds to the decomposition of organic matters. However, the mass loss above 400 °C has been attributed to the decomposition of inorganic matters such as minerals present in the clay material (Favero et al. 2016). This observation indicates that calcination of the pre-calcined Ti-THC sample at a temperature above 400 °C will improve the activity of the sample. This phenomenon agrees with the TGA data reported for other clay-like materials (Bel Hadjltaief et al. 2014; Madikizela et al. 2017). Hence, it can be presumed that titania will be formed at a calcination temperature of 500 °C.

3.1.2 Textural properties and basicity analyses

Figure 2 shows the N₂ adsorption-desorption isotherms of TH and Ti-THC samples. The TH isotherm exhibits type III physical adsorption with hysteresis loops of type H3, which represents the formation of multimolecular layers (Sing and Williams 2004). However, the Ti-THC sample gives pattern similar to type IV isotherm, which corresponds to mesoporous adsorbents with a characteristic feature of the hysteresis loop and is associated with capillary condensation occurring in mesopores. Table 2 presents the specific surface areas and the pore size distributions of the raw termite hill and the modified termite hill materials. Generally, the textural properties of

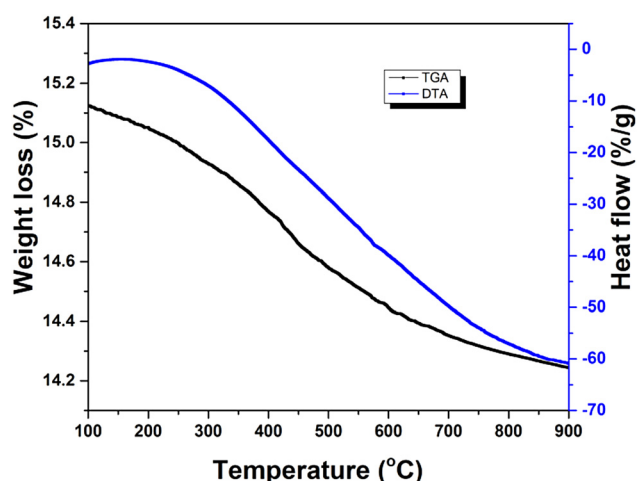


Figure 1: TGA/DTA analysis of pre-calcined titania-termite hill composite at a flow rate of 100 mL/min of N₂ and a heating rate of 15 °C/min from ambient temperature to 900 °C.

the TH sample, which include BET surface area, total pore volume and pore diameter, increase upon impregnation of the titanium. The improvement in these properties indicates that more spaces have been created and more catalytic active sites are present on the catalyst surface. This is corroborated by the SEM results (Figure 3). Furthermore, the significant increase in the surface area suggests that the reaction rate would be favoured as the interaction between the oil and methanol is more rapid in the reaction medium (Tan et al. 2015). The catalytic basic strength that was determined to be $105.3 \pm 0.07 \mu\text{mol/g}$ suggests the presence of basic metal oxides in the as-made catalyst.

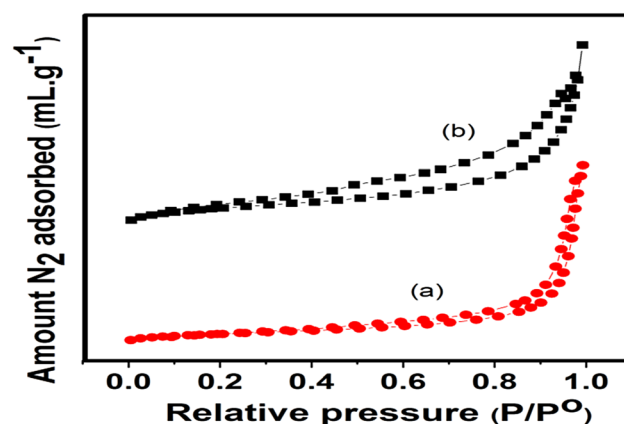


Figure 2: Nitrogen adsorption-desorption isotherm of (a) TH (b) Ti-THC catalyst.

Table 2: Specific surface area, pore size distribution and basicity of raw termite hill and Ti-THC catalyst.

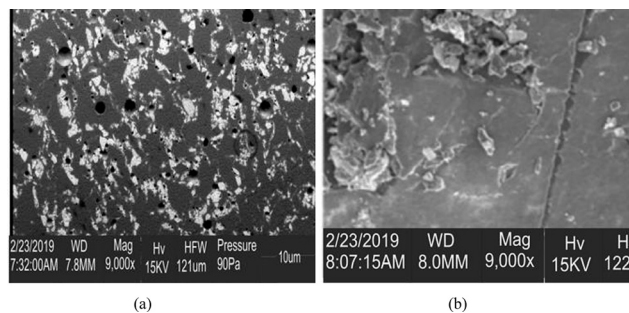
Parameter	Sample	
	TH	Ti-THC catalyst
BET surface area (m ² /g)	13.40	21.10
Total pore volume (cm ³ /g)	0.0582	0.1596
Average pore diameter (nm)	15.789	30.289
Basicity (μmol/g)	–	105.3 ± 0.07

3.1.3 SEM analysis

The surface morphologies of the TH and Ti-THC catalyst were evaluated by SEM analysis and the results are presented in Figure 3. Figure 3a shows the SEM image of TH sample with a magnification of 9000x. From the image, the TH surface is observed to possess an irregular structure and few numbers of non-uniform pores. However, the SEM image of Ti-THC (Figure 3b), which was also captured at a magnification of 9000x, exhibits morphology different from the termite sample. The structure of Ti-THC is seen to be nearly smooth and brighter than termite hill morphology with few pores on its surface. These structural alterations may be due to the impact of the impregnation and calcination processes. A similar observation was also reported by Bel Hadjltaief et al. (2014), in their study on a TiO₂-coated Tunisian clay catalyst.

3.1.4 FTIR analysis

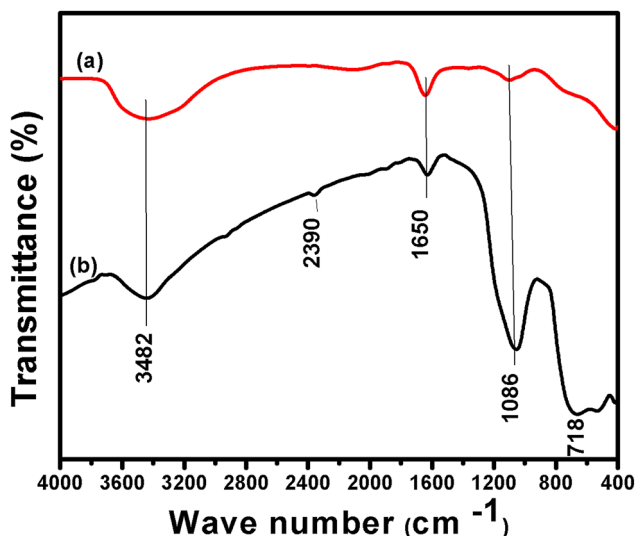
The FTIR spectra of TH and Ti-THC catalyst are presented in Figure 4. The broad absorption band at 3482 cm⁻¹ for both samples can be attributed to the hydroxyl groups (O-H), which confirm the presence of moisture on the samples surfaces. The peak at 2390 cm⁻¹ in the TH and as-synthesized catalyst can be assigned to P-H stretching

**Figure 3:** SEM images of (a) TH; (b) Ti-THC catalyst.

vibration as it is also corroborated by EDX analysis (Figure 6). The sharp peaks at 1650 cm⁻¹ and 1086 cm⁻¹ in both samples are ascribed to Al-OH vibration bands and Si-O-Si deformation bands, respectively (Hassani et al. 2014). However, the new absorption band 718 cm⁻¹ has been noticed in the as-prepared catalyst which corresponds to the out-of-plane vibration bands of Al-O and Si-O (Yusuff et al. 2019; Ritz, Vacula-Kiva, and Plevova. 2011). This result suggests that termite hill is an aluminosilicate material.

3.1.5 XRD analysis

The XRD patterns of the TH and Ti-THC catalyst are presented in Figure 5. The raw termite hill exhibits several diffraction sharp peaks and the presence of a peak at $2\theta = 20.84^\circ$ corresponds to cristobalite. The peaks at $2\theta = 26.56^\circ$, 50.02° , 54.75° and 67.99° are ascribed to quartz structure, while those peaks at $2\theta = 36.56^\circ$ and 59.92° are attributed to tridymite structure (JCPDS No. 46–1045). Another crystalline structure found in the raw anthill sample is kaolinite (8.84° , 17.76° , 45.44° , and 74.92°) as already reported elsewhere (Hassani et al. 2014). However, the XRD diffraction patterns of as-prepared catalyst exhibit the appearance of peaks at $2\theta = 25.28^\circ$, 37.72° , 47.92° , 54.88° , and 62.16° indicating a predominantly anatase phase (JCPDS No. 21–12725) (Bel Hadjltaief et al. 2014; Binitha and Sugunan 2006). The identification of the anatase phase in the Ti-THC sample by XRD measurement indicates the successful dispersion of titania on the termite hill, as also corroborated by the EDX result (Figure 6).

**Figure 4:** FTIR spectra of (a) TH; (b) Ti-THC catalyst.

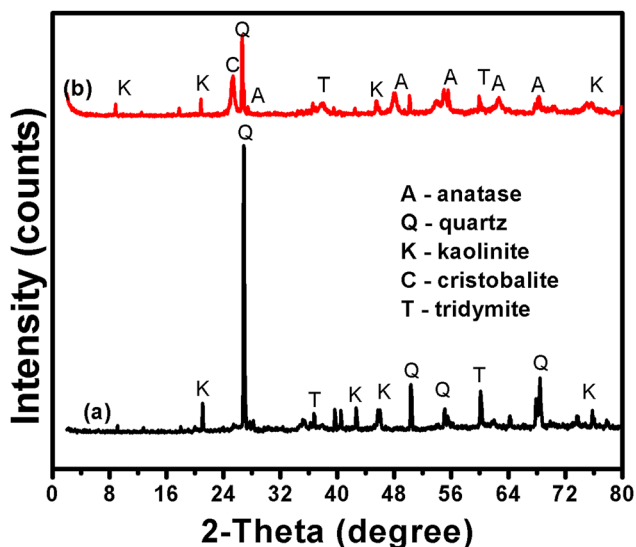


Figure 5: XRD patterns of (a) TH; (b) Ti-THC catalyst.

Furthermore, upon impregnation of titania on termite hill, there is a reappearance of quartz (26.52° and 68.76°) and kaolinite (74.96°) structures indicative of the presence of silicon, aluminum, oxygen, calcium, potassium, sodium, and titanium in the prepared catalyst.

3.1.6 EDX analysis

Figure 6 shows the EDX spectra of the TH and Ti-THC samples. Figure 6a reveals that the termite hill comprises mainly of silicon (Si), aluminium (Al) and calcium (Ca) as similar observations have been reported for natural clay (Madikizela et al. 2017; Mnasri-Ghnimi and Frini-Srasra 2014). The composition of Si increases, whereas the compositions of Al and Ca reduce after the calcination process. Upon impregnation, however, it is observed that titania is successfully inserted into the aluminosilicate layer of the termite hill, as can be seen in Figure 6b.

3.1.7 XRF analysis

The mineralogical compositions of the TH and Ti-THC samples were determined via XRF measurement. Table 3 showed the dominance of silica (SiO_2), alumina (Al_2O_3), calcium oxide (CaO) and iron oxide (Fe_2O_3) in the studied termite hill sample. This observation, as with respect to SiO_2 and Al_2O_3 compositions, agrees with the chemical analysis of clay and is similar to the values obtained by Olutoye et al. (2016) for montmorillonite clay sample. The percentage weights of Al_2O_3 , CaO and Fe_2O_3 decreased after impregnation due to alteration in the composition of the

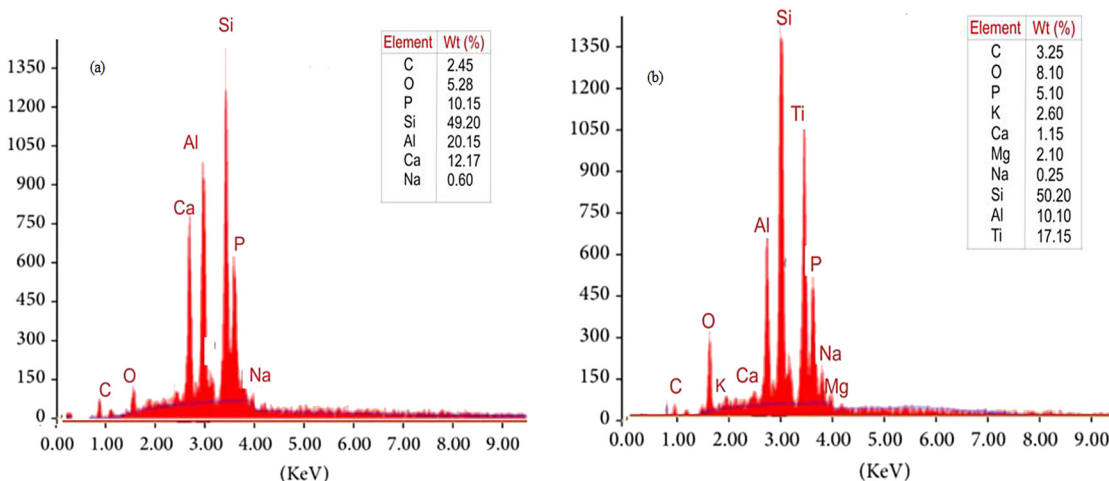


Figure 6: EDX analyses of (a) TH; (b) Ti-THC catalyst.

Table 3: Composition analysis of TH and Ti-THC samples.

Sample	Chemical composition (wt.%)							
	SiO_2	Al_2O_3	CaO	MgO	TiO_2	K_2O	Fe_2O_3	LOI
TH	51.92	21.62	11.43	1.32	2.16	1.31	8.55	1.69
Ti-THC	49.11	13.24	8.71	2.45	16.22	1.93	7.27	1.07

TH. However, the composition of TiO_2 increased upon impregnation, thereby suggesting successful incorporation of titania into termite hill. Based on the XRF result, we presumed that the prepared Ti-THC sample was a dual-site catalyst due to the presence of amphoteric oxides (SiO_2 , TiO_2 and Al_2O_3). The catalyst sample also contains some strong basic oxides (MgO , K_2O and CaO), which provide sufficient adsorption sites for methanol during the transesterification of oil (Refaat 2011).

3.2 Experimental design and statistically analysis

The 4-factor CCD matrix as generated by the design expert software and the experimental results obtained in the transesterification process are depicted in Table 4. The quadratic model (Eq. (2)) was used to correlate the FAME yield and reaction process variables.

$$Y = +54.15 + 2.45T - 9.31t - 3.38C + 20.32M + 6.83Tt - 2.49TC - 5.28TM + 3.47tC - 1.35tM - 1.05CM - 5.51T^2 + 0.52t^2 + 5.08C^2 + 0.76M^2 \quad (2)$$

The FAME yields have been predicted by Eq. (1) and presented in Table 4. The Table reveals that there were good agreements between the predicted and observed values of FAME yield. The correlation between the predicted and experimental results is evaluated by the correlation coefficient (R^2). By comparing the experimental results and the predicted value obtained from the model equation, it was observed that the predicted values agreed with the experimental values of FAME yield with $R^2 = 0.9941$. This indicates that 99.41% of the total variations for the WFO conversion are described by the process variables studied, and this also implies that only 0.59% is not explained by the model. The goodness of the model fit is also measured by the adjusted- R^2 (Adj- R^2). It corrects R^2 -value for the sample size and the number of the model terms based on the degree of freedom. If a model consists of many terms and not a very large sample size, Adj- R^2 may be visibly lesser than R^2 (Giwa, Akpan, and Hameed 2012). In this case, Adj- R^2 value was almost the same as R^2 value (see Table 5).

Furthermore, the model fitness was evaluated by the analysis of variance (ANOVA). Table 5 depicts the ANOVA for the fit of FAME yield from the central composite design. ANOVA is required to evaluate the model's significance and adequacy (Ferreira et al. 2004). The model F-value of 71.64 shows the model is significant. As can be seen in the Table 5, the model comprises of linear, interaction and

quadratic terms. If the model term is significant, P-value should be less than 0.05. In this study, t , C , M , Tt , TC , TM , tC , T^2 and C^2 are significant. More so, the insignificant lack of fit confirms the adequacy of the model fits.

3.2.1 Effect of parameters as response surface

Figure 7(a) shows the interaction effect of reaction temperature and reaction time on FAME yield (%) for catalyst loading of 1.5 wt.% and methanol/WFO ratio of 8:1. As can be seen from Figure 7a, FAME yield decreased with increasing reaction time. This observation may be attributed to the fact that the transesterification reaction is reversible and lower methanol/WFO molar ratio was used; thus, longer reaction duration reduces the FAME yield (Tan et al. 2015). From the same Figure 7a, the FAME yield increases as the reaction temperature increases until it reaches 65 °C, while the temperatures above this value lower the conversion of WFO to biodiesel. This observation indicates that the reaction temperature that exceeds 65 °C will lead to gasification of methanol and reduce the FAME yield as the boiling point of methanol is around 65 °C. Besides, glycerol formed at a temperature above methanol's boiling point is usually viscous because of the esters of intermediate species (mono and diglycerides) likely to dissolve in the glycerol phase, which increases the quantity of glycerol (Bateni et al. 2014; Patil et al. 2019b). Consequently, the FAME yield decreases. Figure 7b shows the response surface plot of FAME yield as a function of catalyst loading and reaction temperature. A slight improvement in FAME yield with increasing catalyst loading has been observed. The reason for this observation is that when the amount of catalyst has increased, the contact between the catalyst and reactants can be improved, which may lead to the favour of FAME yield.

Figure 7c describes the coupled effect of methanol/oil molar ratio and reaction temperature on FAME yield for the reaction time of 3 h and catalyst loading of 1.5 wt.%. The figure shows that the FAME yield sharply increases with an increase in methanol to oil molar ratio. This observation can be ascribed to some reasons. At a higher molar ratio, the contact between oil and methanol is promoted. Besides, the excess alcohol is required to shift the equilibrium for maximum biodiesel yield. The finding is in agreement with some works reported in literature where the higher molar ratio of methanol to oil resulted in higher biodiesel yield (Anwar et al. 2010; Olutoye et al. 2016). However, to study the interaction effect of catalyst loading and reaction time on FAME yield, the transesterification reaction was conducted with catalyst loading varying from 1.0 to 2.0 wt.% and reaction time ranging from 2.0 to 4.0 h

Table 4: Experimental design matrix and expected response.

Run	Transesterification process parameters				FAME yield, Y (%)	
	T (°C)	t (h)	C (wt.%)	M	Predicted	Experimental
1	50(−1)	4(+1)	1 (−1)	10:1 (+1)	59.14	59.22
2	65 (0)	3 (0)	1.5 (0)	11.4:1(+∞)	90.48	90.85
3	65 (0)	3 (0)	1.5(+2)	4.6:1 (−∞)	22.14ii	22.51
4	80(+1)	4(+1)	1 (−1)	6:1 (−1)	42.64	42.72
5	65 (0)	3 (0)	0.7(−∞)	8:1 (0)	74.21	73.76
6	65 (0)	3 (0)	2.3(+∞)	8:1 (0)	62.85	64.04
7	80(+1)	2(−1)	1 (−1)	10:1 (+1)	86.71	86.79
8	50(−1)	2(−1)	2 (+1)	6:1 (−1)	38.43	37.82
9	65 (0)	1.3(−∞)	1.5 (0)	8:1 (0)	71.28	71.65
10	80(+1)	4 (+1)	2 (+1)	6:1 (−1)	39.96	39.35
11	90.2(+∞)	3 (0)	1.5 (0)	8:1 (0)	42.67	43.04
12	50 (−1)	2 (−1)	1 (−1)	6:1 (−1)	45.05	45.13
13	39.8(−∞)	3 (0)	1.5 (0)	8:1 (0)	34.43	34.80
14	50 (−1)	4 (+1)	2 (+1)	10:1 (+1)	62.20	61.59
15	80 (+1)	2 (−1)	2 (+1)	10:1 (+1)	65.94	65.33
16	65 (0)	4.7(+∞)	1.5 (0)	8:1 (0)	39.98	40.35
17	65 (0)	3 (0)	1.5 (0)	8:1 (0)	54.15	56.04
18	65 (0)	3 (0)	1.5 (0)	8:1 (0)	54.15	50.09
19	65 (0)	3 (0)	1.5 (0)	8:1 (0)	54.15	57.02
20	65 (0)	3 (0)	1.5 (0)	8:1 (0)	54.15	52.61
21	65 (0)	3 (0)	1.5 (0)	8:1 (0)	54.15	54.11

Note: actual value (coded value); (0) = center point; ($\pm\infty$) = distance of the axial point from center; (−1) = low level; (+1) = high level; T, temperature; t, time; C, catalyst loading; M, methanol/oil ratio.

Table 5: Analysis of variance for response surface quadratic model.

Source	Sum of squares	Degree of freedom	Mean square	F-value	P-value	Remark
Model	5783.60	14	413.11	71.64	<0.0001	S
T	33.95	1	33.95	5.59	0.0514	NS
t	489.85	1	489.85	84.94	<0.0001	S
C	155.73	1	155.73	27.00	0.0020	S
M	2335.18	1	2335.18	404.94	<0.0001	S
Tt	154.53	1	154.53	26.80	0.0021	S
TC	49.45	1	49.45	8.58	0.0263	S
TM	92.44	1	92.44	16.03	0.0071	S
tC	96.40	1	96.40	16.72	0.0064	S
tM	6.07	1	6.07	1.05	0.3443	NS
CM	8.84	1	8.84	1.53	0.2619	NS
T ²	454.50	1	454.50	78.81	0.0001	S
t ²	4.10	1	4.10	0.71	0.4314	NS
C ²	386.37	1	386.37	67.00	0.0002	S
M ²	8.73	1	8.73	1.51	0.2646	NS
Residual	34.60	6	5.77	—	—	
Lack of fit	4.09	2	2.04	—	0.7776	NS
R ² =0.9941; Adj-R ² =0.9802						

*S, Significance; NS, non-significance.

(Figure 7d). The figure shows that the FAME yield decreased with increasing catalyst loading and reaction time. The reason for this observation is thought to be the

fact that methanol/oil molar ratio determines the extent of reaction (Yin et al. 2012). The authors reported that a higher molar ratio of alcohol to oil, shorter time are required by

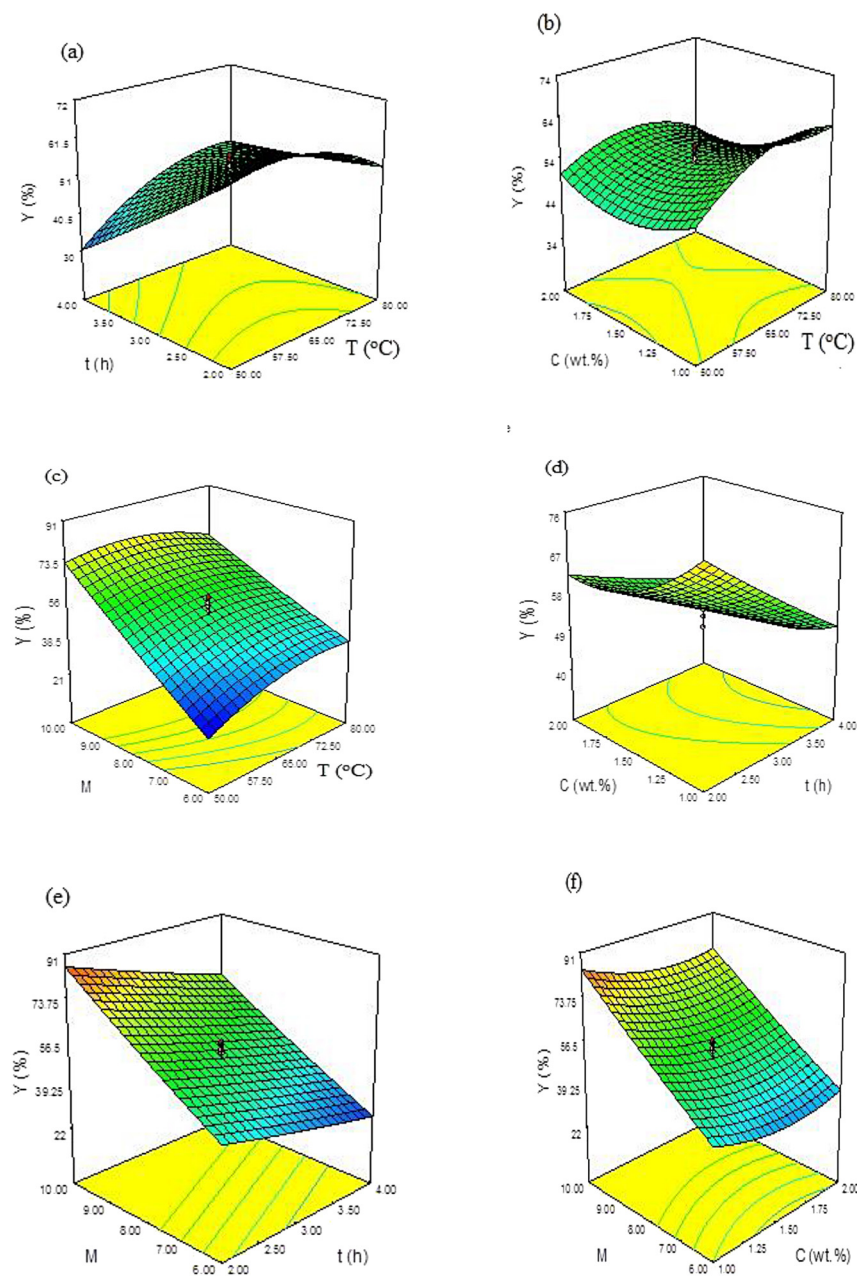


Figure 7: The response surface plots of FAME yield, Y (%) as the function of (a) reaction temperature, T ($^{\circ}\text{C}$) and reaction time, t (h); (b) reaction temperature, T ($^{\circ}\text{C}$) and catalyst loading, C (wt.%); (c) reaction temperature, T ($^{\circ}\text{C}$) and methanol/oil molar ratio, M ; (d) reaction time, t (h) and catalyst loading, C (wt.%); (e) reaction time, t (h) and methanol/oil molar ratio, M ; and (f) catalyst loading, C (wt.%) and methanol/oil molar ratio, M .

transesterification reaction to attain the equilibrium. In this case, however, methanol/oil molar ratio of 8:1 was used, which could be assumed to be lowered. In addition to this, at higher catalyst loading, the FAME yield decreased probably due to the interaction between the remaining FFA in the oil used and catalyst, which results in side reaction (Tan et al. 2015). Furthermore, the statement reported by Yin et al. (2012) that oil conversion to biodiesel largely depends on the methanol/oil molar ratio is corroborated by both Figure 7e and Figure 7f. The figures follow the same trend of increase in methanol/oil molar ratio, which enhances the FAME yield.

3.3 Process optimization

Numerical optimization of transesterification process variables was evaluated using the Design Expert software version 7.0.0 (STAT-EASE Inc., Minneapolis, USA). The desired goal in terms of FAME yield was defined as “maximization” to achieve the best reaction conditions by considering the constraints presented in Table 6. The optimum values of the process parameters for the maximum FAME yield were 71.16 $^{\circ}\text{C}$, 2.12 h, 1.03 wt.% and 9.96:1 for reaction temperature, reaction time, catalyst loading and methanol/oil molar ratio, respectively. The predicted

Table 6: Optimization objective and constraints.

Constraints	Goal	Lower limit	Upper limit
Reaction temperature	In range	50	80
Reaction time	In range	2	4
Catalyst loading	In range	1	2
Methanol/oil molar ratio	In range	6	10
FAME yield	Maximize	22.51	90.85

FAME yield at these optimum conditions was suggested to be 92.73%. However, a further experiment was conducted in triplicate to validate the model and the observed FAME yield was found to be 90.78%. The optimum values of the process parameters and the maximum FAME yield are in the range of values predicted by the model equation.

Table 7 presents a comparison of biodiesel yield by various catalysts. Titania/termite hill composite catalyst is found to have a relatively better performance for biodiesel production and this indicates that it could be regarded as a promising material for the transesterification of triglycerides, mostly when compared with other aluminosilicate based catalysts (Ayoub et al. 2016; Yacob et al. 2017). The catalytic activity in the transesterification of WFO for

precursor (TiO_2) and modified catalyst is also presented in Table 7. Under the same reaction conditions, 51.72% and 90.78% biodiesel yield was achieved respectively for TiO_2 and Ti-THC catalyst. The better performance of Ti-THC material can be simply assigned to the extent of synergy that exist among the mixed metal oxides contained in the modified catalyst.

3.4 Catalyst reusability study

The three successive cycles, which were conducted under the optimum experimental conditions, gave the FAME contents of 73.6%, 68.2% and 51.9%, respectively. The observed decline in the FAME yield could be as a result of blockage of pores on the catalyst surface by oil. Moreover, not the same quantity of catalyst used was recovered during the regeneration process, thereby causing a reduction in the number of active sites on the catalyst. Similar observations have been reported on the reusability studies of clay-based catalysts (Yusuff and Adesina 2020; Liu et al. 2013). Nevertheless, the titania/termite hill composite was found to be stable being able to maintain its activity over three cycles and with minimal leaching.

Table 7: Comparison of FAME yield at optimum reaction conditions using different aluminosilicate based catalysts.

Feedstock	Catalyst	Experimental conditions	Biodiesel yield (%)	Catalyst reusability (cycle)	Reference
Waste cooking palm oil	Clay	T = 150 °C; t = 5 h; M = 15:1; C = 3.5 wt.%	96	3	Olutoye and Hameed (2013)
Waste cooking oil	Barium modified montmorillonite K10	T = 150 °C; t = 5 h; M = 12:1; C = 3.5 wt.%	83.38	3	Olutoye et al. (2016)
CASO	Alkaline modified anthill/	T = 64.82 °C; t = 2 h; M = 8:1; C = 3 wt.%	89.33	3	Yusuff (2019)
<i>Jatropha curcas</i> oil	Na-bentonite	T = 90 °C; t = 6 h; M = 6:1; C = 5 wt.%	84.84	–	Agustian et al. (2016)
Castor oil	HCl-clay	T = 67 °C; t = 3 h; M = 18:1; C = 9 wt.%	83.86	4	Yacob et al. (2017)
Waste frying oil	Montmorillonite clay K-30	T = 90 °C; t = 3 h; M = 12:1; C = 3 wt.%	78.4	–	Ayoub et al. (2016)
Soybean oil	Clay/KF	T = 65 °C; t = 1 h; M = 6:1; C = 15 wt.%	99.7	–	Alves et al. (2014)
Cotton seed oil	Ce/kaolin	T = 60 °C; t = 3 h; M = –; C = 15 wt.%	91	4	Liu, Yun, and Gui (2018)
Marula oil	Impregnated perlite	T = 70.4 °C; t = 3.6 h; M = 29.9:1; C = 4.7 wt.%	91.4	–	Modiba, Osifo, and Rutto. (2014)
Waste cooking oil	Metakaolinite	T = 160 °C; t = 4 h; M = 23:1; C = 5 wt.%	95	8	Ramirez-Ortis, Martinez, and Flores (2012)
Waste frying oil	TiO_2	T = 71.16 °C; t = 2.12 h; M = 9.96:1; C = 1.03 wt.%	51.72	–	Current study
Waste frying oil	Ti-THC	T = 71.16 °C; t = 2.12 h; M = 9.96:1; C = 1.03 wt.%	90.78	3	Current study

T, reaction temperature; t, reaction time; M, methanol to oil molar ratio; C, catalyst loading; CASO, *Chrysophyllum albidum* seed oil.

3.5 Physicochemical properties of FAME produced

The physical and chemical properties of FAME produced were determined and obtained as in accordance with the American Society for Testing and Materials and European Union standards values. The values of the FAME's specific gravity, kinematic viscosity at 40 °C, flash point and cloud point were 0.8762, 5.21 mm²/s, 153 °C and +14 °C, respectively.

4 Conclusions

Titania modified termite hill clay catalyst has been successfully synthesized via an incipient wetness impregnation route. Catalyst characterization results revealed uniform dispersion of titania on the clay material and significant improvement in textural properties of the catalyst upon impregnation. Optimization of the catalytic reaction process parameters by the central composite design showed that reaction time, catalyst loading and methanol/WFO molar ratio had significant effects on FAME yield. The highest FAME yield of 90.78% was obtained under the optimum condition of 71.16 °C reaction temperature, 2.12 h reaction time, 1.03 wt.% catalyst loading and 9.96:1 methanol/WFO molar ratio. The results obtained showed that titania modified termite hill catalyst possessed better activity and relatively stable upon successive recycles.

Author contributions: All authors have accepted responsibility for the entire content of this manuscript and approved its submission.

Research funding: None declared

Competing interests: Authors state no conflict of interest.

References

- Agustian, E., M. Ghazali, and S. R. Wuryaningsih. 2016. "Biodiesel Production of Jatropha Curcas Oil by Bentonite as Catalyst." In *Proceeding of International Conference on Sustainable Energy Engineering and Application 35–40 Indonesian*.
- Alves, H. J., A. M. da Rocha, M. R. Monteiro, C. Morretti, M. D. Cabrelon, C. A. Schwengber, and M. C. Milinsk. 2014. "Treatment of Clay with KF: New Solid Catalyst for Biodiesel Production." *Applied Clay Science* 91–92: 98–104.
- Anwar, F., U. Rashid, M. Ashraf, and M. Nadeem. 2010. "Okra Seed Oil for Biodiesel Production." *Applied Energy* 87: 779–85.
- Ayoub, M., S. Ullah, A. Inayat, A. H. Bhat, and S. Hailegiorgis. 2016. "Process Optimization for Biodiesel Production from Waste Frying Oil over Montmorillonite Clay K-30. 4th International Conference on Process Engineering and Advanced Materials." *Procedia Engineering*, 148 742–9.
- Bateni, H., K. Karimu, A. Zamani, and F. Benakashani. 2014. "Castor Plant for Biodiesel, Biogas, and Ethanol Production with a Biorefinery Processing Perspective." *Applied Energy* 136: 14–22.
- Bel Hadjltaief, H., P. Da Costa, P. Beaunier, M. E. Galvez, and M. Benzina. 2014. "Fe-clay Plate as a Heterogeneous Catalyst in Photo-Fenton Oxidation of Phenol as Probe Molecule for Water Treatment." *Applied Clay Science* 91–92: 46–54.
- Betiku, E., A. A. Okeleye, N. B. Ishola, A. S. Osunleke, and T. V. Ojumu. 2019. "Development of a Novel Mesoporous Biocatalyst Derived from Kola Nut Pod Husk for Conversion of Kariya Seed Oil to Methyl Esters: A Case of Synthesis, Modeling and Optimization Studies." *Catalysis Letters* 1–16, <https://doi.org/10.1007/s10562-019-02788-6>.
- Binitha, N. N., and S. Sugunan. 2006. "Preparation, Characterization and Catalytic Activity of Titania Pillared Montmorillonite Clays." *Microporous and Mesoporous Materials* 93: 82–9.
- Bugaje, I. M., and I. A. Mohammed. 2008. *Biodiesel Production Technology*. Zaria: Science and Technology Forum (STF).
- Calgaroto, S., S. Calgaroto, A. A. Mazutti, D. de Oliveira, S. Pergher, and J. V. de Oliveira. 2013. "Production of Biodiesel from Soybean and Jatropha Curca Oils with KSF and Amberlyst 15 Catalysts in the Presence of Co-solvents." *Sustainable Chemical Processes, Chemistry Central* 1: 17.
- Chouhan, A. P. S., and A. K. Sarma. 2011. "Modern Heterogeneous Catalysts for Biodiesel Production: A Comprehensive Review." *Renewable and Sustainable Energy Reviews* 15: 4378–99.
- Demirbas. 2009. "Characterization of Biodiesel Fuels." *Energy Sources* 31: 889–96. Part A.
- Endalew, A. K., Y. Kiros, and R. Zanzi. 2011. "Inorganic Heterogeneous Catalysts for Biodiesel Production from Vegetable Oils: Review." *Biomass and Bioenergy* 35: 3787–809.
- Favero, J., Parisotto-Peterle, J., Angeli, V. W., Brandalise, R. N., Gomes, L. B., Berymann, C. P., Santos, V. (2016). Physical and Chemical Characterization and Method for the Decontamination of Clays for Application in Cosmetics, 124–125, 252–9.
- Ferreira, S. L. C., W. N. L. dos Santos, C. M. Quintella, B. B. Neto, and J. M. Bosque-Sendra. 2004. "Doehlert Matrix: a Chemometric Tool for Analytical Chemistry-Review." *Talanta* 63: 1061–7.
- Giwa, A., U. G. Akpan, and B. H. Hameed. 2012. "Optimization of Photocatalytic Degradation of an Anthraquinone Dye Using Design of Experiment." *Journal of Engineering Research* 17 (3): 20–31.
- Hassani, M., G. D. Najafpour, M. Mohammadi, and M. Rabiee. 2014. "Preparation, Characterization and Application of Zeolite-Based Catalyst for Production of Biodiesel from Waste Cooking Oil." *Journal of Scientific & Industrial Research* 73: 129–33.
- Kiss, A. A., A. C. Dimian, and G. Rothenberg. 2006. "Solid Acid Catalysts for Biodiesel Production – towards Sustainable Energy." *Advanced Synthesis and Catalysis* 348 (1–2): 75–81.
- Liu, J., Z. Yun, and X. Gui. 2018. "Ce/kaolin Clay as an Active Catalyst for Fatty Acid Methyl Esters Production from Cotton Seed Oil in a New Integrated Apparatus." *Brazilian Journal of Chemical Engineering* 35 (1): 1–12.
- Madikizela, L. M., N. Nkwentsha, N. Y. Mhenguza, and P. Mdhili. 2017. "Physicochemical Characterization and In Vitro Evaluation of the Sun Protection Factor of Cosmetic Products Made from Natural Clay." *South African Journal of Chemistry* 70: 113–19.

- Mnasri-Ghnnimi, S., and N. Frini-Srasra. 2014. "Promoting Effect of Cerium on the Characteristic and Catalytic Activity of Al, Zr, and Al-Zr Pillared Clay." *Applied Clay Science* 88–89: 214–20.
- Modiba, E., P. Osifo, and H. Rutto. 2014. "The Use of Impregnated Perlite as a Heterogeneous Catalyst for Biodiesel Production from Marula Oil." *Chemical Papers* 68 (10): 1341–9.
- Olutoye, M. A., S. W. Wong, L. H. Chin, M. Asif, and B. H. Hameed. 2016. "Synthesis of Fatty Acid Methyl Esters via Transesterification of Waste Cooking Oil by Methanol with a Barium-Modified Montmorillonite K10 Catalyst." *Renewable Energy* 86: 392–8.
- Olutoye, M. A., and B. H. Hameed. 2013. "A Highly Active Clay-Based Catalyst for the Synthesis of Fatty Acid Methyl Ester from Waste Cooking Palm Oil." *Applied Catalysis A: General* 450: 57–62.
- Patil, A. D., S. S. Baral, P. B. Dhanke, C. S. Madankar, U. S. Patil, and V. S. Kore. 2018. "Materials Science for Energy Technologies Parametric Studies of Methyl Esters Synthesis from Thumba Seed Oil Using Heterogeneous Catalyst under Conventional Stirring and Ultrasonic Cavitation." *Materials Science for Energy Technologies* 1 (2): 106–16.
- Patil, A., S. S. Baral, P. Dhanke, and V. Kore. 2019a. "Biodiesel Production Using Prepared Novel Surface Functionalised TiO₂ Nano-Catalyst in Hydrodynamic Cavitation Reactor." *Materials Today: Proceedings* 27: 198–203.
- Patil, A., P. Dhanke, V. Kore, and N. Kanse. 2019b. "Thumba Methyl Ester Production Using Prepared Novel TiO₂ Nano-Catalyst in Ultrasonic Cavitation Reactor." *Materials Today: Proceedings* 18: 4322–9.
- Ramirez-Ortis, J., M. Martinez, and H. Flores. 2012. "Metakaolinite as a Catalyst for Biodiesel Production from Waste Cooking Oil." *Frontiers of Chemical Science and Engineering* 6 (4): 403–9.
- Refaat, A. A. 2011. "Biodiesel Production Using Solid Metal Oxide Catalyst." *International Journal of Environmental Science and Technology* 8 (1): 203–21.
- Ritz, M., L. Vacula-Kiva, and E. Plevova. 2011. "Application of Infrared Spectroscopy and Chemometric Methods to Identification of Selected Materials." *Acta Geodynamica et Geomaterialia* 8: 47–58.
- Sing, K. S. W., and R. T. Williams. 2004. "The Use of Molecular Probes for the Characterization of Nanoporous Adsorbents." *Particle System and Characterization* 21: 71–9.
- Tan, Y. H., M. O. Abdullah, C. N. Hipolito, and Y. H. Taufiq-Yap. 2015. "Waste Ostrich and Chicken-Eggshells as Heterogeneous Base Catalyst for Biodiesel Production from Used Cooking Oil: Catalyst Characterization and Biodiesel Yield Performance." *Applied Energy* 2: 1–13.
- Taufiq-Yap, Y. H., N. F. Abdullah, and M. Basri. 2011. "Biodiesel Production via Transesterification of Palm Oil Using NaOH/Al₂O₃ Catalysts." *Sains Malaysiana* 40 (6): 587–94.
- Yacob, A., A. M. S. Mohmedahmed, M. Azam bin, and M. Zaki. 2017. "Acid Modified Jourdiqia Clay for Methanolysis of castor Oil." *Journal of Pharmacovigilance* 5 (5): 1000240.
- Yin, X. L., H. Ma, Q. H. You, Z. B. Wang, and J. K. Chang. 2012. "Comparison of Four Different Enhancing Methods for Preparing Biodiesel through Transesterification of Sunflower Oil." *Applied Energy* 91: 320–5.
- 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: 24–32.
- Yusuff, A. S., O. D. Adeniyi, O. S. Azeez, M. A. Olutoye, and U. G. Akpan. 2019. "Synthesis and Characterization of Anthill-Eggshell-Ni-Co Mixed Oxides Composite Catalyst for Biodiesel Production from Waste Frying Oil." *Biofuel, Bioproducts & Biorefining* 13: 37–47.
- Yusuff, A. S., O. D. Adeniyi, M. A. Olutoye, and U. G. Akpan. 2018. "Development and Characterization of a Composite Anthill-Chicken Eggshell Catalyst for Biodiesel Production from Waste Frying Oil." *International Journal of Technology* 10 (1): 110–19.
- Yusuff, A. S., and O. A. Adesina. 2020. "Biodiesel Synthesis from Palm Olein Oil Using Anthill as Catalyst." *Journal of Chemical Technology and Metallurgy* 52 (2): 300–6.
- Yusuff, A. S., and K. A. Bello. 2019. "Synthesis of Fatty Acid Methyl Ester via Transesterification of Waste Frying Oil by a Zinc-Modified Pumice Catalyst: Taguchi Approach to Parametric Optimization." *Reaction Kinetics, Mechanisms and Catalysis* 128 (2): 739–61.
- Yusuff, A. S., and J. O. Owolabi. 2019. "Synthesis and Characterization of Alumina Supported Coconut Chaff Catalyst for Biodiesel Production from Waste Frying Oil." *South African Journal of Chemical Engineering* 30: 42–9.
- Yusuff, A. S., and L. T. Popoola. 2019. "Optimization of Biodiesel Production from Waste Frying Oil over Alumina Supported Chicken Eggshell Catalyst Using Experimental Design Tool." *Acta Polytechnica* 59 (1): 88–97.