The potential of composite anthill–waste chicken eggshell as heterogeneous catalyst in biodiesel production

Article *in* Petroleum and Coal · January 2018

Adeyinka S Yusuff
Afe Babalola University

Olalekan David Adeniyi
Federal University of Technology Minna

Moses Olutoye
Federal University of Technology Minna

U.G. Akpan
Federal University of Technology Minna

Petroleum and Coal

Review **Open Access**

THE POTENTIAL OF COMPOSITE ANTHILL-WASTE CHICKEN EGGSHELL AS HETEROGENEOUS CATALYST IN BIODIESEL PRODUCTION

Adeyinka Sikiru Yusuff[1, 2], Olalekan David Adeniyi[2], Sarafa Oluwatosin Azeez[2], Moses Aderemi Olutoye[2] and Uduak George Akpan[2]

[1] Department of Chemical and Petroleum Engineering, Afe Babalola University, Ado-Ekiti, Nigeria
[2] Department of Chemical Engineering, School of Engineering and Engineering Technology, Federal University of Technology, Minna, Nigeria

Received November 22, 2017; Accepted December 23, 2017

Abstract

Biodiesel is an alternative fuel which provides a solution to two main problems associated with petroleum-based diesel. These problems include fossil fuel depletion and environmental degradation. It is commonly produced via transesterification reaction of vegetable oil or animal fat with alcohol in the presence of a catalyst. This catalyst required is either homogeneous or enzyme or heterogeneous. However, amongst these catalysts, heterogeneous catalyst is regarded as most suitable one for the biodiesel production because it discourages the generation of wastewater and also allows catalyst recovery after the reaction process. This present study provides a comprehensive review of different heterogeneous catalysts which have been explored in the past by different researchers in biodiesel production with emphasis on the potential use of mixed anthill clay-eggshell catalyst for biodiesel synthesis. Attention is focused on likely transformation of raw mixed anthill-eggshell sample to highly active metal oxides structure and how to create an environment friendly way of reusing waste eggshells and converting anthill which harbors dangerous animals into worth items. Following this, the mechanism of active phase (CaO) contained in this composite catalyst, the prepa-ration method and characterization techniques for accurate estimation of the physicochemical proper-ties of the solid catalyst are described.

Keywords: *Anthill; eggshell; biodiesel; characterization; preparation*.

1. Introduction

The use of solidly based catalysts in the field of renewable energy to produce renewable fuel has become a significant area of research. This is due to environmental concerns resulting from continual dependence on fossil fuel sources, current industrial energy demands, and upswing in the world population. To this end, current research is focusing on fuel derivable from renewable sources using heterogeneous catalyst and its utilization in the transportation industries and other industrial processes. Development of heterogeneous catalyst from waste and naturally occurring materials doped with metals for hydrocarbon (triglycerides) reactions are a particular area of interest that require more attention of researchers.

The global realization of the finite nature of fossil hydrocarbon and the deleterious effect arising from its consumption has triggered a worldwide search for alternative fuels. The utilization of diesel fuel from petroleum source continues to rise due to increase in population, energy consumption and rapid industrialization [1]. These have triggered a worldwide search for alternative fuels which include biodiesel, bio-alcohol, biogases and other biomass sources. Among the aforementioned renewable fuels, biodiesel has received considerable attention mainly because it provides a solution to problems associated with fossil fuel which include its depletion and environmental degradation [2]. Besides, it could be obtained from biomass [3]. Generally, biodiesel is prepared from vegetable oils and animal fat. However, it can be synthesized from waste oil with same features and ability in minimizing gas emission from the engine without compromising quality [4].

Biodiesel is an alternative and biogenic fuel which comprises of different esters of fatty acid and has been accepted worldwide because of the problems associated with the petroleum derived fuel [5]. Biodiesel can be produced from any fat or oil through transesterification. A transesterification is a form of catalytic reaction whereby triglyceride contained in a vegetable oil or animal fat reacts with primary alcohol commonly methanol to produce esters and glycerol. In biodiesel production, oils and fats are transesterified with methanol in the presence of catalyst [6], to produce fatty acid methyl esters (FAME) and glycerol as a byproduct [7-8]. However, homogeneous catalyzed transesterification process has some disadvantages which include the formation of the unwanted product, corrosion problems, generation of wastewater, and difficult to recycle [3]. Enzymes are also employed in the production of biodiesel.

Enzymes are naturally occurring materials with impressive performance and resistant to compositional changes in a reaction medium. They can enhance biodiesel production via esterification or transesterification process [5]. Enzymatic-catalyzed reaction is carried out at mild and favourable conditions, so as not to denature the enzyme. Enzymatic transesterification has the advantage to provide high yields, but cannot be employed industrially as a result of the exorbitant cost of the enzyme. Another problem is that of deactivation usually caused by impurities contained in reaction feed. Therefore, heterogeneous catalysts are very important for biodiesel production as they possess many advantages over homogeneous catalysts and enzymes [5]. They are noncorrosive, environmentally benign and do not form soaps through free fatty acid neutralization or saponification of triglyceride. Besides, product purity and regeneration of the catalyst are achievable in heterogeneous catalysis [9-10].

Although there is an increasing interest in deriving solid catalysts from naturally occurring and waste materials, locally sourced anthill has not been explored as a catalyst to transesterify vegetable oil to fatty acid methyl esters. This also includes its modification by any of the metal oxides. Moreover, previous research has not provided detailed work on the catalytic performance of two or more of these materials in a combined (composite) form to synthesis fatty acid methyl esters. This present study, therefore, considers the possible development of composite heterogeneous catalyst from anthill and eggshell. Following this, the preparation methods and characterization techniques for accurate estimation of the physicochemical properties of the heterogeneous catalyst are described. Moreover, a possible way of improving the activity of the composite anthill-eggshell with the promoter is described.

2. Heterogeneous catalysis and its fundamental

Heterogeneous catalysis describes the process in which reactant(s) and required catalyst are differed in phase, however, in a heterogeneously catalyzed alcoholysis reaction, in which three-phase system exists, the catalyst is usually solid in nature while oil and alcohol act as reactants. The oil and alcohol are two immiscible liquid phases. Heterogeneous catalysis is of very importance in the field of renewable fuel [11-12]. Heterogeneous catalysts used for biodiesel production are either solid base or acid catalysts. The former is mostly used for biodiesel synthesis because of its better performance and faster rate of reaction as compared to the latter [13]. Meanwhile, the heterogeneous acid catalyst is usually employed, when the feedstock is highly rich in free fatty acid and moisture [14].

Heterogeneous acid catalyst, however, requires elevated reaction time and alcohol to oil molar ratio to enhance the product yield and rate of reaction [13,15]. Nevertheless, heterogeneous catalyzed transesterification process is known for mass transfer (diffusion) limitation, because two different phases (liquid and solid) are involved, and this reduces the reaction rate [12,16]. Hillion *et al.* [15] had identified a way of overcoming diffusion limitation in heterogeneous catalysis. The authors suggested the use of catalytic materials which include promoter and support. These materials provide large specific surface area and pores for active components of the catalyst, thus enhancing methanol adsorption onto active sites. Aluminum oxide (alumina) had been recognized as the suitable promoter for the transesterification reaction without catalyst loss. It has also been widely employed as catalyst support due to its thermal stability [17].

Taufiq-Yap *et al.* [18] investigated the transesterification of palm oil with methanol over $NaOH/Al_2O_3$ catalyst. The catalyst preparation was optimized, and 99% conversion of palm oil to fatty acid methyl esters was achieved under the favourable reaction conditions. More so, Hak-Joo *et al.* [19] investigated the performance of different alumina supported catalysts ($Na/\gamma\text{-}Al_2O_3$, $NaOH/\gamma\text{-}Al_2O_3$, and $Na/NaOH/\gamma\text{-}Al_2O_3$) in the conversion of soybean oil to biodiesel. However, amongst the alumina supported catalysts, $Na/NaOH/\gamma\text{-}Al_2O_3$ showed good catalytic activity by providing highest biodiesel yield under optimum reaction conditions. Furthermore, Arzamendi *et al.* [20] compared the activity of raw and calcined $NaOH/\gamma\text{-}Al_2O_3$ in the transesterification of sunflower oil to biodiesel. However, under the same optimum conditions, raw catalyst achieved nearly 100% conversion, while calcined catalyst provided 86% biodiesel yield. From the aforementioned studies, the results obtained indicate that alumina supported heterogeneous catalysts have good catalytic activity and could be employed for the industrial production of biodiesel.

Many types of heterogeneous catalysts for biodiesel production have been reported ranging from the use of strong acid catalysts to strong base catalysts [21]. Findings have proven that rare earth metals are the most suitable heterogeneous catalyst in biodiesel production [22], but unfortunately, these catalysts are expensive, and their preparation is quite complex [23]. Therefore, to make biodiesel production sustainable, the use of low cost solid heterogeneous catalysts from waste and naturally occurring materials is suggested [24]. These are being investigated to replace the homogeneous catalysts and enzymes, and this research constitutes part of that investigation. These low-cost materials include chicken eggshell [25], Ostrich eggshell [26], Quail eggshell [27], *Pomacea sp*. shell [28], waste animal bone [29], solid waste coral fragment [30], alum [31], montmorillonite clay [32], modified- peanut husk ash [33] and many more. Most of these materials are cheap sources of calcium oxide (CaO) and other alkaline earth metal oxides and reduce the biodiesel production cost [7]. However, anthill which is siliceous fire clay has not been explored as a catalyst for the production of biodiesel. Research has revealed that anthill contains a higher percentage of silica (SiO_2), alumina (Al_2O_2) and iron oxide (Fe_2O_3) [34]. These metal oxides in anthill have high tendency to interact with CaO in eggshell after activation and form a new phase of more active mixed oxides with close interaction.

3. Anthill

Anthill is naturally occurring clay which can serve as a potential starting material for a catalyst in transesterification reaction process. According to Akinwekomi *et al*. [34], anthill sample contains several metal oxides in which some of them in their pure forms have been used as catalysts for biodiesel synthesis. An anthill is a form of siliceous or fire clay which is formed at the entrances of the subterranean dwelling of ant colonies [35]. An ant colony is an underground chamber where ants live and are being built and maintained by worker ants. According to Paton *et al*. [36], an anthill is classified into two categories, namely, type I and type II anthills. Type I nest is less noticeable in the ant territory because it is small in size and shape as shown in Figure 1. However, they are characterized by waste deposition and are easily influenced by erosion [37-38]. By comparison, type II mound as shown in Figure 2, is huge, often sticks together, sometimes surrounded by vegetation and persists for many years [35].

Research has proven that anthill sample has large silica content, follow by alumina and it was also found that chemical compositions of those components contained in anthill samples from different locations vary. The chemical compositions of two different anthills from two different locations in West Africa are presented in Table 1.

Anthill materials are important constituents of the landscape not only because they are readily available, but because of their industrial usefulness. For example, it has been used to make ceramic [35], cement, bricks and sand casting [39], refractories [34] and furnace [35]. More so, due to the presence of silica (SiO_2), alumina (Al_2O_3), iron oxide (Fe_2O_3) and calcium oxide (CaO), anthill has potential ability to be employed as industrial heterogeneous catalyst.

Besides, it is readily available and environmentally benign. However, the potential application of anthill as a catalyst for biodiesel production is attributed to the presence of CaO, Al_2O_3, and SiO_2 which can serve as an active ingredient, promoter and support, respectively.

Table 1. Compositional analysis of anthill from two different locations [34-35]

Constituent	Chemical composition (%)	
	Biadan Ghana Anthill	Akure Nigeria Anthill
SiO_2	68.70	58.83
Al_2O_3	18.43	22.69
Fe_2O_3	2.36	2.42
MgO	0.44	0.84
CaO	0.41	0.01
Na_2O	0.20	0.06
K_2O	1.60	2.10
TiO_2	1.30	0.72
Others	5.56	12.33

Figure 1. Type I Anthill Situated in Front of Owolabi Hall at Afe Babalola University, Ado-Ekiti, Nigeria

Figure 2. Type II Anthill Located at Afe Babalola University, Ado Ekiti, Nigeria on an Elevation of 1165 ft. above sea level, having latitude (N7°36. 409) and longitude (E005°18.627)

4. Chicken eggshell

Chicken eggshells are parts of waste materials from hatcheries, poultry industries, homes, and eateries, which can be easily collected in large amount. Chicken eggs are consumable product worldwide because it is rich in amino acids, vitamin, and minerals [25]. In the past, egg consumption in Nigeria was primarily concentrated in the major urban areas. This is because people from urban areas are better informed about the nutritional value and the protein supply of eggs [40]. In addition, they earn a higher income than the average rural dwellers.

Nowadays, series of awareness on the importance of egg consumption being created by Poultry Association of Nigeria (PAN) and Nutrition Society of Nigeria has made everyone knows the nutritional value of eggs. However, waste chicken eggshells constitute a solid waste disposal problem. Dry chicken eggshell contains nearly 94% of calcium carbonate ($CaCO_3$) by mass, while remaining components are magnesium carbonate ($MgCO_3$), calcium phosphate ($CaPO_4$) and organic matter [41]. Roughly 40% of the poultry wastes are chicken eggshells which are generated as a result of broken eggs and incubation. However, the majority of these waste eggshells are disposed of without further and proper processing by taking to landfill at an exorbitant rate depending on where the landfill site is located [42]. Meanwhile, waste management by landfill method attracts rodents or vermin which in turn spread diseases. Therefore, it is necessary to find a way of converting the waste chicken eggshells into some valueble products [42], as it would help in overcoming the high cost of waste management and environmental concerns.

Several techniques are now being adopted to transform the waste chicken eggshells into valuable items; giving financial benefits to competitive egg processing industries [42]. The various applications in which chicken eggshell could be used include adsorbent for contaminant removal from wastewater [41], stabilizing material for soil properties improvement [43], ink-jet printing paper [44], as a catalyst for lactulosec production from lactose [45], as an excipient for acetaminophen tablet production [42].

Waste bird eggshells have the great unrealized ability as solid heterogeneous catalysts for the synthesis of biodiesel [26]. Calcium trioxocarbonate (IV) constitutes the larger percentage in eggshells and when it is subjected to a thermal treatment; it decomposes into calcium oxide and carbon dioxide. The chemical composition of the thermally treated waste eggshell is shown in Table 2. However, research had proven that calcium oxide (CaO) based catalyst is most widely used catalytic material for the synthesis of fatty acid methyl esters [46-47]. This is attributed to the fact that it is cheap, readily available, low toxicity, slightly soluble in methanol, has the high basic strength and minimum environmental impact. Chicken eggshells as a source of CaO, in particular, had been widely reported in the literature. Meanwhile, CaO based catalysts do leach into the reaction media if they are not anchored by supporting particles [24]. This statement was corroborated by Umdu *et al*. [48], who found that supported CaO showed far more activity and stability than unsupported CaO. Therefore, the authors suggested the use of silica or alumina as a supporting particle, as the basic site density and basic strength which are the factors driving the catalytic activity, get improved [48]. In this present study, however, a possible way of synthesizing supported CaO base catalyst is proposed.

Table 2. Percentage composition of calcined waste eggshell at 900°C (wt %) [49]

Constituent	CaO	MgO	P_2O_5	SO_3	K_2O	SrO	Cl	Fe_2O_3	CuO	Total
Composition	97.42	1.63	0.52	0.26	0.08	0.05	0.02	0.01	0.01	100

5. Composite anthill-eggshell as a supported catalyst

Composite heterogeneous catalyst derived from an anthill and chicken eggshell can be regarded as a supported catalyst. This is because anthill is made up of several metal oxides (Table 1) in which some of these oxides have been used as supports for the solid catalysts [10], besides there is little amount of K, Ca, Mg and Na oxides contained in anthill which have been regarded as super basicity and active species of supported catalysts for biodiesel production [16]. According to Sun *et al*. [50], apart from the specific surface area and pore volume of the catalyst, surface basicity remains the main determinant of catalyst activity. This indicates that anthills could serve as no cost source of super basicity and their supports; same could be said of the waste eggshells. Waste eggshells of chicken were found to be 94% calcium carbonate, 1% magnesium carbonate, 1% calcium phosphate ($Ca_3(PO_4)_2$) and 4% organic matter [51]. It is, therefore, possible to synthesis from eggshell an active phase of composite anthill-eggshell catalyst due to the high $CaCO_3$ composition, the intrinsic pore structure, and its availability in large amount. The successful experiments on the use of waste bird eggshells as cheap sources of CaO for use as low cost solid based catalysts has been reported [25, 46-47, 52-53].

However, when anthill is properly mixed with eggshell in best proportion and well prepared under favourable conditions, the composition of CaO would increase. The presence of the compounds which serve as an active ingredient, support, and promoter for the catalyst justifies the usage of mixed anthill-eggshell for biodiesel production, besides CaO and Al_2O_3 serve as basic and acidic components which make the catalyst to act like dual sites type. Furthermore, a sample containing CaO supported on high surface area materials is regarded as a most active catalyst, besides it minimizes problems of lixiviation. In contrast, non-supported CaO suffers from this disadvantage [54].

6. Preparation of composite anthill-eggshell catalyst

Its preparation is aimed to attach the active phase present in eggshell onto the support particles contained in anthill powder. Several catalyst preparation techniques such as impregnation, sol-gel, precipitation, just to mention but a few, had been described in the literature [55]. Some of these techniques have their own advantages and disadvantages [56]. In preparing supported catalysts, impregnation or precipitation technique is usually employed [57-58]. According to Rojas [58], impregnation is related to ion-exchange or adsorption process, and the interaction with support is prevalent. This method had been widely employed by a lot of researchers to prepare supported heterogeneous catalysts for biodiesel production. Lithium (Li) was impregnated on CaO to catalyze transesterification of high FFA content oil, and its activity was not significantly altered by the vegetable oil containing more than 3 wt. % FFA [59]. More so, Sirichai *et al*. [60] impregnated ZnO with an aqueous solution of $Ca(NO_3)_2.4H_2O$. After pretreatment and calcination steps, CaO-ZnO was liberated and used for transesterification process. Impregnation technique is a simple and commonly used procedure for dispersing active phase over the desired support. Furthermore, it allows rapid deposition of high metal loading [56]. Its disadvantage is that it does not allow uniform deposition of active phase along the pores of the support [61].

Precipitation technique involves the use of the precipitating agent in order to obtain a solid material in a porous form. Sirichai *et al.* [60] made use of Na_2CO_3 as a precipitant to prepare CaO-ZnO catalyst using co-precipitation method and used it to speed up the rate of transesterification reaction between palm oil and methanol. Ammonia solution had also been used as a precipitant for the preparation of CaO-ZrO_2 catalyst using co-precipitation technique [62]. Furthermore, a mixture of Na_2CO_3 and NaOH was used as precipitants to prepare nanometer magnetic solid base catalysts by dispersing CaO on Fe_3O_4 [63]. Meanwhile, the use of single precipitant to precipitate metal ion in solution is not as effective as multi precipitants [64]. The authors proposed triple precipitants that are ammonia solution, carbon dioxide, and ethanol which are base precipitant, acid precipitant, and neutral precipitant respectively. This novel method was applied by same authors to prepare CaO–La_2O_3 and compare with those prepared by impregnation, physical mixing and co-precipitation techniques. The authors observed that there were synergies among the precipitants which provided a better specific BET surface area and a high catalytic activity during biodiesel production.

Based on a preliminary experiment carried out and available literature [60, 65-66], the impregnation by incipient wetness condition was found to be the appropriate and best technique to prepare mixed anthill-eggshell catalyst. This is because it is simple and can also be employed to prepare catalyst industrially the same way it is prepared in the laboratory [56]. More so, apart from being a good and precise method, it is the only method that can be applied to high porous silica where the other methods fail [61]. In preparing mixed anthill-eggshell catalyst by incipient wetness impregnation method, the anthill and eggshell powders have to be mixed in best proportion in such a way that eggshell would constitute larger percentage because the component that will serve as active phase (CaO) is contained in eggshell while supporting particles are present in an anthill. However, the pretreatment steps which include mixing solution or solid, aging, solid-liquid separation and drying have to be carefully and thoroughly carried out so as to obtain homogenize solid mixture at least [58]. More so, calcination which is the final stage during supported catalyst preparation has to be carried out at a very high temperature. Thermal treatment of dried mixed anthill-eggshell catalyst at high temperature would lead to complete removal of adsorbed gases such as CO_2, SO_2, and moisture and change the components into a new phase of more active mixed metal oxides with close interaction [10]. Therefore, thermogravimetric analysis/differential thermal analysis (TGA/DTA) is recommended to determine the thermal stability of the catalyst and also identify various chemical reactions that occur during the thermal treatment process.

7. Characterization of the heterogeneous catalyst

Generally, characterization of the catalyst is necessary so as to gain insight into its physical and chemical compositions. It also helps in correlating catalyst properties to its performance. Thus, different properties of the as-synthesized catalyst can be determined by the following characterization techniques:

8. Determination of physical properties of the catalyst

Catalytic material usually passes through series of stages during preparation, and each of these stages has an influence on its activity, basic strength, and structural stability. To ascertain the effect of these factors, it is pertinent to deduce the physical properties of the as-synthesized catalyst before subjecting it to activity test. However, these properties are often determined using Brunauer-Emmett-Teller (BET) method. This characterization technique helps in determining the distribution properties of the as-synthesized catalyst which include specific surface area, pore size, and pore volume.

The specific surface area is often evaluated by an automatic micrometric surface area machine based on N_2 adsorption and desorption isotherms at 77 K. It is required that the samples should be degassed in a vacuum and at elevated temperature in order to expose the pores and surface of the catalyst. The specific surface area is then calculated based on BET model and also use Barrett-Joyner-Halenda (BJH) method to obtain the pore size distribution. Many researchers had correlated surface area of heterogeneous catalyst to catalytic activity [26, 67-68].

Olutoye *et al.* [68] prepared four different samples of Bi-ZnO catalyst by co-precipitation method by varying ratio of Bi:Zn from 1:49 to 4:.49. After the determination of textural properties comprising of surface area, total pore volume and average pore diameter, the sample with the ratio 2:49 of bismuth loading on zinc has better textural properties with BET surface area of 30.76 m^2/g, and it was chosen amongst all other catalysts prepared for transesterification process. This indicates that surface area is a function of catalyst activity.

This statement was also corroborated by Lopez *et al*. [69] who compared the catalytic activity of two different superacid catalysts (sulfated zirconia and tungstated zirconia) in methanolysis process. Sulfated zirconia exhibited good performance as a result of higher BET surface area (134 m^2/g) as compared to tungstated zirconia which has BET surface area of 89 m^2/g. It is therefore recommended that the preparation condition of a mixed anthill–eggshell catalyst should be optimized in order to identify the optimum conditions that will provide a catalyst with better textural properties.

Furthermore, Tan *et al.* [26] developed CaO based heterogeneous catalysts from ostrich and chicken eggshells and determined their BET surface areas to be 71.0 m^3/g and 54.6 m^3/g, respectively. The FAME contents provided by ostrich and chicken eggshells catalyst were 96% and 94%, respectively. High biodiesel yield obtained was as a result of large surface area possessed by those two synthesized catalysts. However, the higher biodiesel yield provided by calcined ostrich eggshell catalyst was as a result of more active sites present on its surface which allowed better interaction between the CaO-based material and the methanol in the reaction mixture. This is attributed to better textural properties and strong basicity which are possessed by calcined ostrich eggshell compared to that of calcined chicken eggshell [26].

9. Determination of basicity of the catalyst

It is well known that not all catalyst sites participate in transesterification reaction, those that take part in it are referred to as base sites, and they are usually active centers for transesterification [2]. However, the activity of the solid base catalyst is normally evaluated based on its base strength and basicity. Basicity is defined as the number of exposed basic sites per unit weight of catalyst sample. It is linearly related to catalyst surface area [20].

The basic site of solid base catalyst usually alkaline earth metal oxides is oxygen which behaves as proton acceptor [70]. Sun *et al.* [50] in their work investigated the correlation between activity and surface basicity of La_2O_3/ZrO_2 catalyst and the authors concluded that catalytic activity displayed a linear relationship with the basicity towards FAME synthesis, which indicates that high biodiesel yield could be achieved when the basic strength is stronger. However, the high yield in activity observed for the La_2O_3/ZrO_2 catalyst was due to the presence of ZrO_2 which is amphoteric in nature and makes the catalyst to act like dual site type. Therefore, owing to the presence of supports such as SiO_2 and Al_2O_3 in an anthill, it is expected that mixed anthill-eggshell catalyst would exhibit dual sites (acidic and basic centers) behaviour.

The basicity of solid catalyst could be determined by different methods such as Hammett indicator and temperature-programmed desorption (TPD) methods. However, the simplest among the aforementioned methods is the indicator method, according to this method, the colour of acid-base indictors are changed based on the strength of the surface site of the catalysts [70]. The catalyst basic strength is expressed by Hammett function (H) suggested by Paul and Long [71]. When Hammett function (H) of a heterogeneous solid base catalyst is more than 26, such catalyst is referred to as super solid base [2, 71]. Meanwhile, evaluation of basicity via indicator method is always accompanied by the interference of indicators reaction which is not related to acid-base chemistry. Besides, the evidence of reaction is many times provided by a colour change, which may not give an accurate result and also, selective in term of catalyst required [70].

Temperature programmed desorption (TPD) had also been employed by many researchers to measure catalyst basicity and also, evaluate the various number of sites on it. During a TPD operation, the elevated temperature is required in order to desorb strongly bound probes adsorbates. Besides, it is carried out under the same operating conditions so as to compare samples that are involved [70]. Temperature programmed desorption (TPD) technique is of three kinds namely; CO_2-TPD, H_2-TPD, and pyrole-TPD. However, temperature programmed of carbon dioxide (CO_2-TPD) is widely used for probing of basic materials. For instance, super solid base catalysts synthesized from birds' (chicken and ostrich) eggshells have been analyzed using TPD of CO_2. The two catalysts exhibited same desorption behaviour, that is, desorption peak at approximately 600°C. This peak value obtained herein is attributed to CO_2 interaction with strong basic sites. Generally, peak desorption of CO_2 occurs at an elevated temperature as revealed in the case of catalyst synthesized from ostrich eggshell which provided basicity of 595 μmol/g compared to that of catalyst from chicken eggshell which was calculated as 205 μmol/g. However, the higher basic amount of 595 μmol/g obtained for calcined ostrich eggshell catalyst indicated that the more surface area available for CO_2 desorption was as a result of higher surface area possessed by the catalyst. Thus, the results suggested that the surface basicity was the reason for the high yield in activity observed for the catalyst derived from ostrich eggshell [26].

Furthermore, H_2-TPD had been used majorly to characterize such catalysts prepared from γ-alumina supported bimetallic precursors or monometallic precursors. Sirichai *et al.* [60] had successfully used temperature programmed desorption of hydrogen spectroscopy to evaluate the surface basicity and a number of sites found on CaO-ZnO catalyst. Based on the results obtained from H_2-TPD analysis, the authors suggested that the interaction between Ca and Zn at the favourable atomic mixing ratio has great influence on the catalytic activity. Also, the particle size of CaO is identified as one of the crucial factors that determine CaO-ZnO activity.

10. Chemical properties of the catalyst

These properties include composition, structure, and morphology. In catalytic reaction, these properties of the solid catalyst could be significantly altered with repeated experimental runs. The activity, stability and basic strength of the catalyst may change owing to enhanced metal support interactions, the prepared orientation of the active species, accessibility hindrance of the active component and particle size and shape transformation by agglomeration [56]. Consequently, the characterization of chemical properties of the supported catalyst helps to gain insights into the reaction mechanisms encountered in a transesterification process. The heterogeneous catalyst produced could be characterized by its chemical composition using the X-Ray Fluorescence (XRF) or Energy Dispersive X-ray (EDX) machines. The morphologic and crystallographic structure of the catalyst could be examined using X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), and Transmission Electron Microscope (TEM) machine while the surface functional groups will be determined by the Fourier Transform Infrared (FTIR) machine.

11. Future research plan

The promotion of anthill-eggshell by mixed metal oxides has great fulfillment for biodiesel production from low grade feedstock. As discussed in the literature, the activity of bird egg-shells increases with the impregnation of natural material or biomass on them [65-66]. Likewise, modification of eggshell with mixed metal oxide would also improve its performance. Most of the stearate metals (Ca, Ba, Mg, Zn, Co, Ni, Mn, Cd, and Pb) are divalent, and they tend to act as electron-acceptor via formation of a four-membered ring transition state [8, 72-74]. A maximum yield of biodiesel (96%) was reported by Di Serio *et al*. [8] during transesterification of soybean oil with methanol over different stearate metal oxides. Although, both anthill and eggshell do transform into several metal oxides after thermal treatment at elevated tempe-rature, only two stearate metals (calcium and a small amount of magnesium) are present in those catalytic materials.

However, further research is required to get abundant results in using the anthill-eggshell promoted stearate metal oxides catalyst in biodiesel production. Another research which requires urgent attention involves mixed anthill clay (natural occurring item) and eggshell (waste) and its modifications for successful direct conversion of low-grade feedstock such as waste frying oil and other non-edible oils into FAME by one step transesterification method. Present two-step transesterification technique for producing biodiesel from high free fatty acid (FFA) feedstock still not guarantee 100% conversion of triglyceride and complete removal of fatty acid. Currently, research has not been geared towards this direction. But the gathered research findings had shown that the use of modified composite material like mixed anthill-eggshell materials and its modification as a heterogeneous catalyst for high FAME content yield is realistic [75-76].

12. Conclusion

Research nowadays has shown that application of supported heterogeneous catalysts derived from biomass source has unrealized potential to avoid the use of expensive comer-cial rare earth metal oxides in biodiesel production. Transformation of waste eggshell and anthill soil to calcium oxide (active phase) and other metal oxides which are to serve as cata-lyst support and promoter may solve the problem of environmental degradation and also reduce the production cost. The mixed anthill-eggshell catalyst is considered as biomass deri-ved catalyst which is formed from abandoned materials. However, the thermally treated mixed anthill-eggshell might have the great potential to curb leaching of catalyst active species into the reaction media.

Composite anthill-eggshell is a heterogeneous base catalyst which is expected to be tolerant of high free fatty acid vegetable oil and moisture. However, optimization of catalyst prepara-tion condition is necessary in order to obtain best preparation parameters that will give a cata-lyst with good activity for transesterification reaction and thus, should be improved and tested its performance with various oil types.

References

[1] Lin L, Cunshan Z, Vittayapadung S, Xiangqian S, and Mingdong O. Opportunities and challenges for biodiesel fuel. Applied Energy, 2011; 88: 1020-1037.

[2] Refaat AA. Biodiesel production using solid metal oxide catalysts. International Journal of Environmental Science and Technology, 2011; 8(1): 203-221.

[3] Zabeti M, van Daud WMA, and Aroua K. Activity of solid catalysts for biodiesel production: A review. Fuel Processing Technology,2009; 90(6): 770-777.

[4] Refaat AA. Different techniques for the production of biodiesel from waste vegetable oil. International Journal of Environmental. Science and Technology, 2010; 7(1): 183-213.

[5] Basumatary S. Transesterification with a heterogeneous catalyst in the production of biodiesel. A Review. Journal of Chemical and Pharmaceutical Research, 2013; 5(1): 1-7.
[6] Aijaz B, and Flora TTN. A single step solid acid-catalyzed process for the production of biodiesel from the high free fatty acid feedstock. Energy & Fuels, 2010; 24(9): 4712-4720.
[7] Shah B, Sulaimana S, Jamal P, and Alam MZ. Production of heterogeneous catalyst for biodiesel synthesis. International Journal of Chemical and Environmental Engineering, 2014; 5(2): 73-75.
[8] di Serio M, Dimiccoli M, Cammarota F, Nastasi M, and Santacesaria E. Synthesis of biodiesel via homogeneous Lewis acid catalyst. Journal of Molecular Catalysis A: Chemical, 2005; 239(1): 111-115.
[9] Alonso DM, Mariscal R, Granados ML, and Maireles-Torres P. Biodiesel preparation using Li/CaO catalysts: Activation process and homogeneous contribution. Catalysis Today,2009; 143(1-2): 167-171.
[10] Olutoye MA, and Hameed BH. A highly active clay-based catalyst for the synthesis of fatty acid methyl ester from waste cooking palm oil. Applied Catalysis A: General,2013; 450: 57-62.
[11] Kim HJ, Kang BS, Kim MJ, Park YM, Kim DK, Lee JS, and Lee KT. Transesterification of vegetable oil to biodiesel using a heterogeneous base catalyst. Catalysis Today, 2004; 93(95): 315-320.
[12] Mbaraka IK, and Shanks BH. Conversion of oils and fats using advanced mesoporous heterogeneous catalysts. Journal of the American Oil Chemists' Society, 2006; 83: 79-91.
[13] Yun JT, Dehkhoda AM, and Ellis N. Development of biochar-based catalyst for transesterification of canola oil. Energy & Fuels, 2011; 25: 337-344.
[14] Boz N, and Kara M. Solid base catalyzed transesterification of canola oil. Chemical Engineering Communications, 2009; 196: 80-92.
[15] Hillion G, Delfort B, le Pennee D, Bournay L, and Chodorge J. Biodiesel production by a continuous process using a heterogeneous catalyst. Prepr. Pap. - American Chemical Society, Division of Fuel Chemistry, 2003; 48(2): 636-638.
[16] Sani YM, Daud WMAW, and Abdul Aziz AR. Biodiesel feedstock and production technologies, successes, challenges and prospects. Intech, 2013; 4: 77-101.
[17] Furuta S, Matsuhashi H, and Arata K. Biodiesel fuel production with solid super acid catalysis in fixed bed reactor under atmospheric pressure". Catalysis Communication, 2004; 5(12): 712-723.
[18] Taufiq-Yap YH, Abdullah NF and Basri M. Biodiesel production via transesterification of palm oil using $NaOH/Al_2O_3$ catalysts. Sains Malaysiana, 2011; 40(6): 587-594.
[19] Hak-Joo K, Bo-Seung K, Min-Ju K, Young P, Deog-Keun K, Jin-Suk L and Kwan-Young L. Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst. Catalysis Today, 2004; 93(95): 315-320.
[20] Arzamendi G, Arguinarena E, Camp I, Zabala IS and Gandia LM. Alkaline and alkaline-earth metals compounds as catalysts for the methanolysis of sunflower oil. Catalysis Today, 2008; 133(135): 305-313.
[21] Kondamudi N, Mohapatra S, and Misra M. Quintinite as a bifunctional heterogeneous catalyst for biodiesel synthesis. Applied Catalysis A, General, 2011; 393(1-2): 36-43.
[22] Pinzi S, Gandia LM, Arzamendi G, Ruiz JJ, and Dorado MP. Influence of vegetable oils fatty acid composition on reaction temperature and glycerides conversion to biodiesel during transesterification. Bioresource Technology, 2011; 102: 1044-1050.
[23] Leung DYC, Wu X, and Leung MKH. A review on biodiesel production using catalysed transesterification. Applied Energy, 2010; 87: 1083-1095.
[24] Boey PL, Mariam G, Hamid SA, and Ali DMH. Utilization of waste cockle shell (Anadara granosa) in biodiesel production from palm olein optimization using response surface methodology. Fuel, 2011; 90: 2353-2358.
[25] Sharma YC, Singh B and Korstad J. Application of an efficient nonconventional heterogeneous catalyst for biodiesel synthesis from Pongamia pinnata oil. Energy & Fuels, 2010; 24: 3223-3231.
[26] Tan YH, Abdullah MO, Hipolito CN, and Taufiq-Yap YH. Waste ostrich and chicken-eggshells as heterogeneous base catalyst for biodiesel production from used cooking oil: catalyst characterization and biodiesel yield performance. Applied Energy, 2015; 2: 1-13.
[27] Cho YB, and Seo G. High activity of acid treated of quail eggshell catalysts in the transesterification of palm oil with methanol. Bioresource Technology, 2010; 101: 8515 -8524.

[28] Margaretha YH, Prastyo HS, Ayucitra A and Ismadji S. Calcium oxide from pomacea sp. shell as a catalyst for biodiesel production. International Journal of Energy and Environmental Engineering, 2012;3: 1-9.
[29] Obadiah A, Swaroopa GA, Kumar SV, Jeganathan KR, and Ramasubbu A. Biodiesel production from Palm oil using calcined waste animal bone as catalyst. Bioresource Technology, 2012; 116(2): 5-16.
[30] Roschat W, Kacha M, Yoosuk B, Sudyoaduk T, and Promarak V. Biodiesel pr production based on heterogeneous process catalyzed by solid waste coral fragment. Fuel, 2012; 2: 194-202.
[31] Aderemi BO, and Hameed BH. Alum as a heterogeneous catalyst for the transesterification of palm oil. Applied Catalysis. A General, 2009; 370: 54-58.
[32] Olutoye MA, Wong SW, Chin LH, Asif M, and Hameed BH. Synthesis of fatty acid methyl esters via transesterification of waste cooking oil by methanol with a barium-modified montmorillonite K10 catalyst. Renewable Energy, 2015; 86: 392-398.
[33] Dai Y, Chen K, Wang Y, and Chen C. Application of peanut husk ash as a low-cost solid catalyst for biodiesel production. International Journal of Chemical Engineering and Applications, 2014; 5(3): 276-280.
[34] Akinwekomi AD, Omotoyinbo JA, and Folorunso D. Effect of high alumina cement on selected foundry properties of anthill clay. Leonardo Electronic Journal of Practices and Technology, 2012; 1: 37-46.
[35] Henne GA. Anthill as a resource for ceramics. Published PhD Thesis, Faculty of Fine Art, Kwame Nkrumah University of Science and Technology, Ghana, 2009.
[36] Paton TR, Humphreys GS, and Mitchel PB. Soils ± A Global View: London: UCL Press, 1995.
[37] Sharma V, and Sumbali G. An overview of the symbiotic interaction between ants, fungis and other living organisms in ant-hill soil. International Journal of Environmental Science, 4(3) (2013) 432-443.
[38] Kristiansen SM, and Amelung W. Abandoned anthill in a temperate deciduous forest morphology and organic matter composition. European Journal of Soil Science. 52 (2001) 355– 363.
[39] Olusegun HD, and Ajiboye TK. Design construction and testing of vibrator-compactor block making machine for rural application. International Journal of Engineering, 3(1) (2009) 1-14.
[40] Elufisan MO. Determinants of household consumption-expenditure on egg in Ilorin east and west local Areas, Kwara State, Nigeria. Unpublished B. Agric Thesis, Department of Agricultural Economics and Farm Management, University of Ilorin, Nigeria. 1994: 1-168.
[41] Tsai WT, Yang JM, Lai CW, Cheng YH, Lin CC and Yeh CW. Characterization and adsorption properties of eggshells and eggshell membrane. Bioresource Technology, 2006; 121: 167-173.
[42] Than MM, Lawanprasert P, and Jateleela S. Utilization of eggshell powder as excipient in fast and sustained release of acetaminophen tablet. Mahidol University Journal of Pharmaceutical Sciences, 2012; 39(3-4): 32-38.
[43] Amu OO, Fajobi AB and Oke BO. Effect of eggshell powder on the stabilizing potential of lime on expensive clay oil. Research Journal of Agricultural and Biological Science, 2005; 1: 80-84.
[44] Yoo S, Hsieh JS and Zou P and Kokoszka J. Utilization of calcium carbonate particles from eggshell waste as coating pigments for ink-jet printing paper. Bioresource Technology,2009; 100: 6416-6421.
[45] Montilla A, del Castillo MD, Sanz ML and Olano A. Egg shell as catalyst of lactose isomerisation to lactulose. Journal of Food Chemistry, 2005; 90: 883–890.
[46] Nakatani N, Takamori H, Takeda K, and Sakugawa H. Transesterification of soybean oil using combusted shell waste as a catalyst. Bioresource Technology, 2009; 100:1510-1513.
[47] Wei Z, Xu C, and Li B. Application of waste eggshell as low-cost solid catalyst for biodiesel production. Bioresource Technology, 2009; 100: 2883–2885.
[48] Umdu ES, Tuncer M, and Seker E. Transesterification of *Nannochloropsis aculata* microalga's lipid to biodiesel on Al_2O_3 supported CaO and MgO catalysts. Bioresource. Technology, 2009; 100: 2828-2831.
[49] Witoon T. Characterization of calcium oxide derived from waste eggshell and its application as CO_2 sorbent. Ceramics International, 2011; 37: 3291-3298.
[50] Sun H, Ding Y, Duan J, Zhang Q, Wang Z, Lou H, and Zheng X. Transesterification of sunflower oil to biodiesel on ZrO2 supported La_2O_3 catalyst. Bioresource Technology, 2010; 101:(2010) 953-958.
[51] K. Chojnacka, Biosorption of Cr(III) ions by Eggshells. Journal of Hazardous. Materials. 121 (2005) 167–169.

[52] R. Chakraborty, S. Bepari and A. Banerjee, Transesterification of soybean oil catalyzed by fly ash and egg shell derived solid catalysts. Chemical Engineering Journal, 165 (2012) 798–801.
[53] N. Viriya-empikul, P. Krasae, W. Nualpaeng, B. Yoosuk, and K. Faungnawakij, Biodiesel production over Ca-based solid catalysts derived from industrial wastes. Fuel. 92 (2012) 239-344.
[54] A. Sivasamy, K.Y. Cheah, P. Fornasiero, F. Kemausuor, S. Zinoviev and S. Miertus, Catalytic applications in the production of biodiesel from vegetable oils. ChemSusChem, 2 (2009) 278-300.
[55] C.H. Bartholomew, and R.J. Farrauto, Fundamentals of Industrial Catalytic Processes. John. Wiley & Sons Inc., Hoboken, New Jersy, (2006).
[56] Q.M. Quddus, A novel mixed metallic oxygen carriers for chemical looping combustion: Preparation, characterization and kinetic modeling, published PhD thesis. Department of Chemical and Biochemical Engineering, University of Western Ontario London, Ontario Canada, 2013.
[57] K. Koeler, Modern methods in heterogeneous catalysis research", Fritz Haber Institute, TU Berlin & HU Berlin, p.1-35, 2006.
[58] S. Rojas, Preparation of Catalysts: Heterogeneous catalysts, CSIC. 1-52, 2013.
[59] A. D'Cruz, M.G. Kulkarni, L.C. Meher, and A.K. Dalai, Synthesis of biodiesel from canola oil using heterogeneous base catalyst. Journal of American Oil Chemical Society. 84 (2007) 937-943.
[60] C.A. Sirichai, C.A. L. Apanee, and J. Samai, Biodiesel production from palm oil using heterogeneous base catalyst. International Journal of Chemical and Biological Engineering. 6 (2012) 230-235.
[64] G. Leofanti, G. Tozzola, M. Padovan, G. Petrini, S. Bordiga, and A. Zecchina, 1997. Catalyst characterization: characterization techniques. Catalysis Today. 34 (1997) 307-327.
[62] H. Wang, M. Wang, S. Liu, N. Zhao, W. Wei, and Y. Sun, Influence of preparation methods on the structure and performance of CaO–ZrO2 catalyst for the synthesis of dimethylcarbonate via transesterification. Journal of Molecular Catalysis A: Chemical. 258 (1-2) (2006) 308-312.
[63] K. Liu, H. He, Y. Wang, S. Zhu, and X. Ziao, Tansesterification of Soybean Oil to Boidiesel Using CaO as A Solid Base Catalyst. Fuel. 87 (2008) 216-221.
[64] S.L. Yan, S.O. Salley, and K.Y. Simon Ng, Simultaneous transesterification and esterification of unrefined or waste oils over ZnO-La_2O catalysts. Applied Catalysts A: General. 353(2) (2009) 203-212.
[65] J.K. Lakhya, C. Singh, B. Jutika, K. Rupam, and D. Dhanapati, Biochar supported CaO as heterogeneous catalyst for biodiesel production. International Journal of Innovative research & Development. 1(7) (2012) 186-195.
[66] M.A. Olutoye, O.D. Adeniyi, and A.S. Yusuff, Synthesis of biodiesel from palm kernel oil using mixed clay-eggshell heterogeneous catalyst. Iranica Journal of Energy and Environment. 7(3) (2016) 308-314.
[67] D. Kumar, and A. Ali, Nanocrystalline KeCaO for the transesterification of a variety of feedstocks: structure, kinetics and catalytic properties. Biomass Bioenergy. 46 (2012) 459-468.
[68] M.A. Olutoye, B. Sulaiman and A.S. Yusuff, Bi-ZnO heterogeneous catalyst for transesterification of crude jatropha oil to fatty acid methyl ester". Advances in Research 7(1) (2016) 1-8.
[69] D.E. Lopez, J.G. Godwin Jr., O.A. Bruce and E. Lotero, Transesterification of triacetin with alcohol on solid acid and base catalysts. Applied Catalysis A: General, 2 (2005) 97-105.
[70] M. Alsawalha, Characterization of acidic and basic properties of heterogeneous catalysts by test reactions. PhD dissertation, University of Oldenberg Germany. 2004 1-121.
[71] F. Audry, P.E. Hoggan, J. Saussey, J.C. Lavalley, H. Lauron-pernot, and A.M. Le Govic, 1997. Infrared study and quantum calculation of the conversion of methylbutynol into hydroxymethylbutanone on Zirconia. Journal of Catalysis. 168 (1997) 471-481.
[72] Y. Li, F. Qiu., D. Yang, X. Li, and P. Sun, Preparation, characterization and application of heterogeneous solid base catalyst for biodiesel production from soybean oil. Biomass Bioenergy. 35 (2011) 2787–2795.
[73] V. Kumar, and P. Kant, Biodiesel production from sorghum oil by transesterification using zinc oxide as catalyst. Petroleum & Coal. 56(1) (2014) 35-40.

[74] G. Feng, and F. Zhen, 2011. Biodiesel production with solid catalysts, biodiesel- feedstocks and Processing Technologies, Dr. Margarita Stoytcheva (Ed.), ISBN: 978-953-307-713-0, InTech.
[75] A.S. Yusuff, O.D. Adeniyi, M.A. Olutoye, and U.G. Akpan, A review on application of heterogeneous catalyst in the production of biodiesel from vegetable oil. Journal of Applied Science and Process Engineering. 4(2) (2017) 142-157.
[76] A.S. Yusuff, O.D. Adeniyi, M.A. Olutoye, and U.G. Akpan, Performance and emission characteristics of diesel engine fuelled with waste frying oil biodiesel-petroleum diesel blend. International Journal of Engineering Research in Africa. 32 (2017) 100-111.

To whom correspondence should be addressed: Dr. Adeyinka Sikiru Yusuff, Department of Chemical and Petroleum Engineering, Afe Babalola University, Ado-Ekiti, Nigeria, yusuffas@abuad.edu.ng