BIODIESEL SYNTHESIS FROM PALM OLEIN OIL USING ANTHILL AS CATALYST

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ABSTRACT

In the present study, heterogeneous catalyst was synthesized from type II anthill, characterized and used to catalyze transesterification of palm olein oil with methanol. The influence of reaction parameters, including reaction temperature, reaction time and catalyst dose at fixed methanol/oil molar ratio of 6:1 on biodiesel yield was investigated. The results obtained showed that maximum biodiesel yield of 78.2 % was achieved at the optimum conditions of 70^{o}C reaction temperature, 3 h reaction time and 2 wt % catalyst dose. This study revealed the potential of anthill as a catalytic material for biodiesel production.

Keywords: Anthill, biodiesel, heterogeneous catalyst, palm olein oil, transesterification.

INTRODUCTION

In recent time, biodiesel has gained tremendous popularity because it can be made from biomass and it is environmentally benign. Besides, it provides solution to the double crisis of fossil hydrocarbon depletion and environmental deterioration [1]. According to Kurki et al. [2], biodiesel emits lower gaseous pollutants when used in compression ignition or vehicular engine compared to fossil hydrocarbon fuel.

Generally, there are several ways by which biodiesel could be produced. They include blending, pyrolysis, microemulsification, esterification and transesterification. Among these methods, transesterification is the most commonly used technique for biodiesel production because it is simple and cheaper [3]. Biodiesel production via transesterification process is usually carried out by reacting triglyceride contained in plant oil or animal fat with simple alcohol such as methanol in the presence of liquid (homogeneous) or solid (heterogeneous) catalyst [4] as can be seen in Fig. 1. However, homogeneous catalyzed transesterification often generates wastewater and does not allow catalyst reusability [5]. Thus, the application of solid heterogeneous catalyst is a possible way of overcoming those aforementioned problems. Several materials have been applied as heterogeneous catalysts for the production of biodiesel [6]. They include pure metal oxides [7], mixed metal oxide [8], sulphated/metal oxide [9], agricultural waste [3], domestic waste [10], construction waste [11] and naturally occurring materials [12].

In the industry where sustainability and large output is required, derivation of heterogeneous catalyst from low cost and readily available naturally occurring materials with high activity for biodiesel synthesis is beneficial to the entire process. Anthill is a naturally occurring material formed by ants at their entrances. Anthill is classified into type I and type II. Type I anthill is less noticeable in environment because it is smaller in size and influenced by erosion, while type II anthill is huge, surrounded by vegetation and can persist for several years [13]. Anthill material has several industrial usefulness, for example, it has been used to make ceramics, cement, furnace, sand casting and as an adsorbent to remove both organic and inorganic contaminants from wastewater [14 - 16].

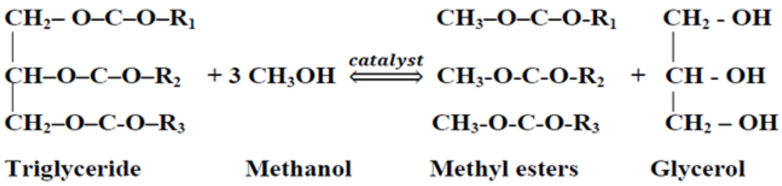


Fig. 1. Transesterification of oil with methanol.

In this study, type II anthill was used as heterogeneous catalyst in converting palm olein oil to biodiesel and was evaluated based on its morphological and chemical properties. The influence of reaction variables such as reaction temperature, time and catalyst loading on biodiesel yield, were investigated. Moreover, the biodiesel produced under optimum reaction conditions, was characterized using FTIR and physicochemical properties techniques.

EXPERIMENTAL

Materials

Type II anthill situated beside the Guest house, Afe Babalola University (ABUAD), Ado-Ekiti, Nigeria, was harvested. The palm olein oil with specific gravity, kinematic viscosity and acid value 0.913, 10.96 mm^2/s and 2.83 mgKOH/g, respectively, were purchased from King's market, Ado-Ekiti, Nigeria. The methanol used was of synthesis grade (99.9 %) and all other chemicals used for characterization of palm olein oil and the biodiesel were of analytical grade.

Catalyst Preparation and Characterization

The harvested anthill was gently pulverized with the aid of mortar and pestle. It was later sieved to obtain particle sizes between 150 - 220 µm. The raw anthill was then calcined at 900^{o}C for 4 h in a muffle furnace with a heating rate of 10^{o}C/min. The morphological structure, surface functional groups and chemical compositions of the prepared sample were determined via scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy and X-ray fluorescence, respectively.

Biodiesel Production Process

The conversion of palm olein oil to the biodiesel was carried out in a batch reactor consisting of a 250 mL flat-bottomed flask equipped with a magnetic stirrer and a thermometer. The reaction mixtures comprising of oil, methanol and catalyst were all weighed, charged into a reaction vessel and agitated vigorously at constant stirring speed of 250 rpm. The reactions were performed at different conditions, considering reaction temperature (60 - 80^{o}C), reaction time (1 - 5 h) and catalyst loading (0.5 - 2.5 wt %), while keeping methanol/oil molar ratio and stirring rate constant.

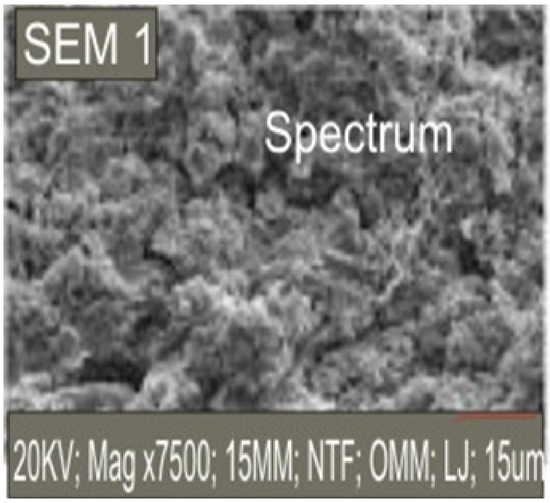
After the end of the reaction, the product mixtures consisting of unreacted methanol, biodiesel, glycerol and catalyst were poured into a separating funnel and left overnight for proper separation. Glycerol and catalyst were thereafter removed from the mixture, while the mixtures of biodiesel produced and unused methanol left in the funnel were poured into a beaker and heated at 65^{o}C to evaporate the unused methanol. The yield of biodiesel was determined by Eq. (1).

$$\text{Biodiesel yield, Y \%} = \left[\frac{weight\ of\ biodiesel}{weight\ of\ palm\ olein\ oil}\right] x\ 100\% \quad (1)$$

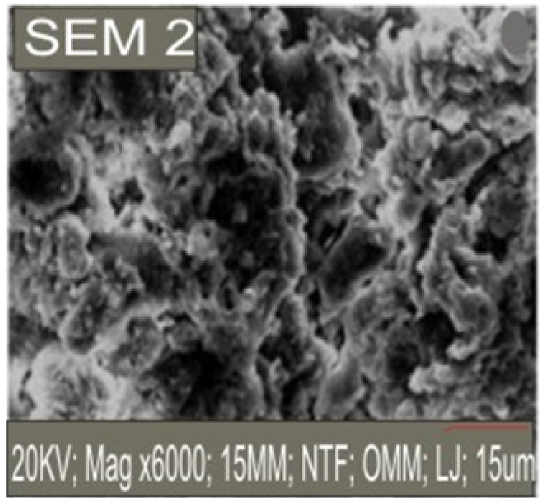
RESULTS AND DISCUSSION

Catalyst Characterization

Fig. 2 shows the SEM images of raw and calcined anthill samples. As can be seen in Fig. 2(a), the raw catalyst possesses irregular small particles and rough surface without voids. This observation could be attributed to the presence of sand. However, upon calcination of the raw catalyst, there was formation of different layer of pores on the surface of the calcined catalyst as can be observed through SEM image shown in Fig. 2(b). This indicates that there was decomposition of the catalyst major components into mixed metal oxides and carbon dioxide which occupy and fill up the available pores for possible reaction. This is corroborated by FTIR and XRF analyses. A similar observation was reported by Olutoye and Hameed [12] who studied the conversion of waste cooking palm oil to biodiesel using clay as catalyst.



(a)



(b)

Fig. 2. SEM images of (a) raw and (b) calcined anthill.

Fig. 3 shows various functional groups present on the surface of the calcined anthill. The broad band around 3445 cm^{-1} is attributed to O-H stretching vibration, which indicates the presence of moisture on the catalyst surface. The band at 2927.76 cm^{-1} is due to –CH_2 stretching vibration, while a band at 1631.73 cm^{-1} corresponds to OH deformation of water. The bands at 1056 cm^{-1} and 780.48 cm^{-1} can be respectively assigned to the Al-Al-OH and Al-Mg-OH vibration of the clay sheet [12]. The short peak at 685.36 cm^{-1} is attributed to combined Al-O and Si-O out of the plane [11]. The observed band at 451.65 cm^{-1} is due to Si-O-Al vibration mode [17]. All these surface functional groups are responsible for the effective performance of anthill in transesterification of palm olein oil.

The mineral compositions of the raw and calcined anthill are presented in Table 1. The XRF results showed that the major chemical composition of anthill were silica (SiO_2), alumina (Al_2O_3), zirconia (ZrO_2), iron (III) oxide (Fe_2O_3) and titanium oxide (TiO_2). However, the composition of SiO_2 and Al_2O_3 decreased after thermal treatment of the anthill, while those of ZrO_2 and Fe_2O_3 increased. This observation is attributed to the elimination of adsorbed gases such as CO_2, SO_2, moisture and organic matter. This study revealed the unique difference between anthill and natural clay as the former contains ZrO_2 which is not present in the latter. However, Zirconium is like gold, that is, it is scarce and can withstand high temperatures [18]. This indicates a good discovery.

As reported in the literature, SiO_2, ZrO_2, Al_2O_3 and TiO_2 have been employed in pure and combined forms as catalysts in the transesterification of plant oils and animal fats [6, 19 - 21]. Thus, these metal oxides are active in nature for catalysis irrespective of their quantity and are responsible for the better activity of the calcined anthill for transesterification.

Transesterification reaction

Various reaction parameters affecting biodiesel yield in transesterification process, which include reaction temperature, time and catalyst dose at fixed methanol/palm olein oil molar ratio were investigated in details.

Reaction temperature

The transesterification reaction was carried out at different reaction temperatures (60°C - 80°C) while keeping other process variables constant. Fig. 4 shows the yields of palm olein oil biodiesel at different temperatures. It was observed that the biodiesel yield increased

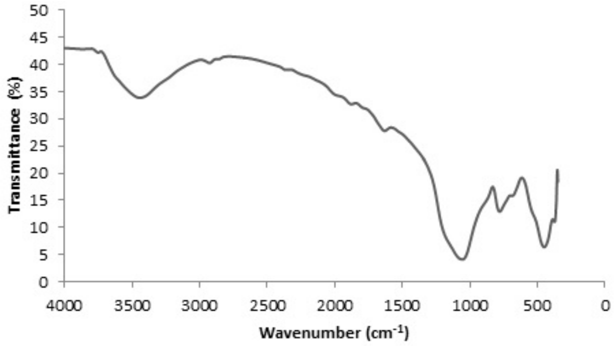


Fig. 3. FTIR spectrum of calcined anthill.

Table 1. XRF analysis of raw and calcined anthill.

Constituent	Chemical composition of anthill (wt. %)	
	Raw	Calcined
SiO_2	65.02	63.68
Al_2O_3	17.89	13.41
Fe_2O_3	2.56	3.13
ZrO_2	7.37	8.28
MgO	0.54	2.08
CaO	0.76	0.23
Na_2O	0.31	1.22
K_2O	1.93	1.13
TiO_2	4.76	0.72

steadily from 55.7 % at 60°C to 78 % at 70°C. However, there was a drop in the yield of biodiesel when the reaction was conducted at temperature above 70°C. This observation is due to the total gasification of methanol which inhibits the reaction on the catalyst-oil-gaseous methanol interface [3].

Reaction time

Reaction time is one of the factors affecting the yield of biodiesel in transesterification process. Conversion of palm olein oil to its biodiesel was carried out at different periods of reaction, while keeping other variables constant. Fig. 5 shows the influence of reaction time on biodiesel yield. It was observed that the biodiesel yield increased from 1 h to 3 h. However, as the reaction time prolonged, biodiesel yield was reduced. The result obtained herein reaffirmed the fact that shorter reaction time increases the biodiesel yield during the transesterification process [22]. Therefore, reaction time of 3 h was considered as optimum point. The highest biodiesel yield obtained in 3 h at 70°C was 76.12 %.

Catalyst dose

The influence of the catalyst dose on the heterogeneous catalyzed transesterification process was investigated. The quantity of calcined anthill was varied from 0.5 wt. % to 2.5 wt. % in respect to the amount of palm olein oil used in the process. As can be seen in Fig. 6, the yield of biodiesel increases as the catalyst dose increases from 0.5 wt % to 2 wt. % indicative of the intimate contact between catalyst and reactants. However, loading of catalyst above 2 wt. % decreased the biodiesel yield. This is because reaction mixtures become more viscous at higher catalyst loading, thus resulting in formation of more glycerol and inhibition of biodiesel separation from the product mixtures. Similar results have also been reported [3, 23]. This implies that increasing the quantity of catalyst in biodiesel production process has negative effect on its cost of production. Therefore, maximum conversion of palm olein oil to biodiesel is achievable,

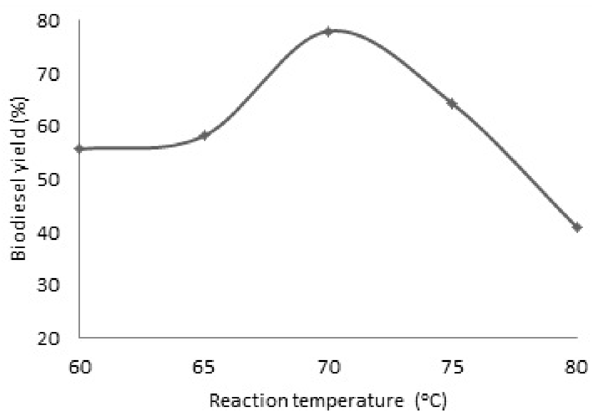


Fig. 4. Biodiesel yields at different reaction temperatures at fixed reaction time = 3 h, catalyst dose = 2.0 wt. % and methanol/oil molar ratio of 6:1.

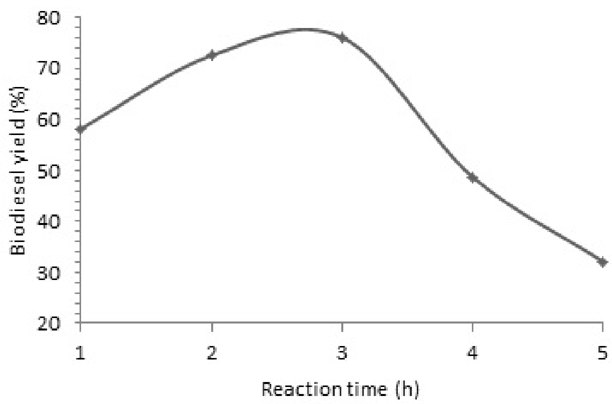


Fig. 5. Biodiesel yields at different reaction time at fixed reaction temperature = 70°C, catalyst dose = 2.0 wt. % and methanol/oil molar ratio of 6:1.

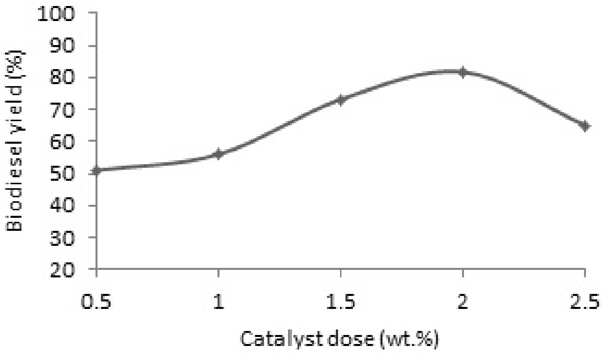


Fig. 6. Biodiesel yields at different catalyst doses at fixed reaction temperature = 70°C, reaction time = 3 h and methanol/oil molar ratio of 6:1.

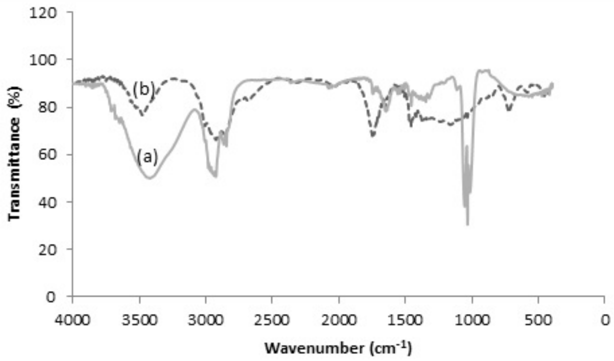


Fig. 7. FTIR spectra of (a) palm olein oil and (b) palm olein oil biodiesel.

if 2 wt. % of calcined anthill is used as catalyst.

Characterization of palm olein oil biodiesel

Palm olein oil biodiesel produced under the optimum reaction conditions was analyzed in order to ascertain its quality and constituents using FTIR spectroscopy and physicochemical analysis technique. Thus, the results of analyses were explained in details.

FTIR analysis

Palm olein oil and its biodiesel were analyzed using FTIR spectroscopy in order to identify the functional groups. Fig. 7 and Table 2 show the FTIR spectra of palm olein oil and the biodiesel. It was observed that some of the peaks in the feedstock disappeared or switched and new peaks were also formed upon conversion to the biodiesel. The changes observed in the peaks of feedstock after reaction implied conversion of triglycerides into esters as confirmed by appearance of sharp peak at 1746.57 cm^{-1} [17]. Possible participation of functional groups associated with palm olein oil in transesterification reaction could be responsible for the observed changes as well.

Physicochemical properties determination

Table 3 depicts the physicochemical properties of palm olein oil biodiesel which was compared to ASTM/EN biodiesel standard. The relative density at room

Table 2. FTIR spectra of palm olein oil and the biodiesel.

IR Band	Wavenumber (cm^{-1})		Assignment/Vibration mode
	Palm olein oil	Palm olein oil biodiesel	
1	3414.90	3473.91	O-H stretching vibration
2	2924.18	2922.25	Two bands for $–CH_2$- groups
3	2845.10	2852.81	CH stretching vibration
4	-	2681.14	Overtone of CH bending
5	-	2318.51	P-H stretching
6	-	2031.11	C≡C stretching
7	1739.01	1746.57	C=O stretch of ester carbonyl
8	1647.26	1653.05	C=N or two bands from C=O stretching
9	1456.30	1456.30	CH_3 antisym deformation
10	1346.36	-	NO_2 sym stretching
11	1112.96	1163.11	C-O stretch of ester
12	1055.10	1033.88	P-O-C antisym stretching
14	1016.52	-	C-C stretching
15	-	721.40	C-H_2 methylene rock
16	-	584.45	C-C-CN bending

Table 3. Physicochemical and fuel properties of palm olein oil derived biodiesel compared to ASTM .

Property	Palm olein oil Biodiesel	Biodiesel Standard ASTM/EN
Relative density	0.891	0.86 - 0.90
Kinematic viscosity (mm^2/s)	5.06	1.9 - 6.0
Acid value (mgKOH/g)	0.92	0.8 max
Flash point (^oC)	155	≥ 130^oC
Pour point (^oC)	-13	-15 - 10

temperature was obtained to be 0.891, the result falls within the range of ASTM D6751 and European standard EN14214 (0.860 - 0.90). The biodiesel produced in this study has kinematic viscosity of 5.06 mm^2/s at 40^oC. The value obtained herein was similar to those reported in the literature [3, 24] and also agreed with ASTM D445 biodiesel standard (1.9 - 6.0 mm^2/s).

The number of milligram of alkaline solution necessary to neutralize the fatty acid contained in a gram of fat or oil is referred to as acid value. As shown in Table 3, the acid value obtained for palm olein oil biodiesel in this study was found to be 0.92. The result exceeds the ASTM standard of 0.8 mgKOH/g. Nevertheless, 72.5 % of free fatty acid (FFA) contained in the feedstock was converted to biodiesel, which indicates that the anthill is an effective catalyst for biodiesel production from high FFA content feedstock.

Flash point of a fuel is the temperature at which fuel is ignited or sparked when exposed to fire. The value of flash point for palm olein oil biodiesel obtained in this study was 155^oC, which is agree with ASTM D93 biodiesel standard (100 - 170^oC). The result obtained is quite high which indicates that the biodiesel produced is safe from handling [25]. From this study as well, the pour point of biodiesel of palm olein oil was obtained to be -13^oC and found to be comparable with those values reported in the literature [3, 26] and it also agreed with ASTM D2500 biodiesel standard (-15 - 10).

CONCLUSIONS

The present study had revealed the potential of anthill as a low-cost heterogeneous catalyst for biodiesel production. From the SEM results, the particle size of anthill reduced after calcination indicative of complete decomposition, while the functional groups present on the surface of the activated anthill was similar to natural clay as revealed by FTIR analysis. The XRF analysis on anthill catalyst revealed several active sites, including SiO_2, Al_2O_3, ZrO_2 and TiO_2. The maximum biodiesel yield was obtained at optimum reaction conditions of 70^oC reaction temperature, 3 h reaction time, 2 wt. % catalyst loading and methanol/palm olein oil molar ratio of 6:1. The physicochemical properties of palm olein oil biodiesel agreed with ASTM/EN standard, thus confirming the quality of the product.

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