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A Comparative Study of Transesterification of *Hydnocapus weightiana* Seed Oil Using Calcined and Acid Activated Natural Heterogeneous Catalyst and Its Kinetic Study

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Abstract

The world's total fossil fuel consumption has been significantly increasing with consequential increased environmental catastrophes. A hunt for an alternate energy source was stimulated. Biofuel is a plausible option in this pursuit due to its ideal qualities which included but are not limited to renewability and environmental friendliness. However, the pump price of biodiesel is still very high due mainly to the high cost of the production of the commodity which is influenced by the feedstock and the homogeneous nature of catalyst used. Heterogeneous catalyst was prepared by using *Pila globosa* sea snail shells prepared by calcination (CP8) and by acid activation (PTW1M). *Hydnocapus weightiana* seed oil (Non-edible feedstock) was extracted using the soxhlet extraction method and was used for biofuel production with a methanol oil ratio of 3:1. Agitation speed 800, 600 rmp, reaction temperatures of 70˚C, 60˚C, catalyst concentration (3.00, 2.00 wt%) and reaction time (70 and 60 min) was maintained for CP8 and PTW1M respectively. The rate of the reaction followed a reversible second-order reaction rate. Re-usability accessed. From TGA analysis, the best calcination temperature was 800˚C. SEM results showed improved surface morphology after calcination, especially for CP8. FTIR analysis showed the elimination of volatiles and formation of CaO and CaO_4Te after calcination. The reaction rate constant at different temperatures was 0.0287 at 30˚C, 0.1200 at 50˚C and 0.1142 at 70˚C and activation energy of the ethyl ester was 49.49 KJ/mol. Using CP8. Most of the fuel properties met with ASTM 6751 standard. The result of the re-usability showed that the biodiesel yield declined as follows: 92, 86, 80, 73 and 69 % for CP8 and 85, 84, 81, 76, 65. For PTW1M. After the fifth regeneration cycle, both CP8 and PTW1M samples of *Pila globosa* sea snail shell catalyst proved effective in transesterification reaction of *Hydnocapus weightiana* seed oil using ethanol. It was observed that the calcined catalyst (CP8) showed a superior catalytic performance.

Keywords

Bio-Fuel, *Hydnocapus weightiana* Calcined/Acid-Activated *Pila globosa*, Seed-Oil

1. Introduction

Alternative energy is renewable [1] [2]. However, the pump price of biodiesel is still very high due mainly to the high cost of the production of the commodity which is influenced by the feedstock and the homogeneous nature of catalyst used [3]. In the production of biodiesel, the raw material to be used has faced an obstacle because; most of the vegetable oils used compete with food security thereby creating scarcity in food sector and causing an increase in the pump price of the biodiesel [4]. Fresh edible oils are used as feedstock made up more than 80% of biodiesel production. Thus, it is very important to identify and use unconventional vegetable oils, which are not edible. This will help prevent fuel/food crisis and the price of biodiesel produced will be cheaper [5]. Being biodegradable and clean to the environment, vegetable oils have always been considered as good alternatives that can solve problems related to environmental pollution [1] due to high densities and viscosities, natural vegetable oils needed to be modified before they can be used directly in diesel engines. The modification can be achieved through the transesterification or alcoholysis process, which is usually facilitated by acids, bases, enzymes, and other types and forms of catalysts [6]. The catalysts can be either in a homogeneous or a heterogeneous phase. If the catalyst remains in the same phase (usually liquid) as the reactants during alcoholysis, then that is the homogeneous catalyst. If the catalyst is in a different phase (usually non-liquid) to the reactants, then that is the heterogeneous catalyst [7]. The appropriate catalyst selection depends on several factors, namely, the amount of free fatty acids (FFAs) in the oil, the water content, etc. Homogeneous catalysts are generally efficient in converting biodiesel with low FFA and water containing single-origin feedstock [8]. Oils with higher FFA content leads to the formation of soap, consequently affecting the activity of the catalyst [9]. Besides, the catalyst is partially miscible in biodiesel and miscible in glycerol, which results in problems of product separation from the reactant mixture Heterogeneous catalysts, on the other hand, provides high activity, selectivity, and water adaptability due to the presence of a large number of active acid or basic sites. Various reviews have been published on the topic of catalysts, especially heterogeneous catalysts [10] [11] [12] [13]. Heterogeneous catalysts can either be acidic or basic. Base catalysts are especially appropriate for good purity oils with low FFA contents because they are more vigorous than acids in transesterification. Continuous flow and a packed bed arrangement are generally employed for synthesizing biodiesel using solid base catalysts which ultimately facilitate both coproductions of glycerol with good purity and catalyst separation [14]. Some examples of Solid basic catalysts are: ZnO, CuO, zeolites, CaO, SrO, MgO, BaO, basic polymers and carbonates such as $MgCO_3$, $CaCO_3$, $BaCO_3$ and $SrCO_3$ have drawn interest as heterogeneous transesterification catalysts [15] [16]. Waste derived from industrial processes and surrounding environment can aid in the development of a low-cost solid base catalyst. These catalysts can promote a sustainable and environment-friendly approach toward biodiesel production [17]. Calcium-enriched waste products, namely, shells of mussels, eggs, cockles, snails, and oysters; fish scales; animal bones; and ash derived from plant species, etc. are easily available at low cost Calcium obtained from these waste materials could be converted to CaO, which is the most versatile heterogeneous base catalyst [18]. The maximum yield for these conditions was 96.81% and 95.12% for CaO and waste-eggshell-based CaO, respectively [17] [18]. Heterogeneous acid catalysts have a less corrosive and toxic effect and give rise to fewer environmental problems compared to homogeneous acid catalysts These catalysts contain a variety of acidic sites with different strengths of Brønsted or Lewis acidity. While these catalysts provide encouraging results under moderate reaction conditions, they react very slowly compared to solid base catalysts. In addition, high catalyst loading, high temperature, and long reaction time are required to employ this type of catalyst [19]. Sulfated metal oxides generally work as an acid heterogeneous catalyst in esterification reactions examples are $Ce/ZrO_2\text{-}TiO_2/SO_4^{2-}$, as well as sulfuric acid $TiO_2/SO_4^{2-}\text{-}(NH_4)_2SO_4$ [20] [21]. Biodiesel can be produced from different feedstocks ranging from vegetable oil, animal fats, waste cooking oil and algae However, the use of edible vegetable oils as biodiesel feedstock has been of concern as its requirement is increasing, competing with the food supply and pump price is also increasing. Prime importance is given to non-conventional seed oils as they will not cause a food/fuel crisis [2]. Also to natural catalyst from *Pila globosa* sea snail shell. This research is focused on the comparison of the yield of biodiesel from *Hydnocapus weightiana* seed oil using acid activated and calcined (alkaline based) natural heterogeneous catalyst from *Pila globosa* sea snail shell. It will guide researchers on which of the catalyst can be more effective in biodiesel production using *Hydnocapus weightiana* seed oil as feedstock.

2. Materials and Methods

2.1. Materials

All the reagents were obtained from Sigma Aldrich and used without further purification. The flash point was recorded with a Pensky Martens flash point tester, while the Soxhlet extractor was used to extract the oil from the raw seeds. Calcination was achieved with a Muffle furnace.

A digital density meter (model AP PAAR DMA 35) and a viscometer were used to test the seed oil and ester blends' densities and viscosity. Fourier-Transform Infrared Spectroscopy (FTIR) was used to analyse the catalyst and seed oil functional group. A spectrophotometer (8400SSHIMADZU) and Emission Scanning Electron Microscope (JSM-670IF) were used to check the morphology of the catalyst Emission Scanning Electron Microscope (JSM-670IF), for SEM/EDX and hang down lyrics TGA equipment from Perkin Elmer with balance precision of 0.001.

2.2. Methods

2.2.1. Sample Collection and Oil Extraction

1) Collection of Samples

Fruits of *Hydnocapus weightiana* were collected from surrounding villages around Oji urban in Oji River L.G.A of Enugu where they are abundant. The sample was identified by a taxonomist. The seeds were separated, dried in an oven at 106˚C during 24 h and finely ground into powder.

2) Seed Oil Extraction

Oil was extracted from the sample by soxhlet extraction. The sample was weighed into a semi-permeable cotton material and placed into the timbale of a 500 mL soxhlet extractor. 400 mL petroleum ether with boiling point range of "50˚C - 80˚C" was measured into a 500 mL round bottom round flask. The soxhlet extraction system was heated on a heating mantle while water was allowed to circulate at the outer jacket of the condenser. The extraction was discontinued when oil was completely extracted from the sample. The de-fatted sample in the semi permeable membrane was discarded, while the oil and n-hexane mixture in the flat bottom flask were separated using a rotary evaporator apparatus. The percentage yields were determined; the extracted oil was characterized to determine their density, moisture content, saponification value, viscosity, acid value, peroxide value and iodine etc. The percentage oil yield was calculated using the formula:

$$\%\ \text{Oil content} = \frac{\text{weight of oil extracted}}{\text{weight of seed sample}} \times \frac{100}{1} \tag{1}$$

The Physicochemical Properties

2.3. Catalyst Preparation and Characterization

2.3.1. Catalyst Preparation

The samples of the *Pila globosa* sea snail were sourced from Afor Oduma. A local market in Oduma, Aninri Local Government Area of Enugu state Nigeria. The sample was authenticated by a Botanist. The shell was isolated washed dried in the oven at 105˚C. The dried shells were mashed to powder in a mortar, then ground in a grinding machine and sieved with "105 µm - 110 µm" range mesh size. 50 g of the sample was calcined at temperatures of 800˚C at a heating rate of

4˚C per min in a Carbolite furnace for 1 hr. another 50 g was treated with 1 molar solution of H_2SO_4. The slurry was stirred continually for 10 minutes then, washed with water, then, heated in the oven at 600ºC for 1 hr.

Table 1 showed that catalyst 1 has a code PTW1M while catalyst 2 has the code CP8. Catalyst 1 was activated by acid then heated to 600˚C while catalyst 2 was activated by calcined at 800˚C.

2.3.2. Catalyst Sample Characterization

The prepared powdered *Pila globosa* sea snail shell was kept in a desiccator to prevent moisture. It was initially subjected to thermogravimetric analysis (TGA) to determine the calcination temperature and time. After calcination, they were packaged and sent for further characterization and analysis. The elemental composition of the calcined powdered shells was determined using Energy Dispersive X-Ray Spectroscopy (EDX), the functional group was analyzed using Fourier Transformed Infrared Spectroscopy (FTIR). The morphology was analyzed using scanning electron microscopy (SEM).

2.3.3. Transesterification Using 2 Heterogeneous Catalysts Prepared from *Pila globosa* Sea Snail Shell

Procedure: The oil extracted was heated to about 100˚C for 20 minutes and allowed to cool. This is to ensure that all the residual solvent water and other volatile were evaporated away. 100 ml of oil was measured into a three necked flask, 2.5 g of each of the catalyst prepared from *Pila globosa* sea snail shells (CP8 and PT1M@6) catalysts were measured into a beaker respectively. 300 ml of methanol was measured out. Part of the methanol was used to dissolve the catalyst and the mixture was poured into the three arms flask. The remaining methanol was used to rinse the catalyst in the beaker into the three necked flasks. Thermometer was fitted into a rubber stopper which was eventually fitted into one of the arms of the three necked flasks. The transesterification reaction was carried out using a 500 mL round bottom three necked glass reactor into which the calculated amount of the oil, methanol and catalyst were added as well as magnetic stirrer for homogeneity. A reflux condenser was attached to the middle arm of the reactor while a thermocouple was inserted through the other necks to make enough contact with the reactant to help regulate the reaction temperature. The glass reactor with the content was mounted onto a heating mantle. The temperature, stirring speed and reaction time was kept constant. The temperature was kept at 60˚C while the rotation speed of 600 rpm was maintained and the reaction time of 60 hr was kept constant. Thereafter, the mixture was poured into the separating funnel and allowed to separate. There were three layers in the

Table 1. Shows catalyst source calcination temperature and codes.

Catalyst source,	calcined temperature	codes
Pila globosa shell treated with 1 M H_2SO_4. Catalyst 1	600˚C	(PTW1M)
Pila globosa shell Catalyst 2	800˚C	(CP8)

funnel. The first layer was the catalyst layer. The second was the frost the third was the FAME Produced The percentage of FAME yield or conversion was calculated. The produced biodiesel (methyl ester) was characterized for its biodiesel properties according to ASTM standards [19].

$$\text{FAMEYield}(\%)=\frac{\text{Weight of Raw seed oil}(\text{g})}{\text{Weight of biodiesel}}\times\frac{100}{1} \tag{2}$$

3. Result and Discussion

All the tests done for physicochemical chemical properties of *Hydnocarpus weightiena* oil were according to standards [22]. **Table 2** showed the characteristics of *Hydnocarpus weightiena* seed oils. The oil from *Hydnocarpus weightiena* was dark red in color. The percentage oil yield of *Hydnocarpus weightiena* was 55.00%. The percentage oil yield of *Hydnocarpus weightiena* seed oil compared favorably with majority of the known seeds oils like soya bean (11.25%) cotton (18.28) *Afzelia africana* (30.5) *Triculia africana* (45.00%). The result of the physicochemical properties shows that the seed contains an excellent quantity of oil. It is among the top oil containing seeds ideal for commercial biodiesel production. The oil yield was high and commercial extraction of the oil is possible. The oil will be best extracted by solvent extraction [23].

The saponification value of the seed oil of *Hydnocarpus weightiena* suggests that the oil will be good for making liquid soap and shampoo due to its high saponification value. The seed oil of *Hydnocarpus weightiena* is not edible due to its relatively high acid value. The high acid value of 33.66 mg/g for *Hydnocarpus weightiena* was recorded, which is high compared to that of breadfruit seed oil is 7.38 mgKOH/g, butter oil which is 1.79 mgKOH/g and cashew, 10.7 mgKOH/g 18

Table 2. Physiochemical properties of *Hydnocarpus weightiena* seed oils.

Parameters	*Hydnocarpus weightiena*
Appearance	Dark red.
Acid value	33.66
Free fatty acid	16.83
Iodine value	99.37
Saponification value (mgKOH)	2552.55
Peroxide value (meq·Kg^{-1})	5.60
Calorific value	45.12
Oil yield	55.00%
Flash point (˚C)	56.00
PH	6.40
Viscosity mm^2/s	24.62
Ash content	0.01

avocado seed oil 16.8 mgKOH/g. Excess of acid vale could be removed by alkaline wash (purification) [24]. The peroxide value obtained in the analysis is below those reported by Akpan *et al.* [25]. Which was 28.8 mg/kg and 126.4 mg/kg for avocado and native pears respectively. Peroxide value correlates with the extent to which oxidative rancidity has taken place in oil, and thus a measure of the shelf life of the vegetable oil. With the low peroxide value obtained shows that the oil is not highly oxidized and therefore will be generally acceptable for the absence of odor and flavour in its content. Otorio [24] reported that oil becomes rancid when peroxide value range from 20.0 to 40.0 mg/g. Therefore it has a low susceptibility to oxidative rancidity and deterioration as confirmed by the peroxide value which also serves as indicators of the presence or high levels of anti-oxidants in the oils [24].

The low iodine value of the samples placed the oils as non-drying oils, and such, they could not be used for the production of resin as plasticizers in plastics or vanishes. *Hydnocarpus weightiena* has iodine value of 99.37. Ogbu and co-workers said that such oils are not likely to polymerize and oxidize at higher temperature. Iodine value is used to determine the level of unsaturation in fatty acids. The higher the iodine value, the more unsaturated then the faster the oil can oxidize and polymerize. The greater the degree of unsaturation, the more vulnerable the oil is to lipid peroxidation unless antioxidant was used to remedy the situation. High iodine values are always reported as being associated with polymerization and subsequent engine damage. Biodiesel made from this oil can pass on the same effect as the vegetable oil when they are used as feedstock Vegetable oils with low iodine value like *Hydnocarpus weightiena* can be used directly in the diesel engine without further processing due to their low iodine value [25]. All that is required is just extraction and purification. Vast majority of vegetable and animal oils have iodine value that can cause problem in the engine if used as neat fuel. Iodine values are very important because many fuel standard for iodine value for biodiesel is highly dependent on the nature of the feed [25].

Hydnocarpus weightiena oil had an ash content of 0.1 % which showed that it had low quantity of microelements. The low ash content also confirmed that the oil contained burnable materials which make them less likely to contribute to injector, fuel pump, piston and ring wear. Ejija *et al.* in a separate study reported an ash content of 1.4% for Sclerocarya birrea seed oil [24]. The high calorific values for the samples showed that the seed oil has high energy content hence it will give off energy that will be utilized to power the engine [23]. The pH value of the oil as presented in **Table 3** is (6.4). This value is within the range according to Elijah [26] for biodiesel production. The pH for this oil is less than seven due to the presence of fatty acid content [26].

3.1. Characterization of *Pila glabosa* Sea Snail Shell

RPGS from the EDX analysis results in **Table 3**, it was observed that the raw *Pila globosa* shell contained carbon Atomic conc. 32.37%, Oxygen Atomic conc. 40.27% Calcium contained Atomic conc. 13.64. Finally Tellurium contained atomic conc. of 13.37. They are the elements present in the samples. Element presents are represented in the peaks. The height of the peak represents the concentration. The raw sample contains a lot of calcium carbonate. Tellurium was also present in the sample. Furthermore, **Figure 2** shows the EDX Spectrum of the elemental composition of *Pila globosa* sea snail shell calcined at 800˚C (CP8). **Table 4** shows the EDX result of the elemental composition of *Pila globosa* sea snail Shell calcined at 800˚C (CP8). From the EDX analysis results, it was observed that in the calcined sample, the elements contained are oxygen Atomic conc. 21.85%. Then, calcium Atomic conc. of 37.83% and Tellurium contained atomic conc. of 40.32 weight conc. Those elements are traditionally present in any snail shell as reported by Otori [24]. Volatiles like carbon were vaporized and calcium oxide was formed [24]. Tellurium remained in the *Pila globosa* after calcination. Panel *et al.* [26] argued that such an element can induce synergetic effect and make the catalyst better. The result shows that ash from snail shells contained CaO considered a favorable base catalyst in biodiesel production with high basic strength, minor toxicity and easy reactions [24]. **Table 5** showed the EDX analysis results. It was observed that *Pila globosa* Shell treated with 1 M H_2SO_4 acid and calcined at 600˚C contained the following elements, sulphur of atomic conc. 9.09%, oxygen, oxygen Atomic conc. 46.39% Calcium, Atomic conc. of 26.55% and Tellurium contained atomic conc. of 17.97. Due to the element sulphur present. PTW1M6 is an acid catalyst [19]. It could be argued that Calcium sites were basic and that sulphur sites could be regarded as Lewis acidic and surface containing hydroxyl group acted as the Brönsted acids [27] [28]. Heterogeneous acid catalysts have a less corrosive and toxic effect and give rise to fewer environmental problems compared to homogeneous acid catalysts. Treatment with 1 M H_2SO_4 acid did not interfere with Calcium Telluride hence the special qualities it conferred in the catalyst made it very active. [28]. Faruque *et al.* agree with this [29].

Table 3. The elemental composition of raw catalyst (RPGS).

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
52	Te	Tellurium	13.72	52.57
8	O	Oxygen	40.27	19.34
20	Ca	Calcium	13.64	16.41
6	C	Carbon	32.37	11.67

Table 4. Showed the elemental composition of *Pila globosa* sea snail Shell calcined at 800˚C (CP8).

Element Number	Element Symbol	Element Name	Atomic Conc.%	Weight Conc.%
52	Te	Tellurium	40.32	73.39
20	Ca	Calcium	37.83	21.63
8	O	Oxygen	21.85	4.99

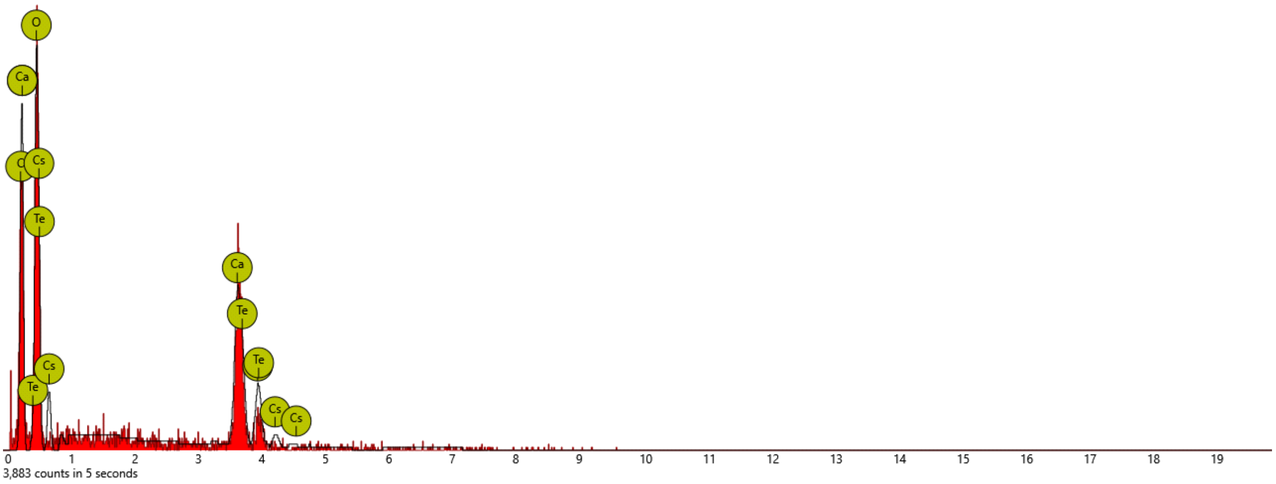

Figure 1. EDX spectrum. The elemental composition of raw *Pila globosa* shell.

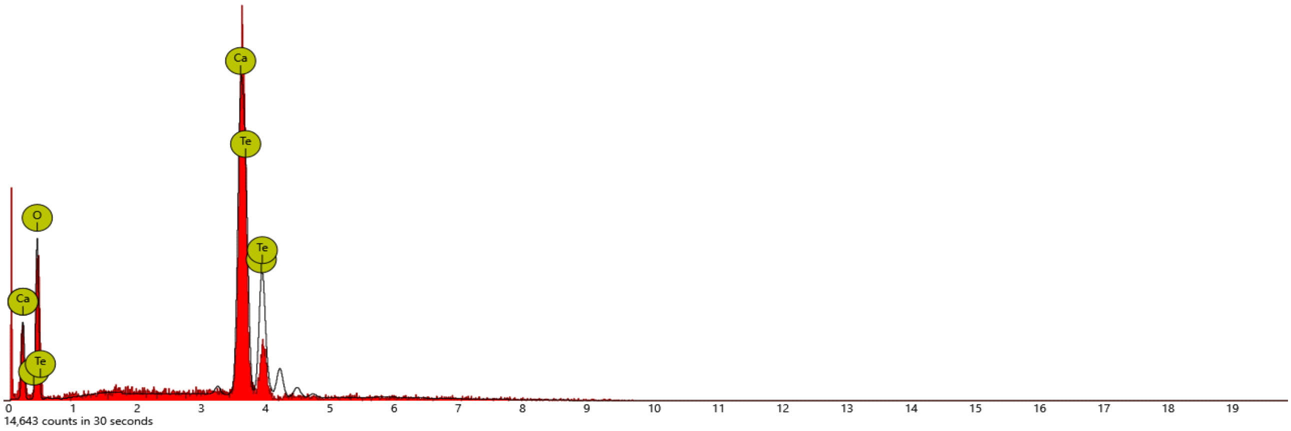

Figure 2. The plot of the elemental concentration of of *Pila globosa* sea snail Shell calcined at 800˚C (CP8). The height of the plot represents the concentration.

Table 5. shows the elemental composition of the catalyst treated with 1 M H_2SO_4 acid and calcined at 600˚C (PTW1M@6.)

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
52	Te	Tellurium	17.97	52.22
20	Ca	Calcium	26.55	24.23
8	O	Oxygen	46.39	16.91
16	S	Sulfur	9.09	6.64

3.2. Scanning Electron Micrograph of the Shell Raw Calcined and Acid Treated *Pila globosa* Sea Snail Shell Catalyst

Figure 4. Showed The Scanning electron micrograph of the Raw *Pila globosa*

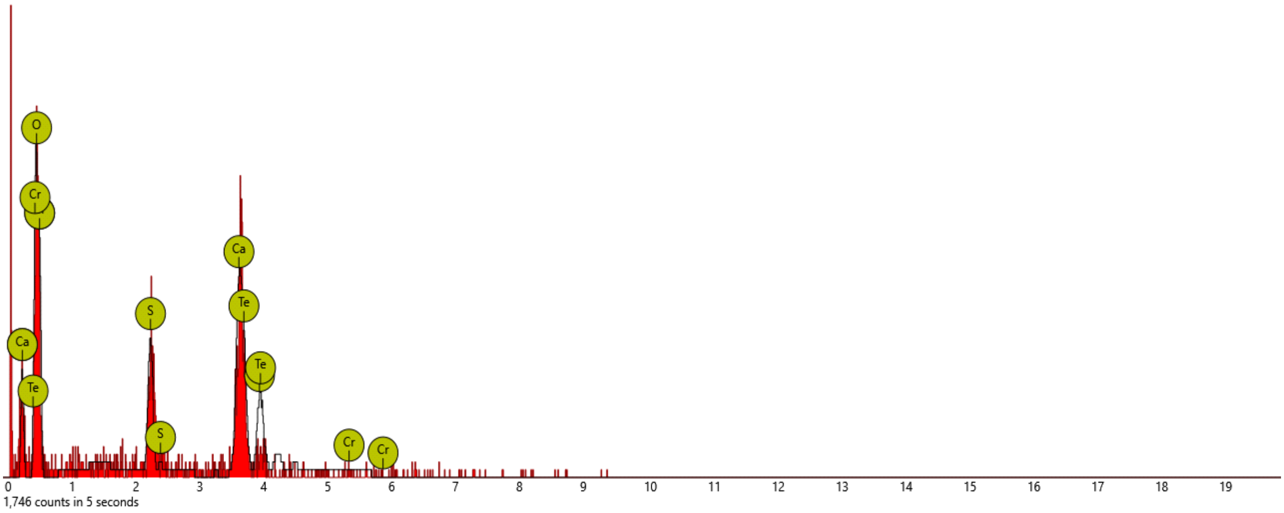

Figure 3. EDX Spectrum The elemental composition of *Pila globosa* Shell treated with 1 M H_2SO_4 acid and calcined at 600˚C (PTW1M).

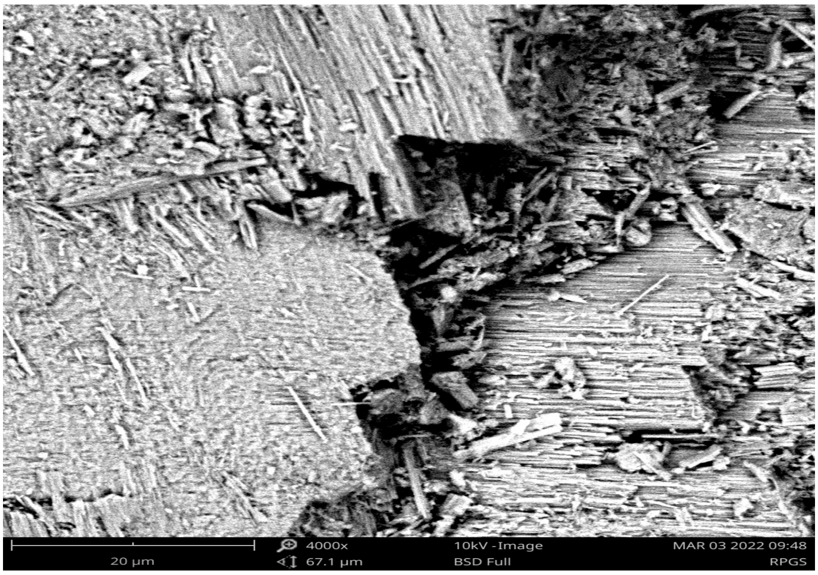

Figure 4. Scanning electron micrograph of the Raw *Pila globosa* shell (RPGS).

shell (RPGS The morphology of the raw showed agglomeration with little or no pores. **Figure 5** and **Figure 6** showed the micrograph of the calcined and acid treated sea snail shells respectively. From the micrograph, raw sample contrasts strongly with that of the calcined and acid treated sample [23]. The catalyst samples at similar magnification showed bulk agglomeration with fine pours for calcined and acid treated. Whereas the raw sample showed little or no pours at all. [24]. The morphology of CaO CaO_3Te with irregular pores, shapes and size, varying from one surface to another (at a magnification of 4000 µm). The shape of the calcined and acid treated shell was formed by tiny crystals embedded in the large particles; probably due to the heterogeneous distribution in the mechanical properties of the sea snail shell used which can be regarded as an

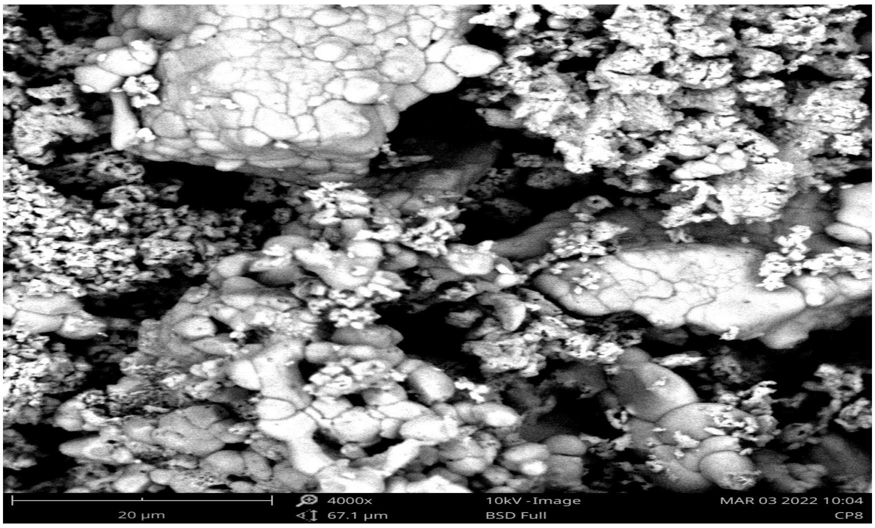

Figure 5. Scanning electron micrograph of the *Pila globosa* shell shell Calcined at 800˚C (CP).

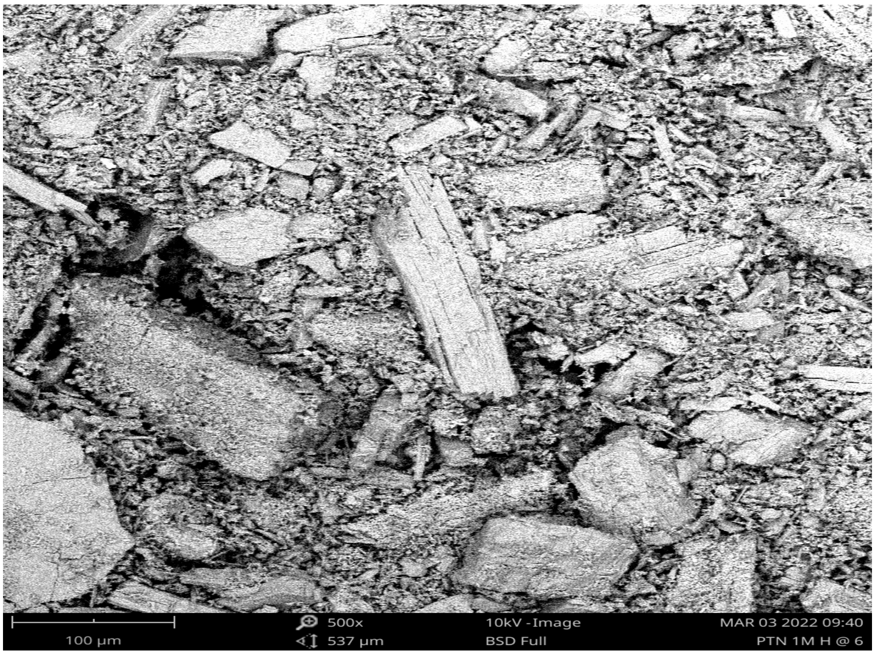

Figure 6. Scanning electron micrograph of Acid treated *Pila globosa* shell Calcined at 600˚C The micrograph of raw (PTW1M).

attribute of high catalytic activity as reported by Otiro and Ekeoma in their separate studies [23]. This characterization of the heterogeneous morphology of CaO from the uncalcined sea snail shell has been noted previously under similar conditions [23] [24].

3.3. Results of the (DTA/TGA) Analysis for Raw, Calcined and Acid Treated *Pila globosa* Shell

Figure 7 showed the thermogram, of raw *Pila globosa* sea snail shells. From the thermogramme, (the green line) it could be observed that 100% of the sample

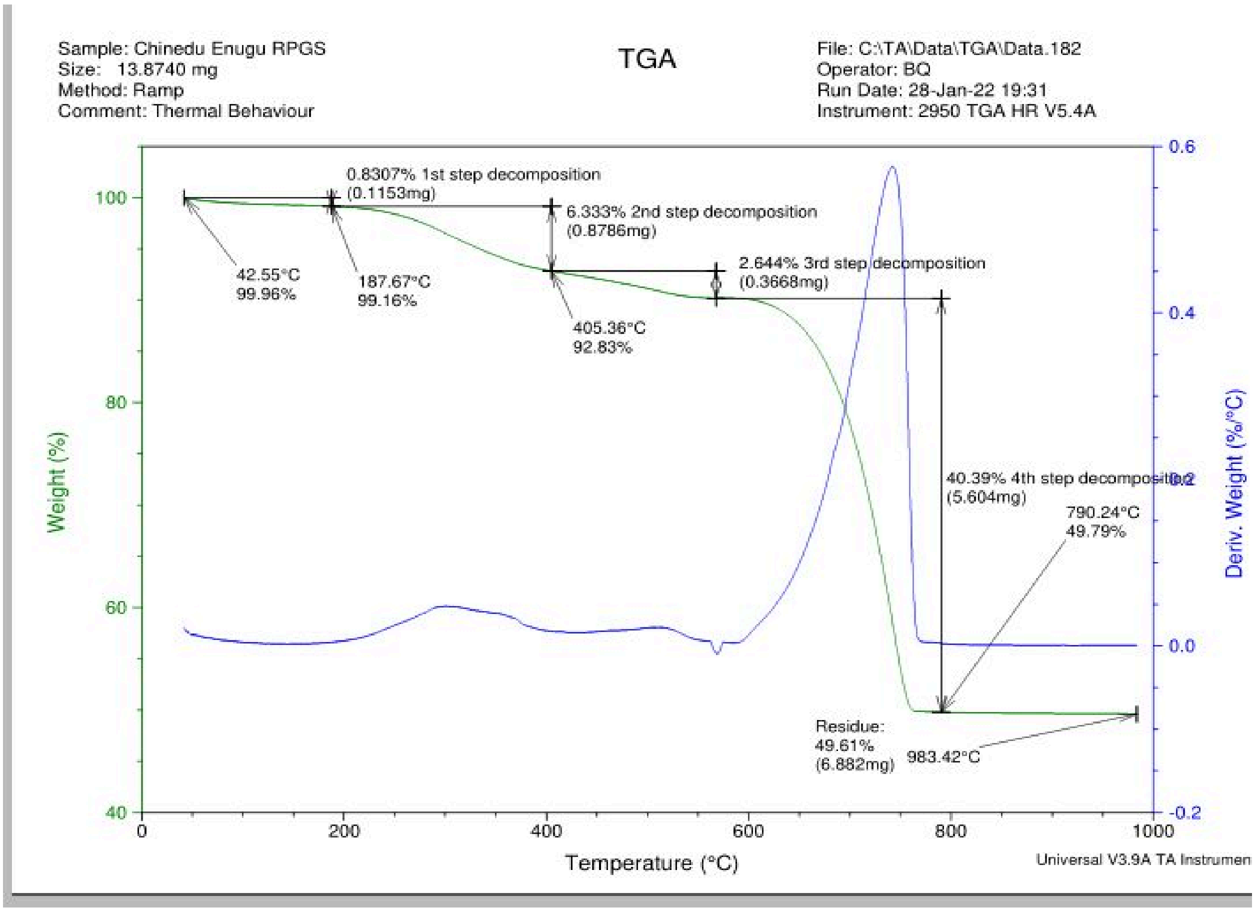

Figure 7. Shows the results of the (DTA/TGA) analysis for Raw *Pila globosa* shell.

was Stable at 42.55˚C. However there was the slight weight loss that started at 42.55˚C where 0.8307% of the sample representing 0.1158 mg of the sample was decomposed. A residue of 99.96% remained. It was also shown by the derivative (the blue line) as a slight peak at the same temperature. That was recorded as first step of decomposition. There was another weight loss at the temperature of 187˚C where 6.333% of the sample representing 0.8766 mg of the sample was decomposed. A residue of 92.83% remained. It was also shown by the derivative (the blue line) as a slight peak at the same temperature. That was recorded as 2nd step of decomposition. There was yet another weight loss at the temperature of 405.36˚C where 2.644% of the sample representing 0.3668mg of the sample was decomposed. It was also shown by the derivative (the blue line) as a slight peak at the same temperature. That was recorded as 3rd step of decomposition. Finally another weight was lost at the temperature of 790.24˚C where 40.39% of the sample representing 5.604 (mg) of the sample was decomposed. A residue of 49.79% remained. It was also shown by the derivative (the blue line) as a bold peak at the same temperature. That was recorded as 4th step decomposition. That was major exothermic weight loss. TGA curve corresponded to the decomposition and desorption of the sample. The TGA analysis Confirmed that the proper temperature for calcination was 800˚C which was the position of Okeahialam and co-workers [30]. $CaCO_3$ and CaO_3Te are believed to be the major component of the sample as revealed by SEM EDX analysis. $CaCO_3$ was converted to CaO and CO_2 at that temperatures range [24]. **Figure 8** showed the results of the (DTA/TGA) analysis of Calcin [ed *Pila globosa* shell @ 800˚C (CP8). From the thermogram, (the green line) it could be observed that 100% of the sample was Stable at 34.68˚C. However, there was a weight loss that started at 587.83˚C and continued till 783.93˚C. At 587.83˚C, 0.0933 mg of the sample representing 1.097% of the sample was decomposed. A residue of 98.90% remained. It cannot be quite identified by the derivative (the blue line) as a peak at the same temperature range because it is very small. It was recorded as first decomposition peak. At 783.93˚C, 2.909 mg of the sample representing 43.55% of the sample was decomposed. A residue of 55.34% remained. It was recorded at the derivative (the blue line) as a bold peak at the same temperature range of 587.83˚C and 783.93˚C. It was recorded as second decomposition peak which was a major exothermic weight loss. It was recorded as the TGA curve corresponded to the decomposition and desorption of the sample. Sample almost did not decompose except at 783.93˚C. So 800˚C is proved to be the correct temperature for calcination.

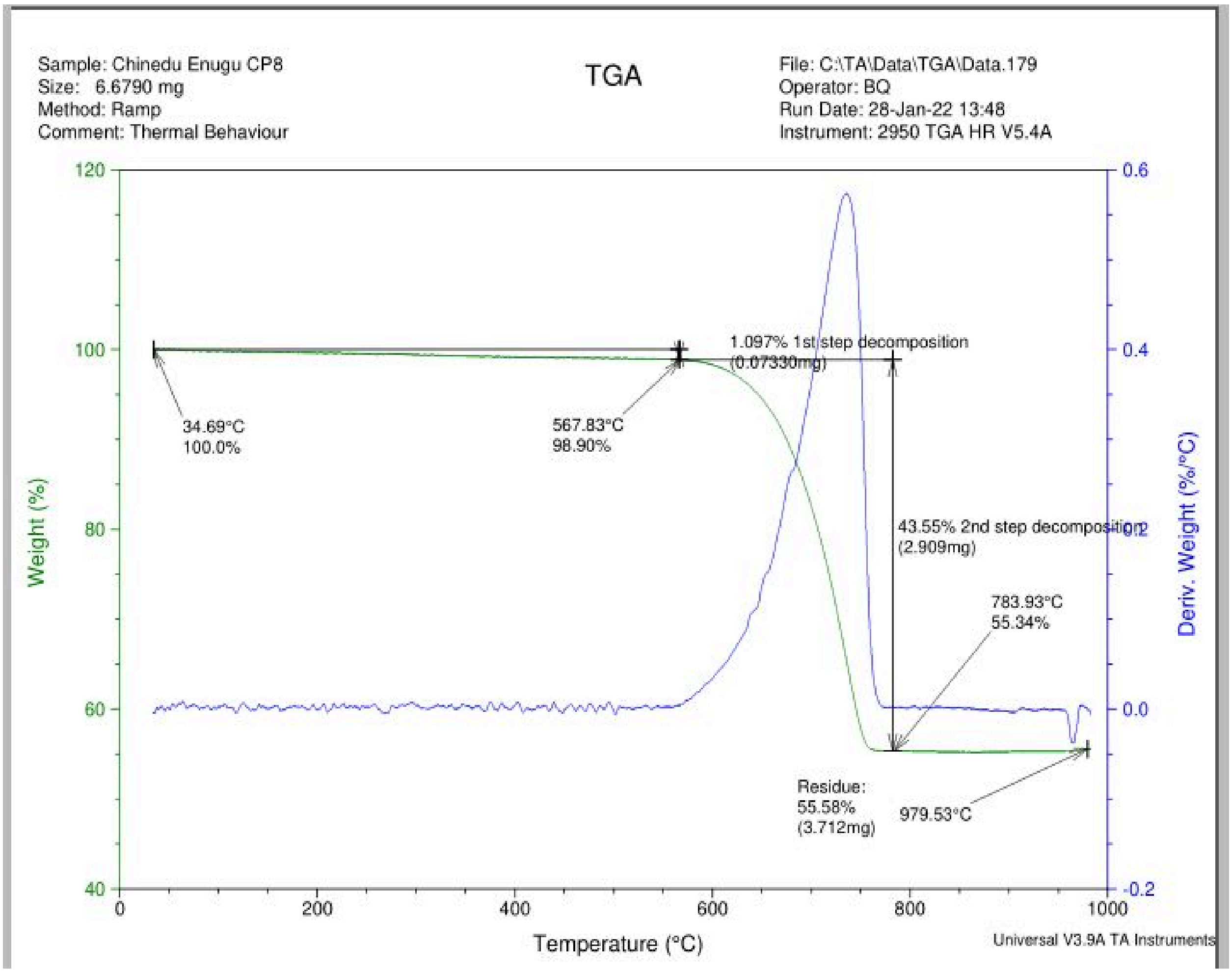

Figure 8. Shows the results of the (DTA/TGA) analysis for *Pila globosa* shell calcined @ 800˚C (CP8).

Similar trend was reported by Odude *et al.* [31]. **Figure 9** also showed the results of the (DTA/TGA) analysis of *Pila globosa* shell treated with 1 M H_2SO_4 (PTW1M6) Calcined at 600˚C. From the thermogram, (the green line) it could be observed that 100% of the sample was stable at 34.68˚C. However there was a weight loss that started at 594.64˚C and continued till 787.09˚C. 4.075 mg of the sample representing 37.84% of the sample was decomposed. A residue of 63.03% remained. The thermogram is similar to that of CP8. This shows that calcination gets rid of impurities like water and volatile matter and opens up the pores as active sites for reaction [24] [30] [31].

3.4. Infra-Red Spectra of Raw *Pila Globoa* Shell (RPGS)

The Infra-Red spectra of Raw *Pila globosa* Shell (RPGS) were shown in **Figure 10** major absorption bands were observed at 2915 which are attributed to the asymmetric stretching vibration, and mode of carbonate species. (CO_3^{2-}) in the catalyst surface [30]. Other bonds occurred at wavenumber 1785cm^{-1}, 1448 cm^{-1}, 1082 cm^{-1}, 857 cm^{-1} and 712 cm^{-1}. The wavenumbers that are signature or characteristic absorption for carbonate ions are 1792, 1479, 1082, 855, 711, cm^{-1} [31]. The non-alignment of the wave number can be attributed to the presence

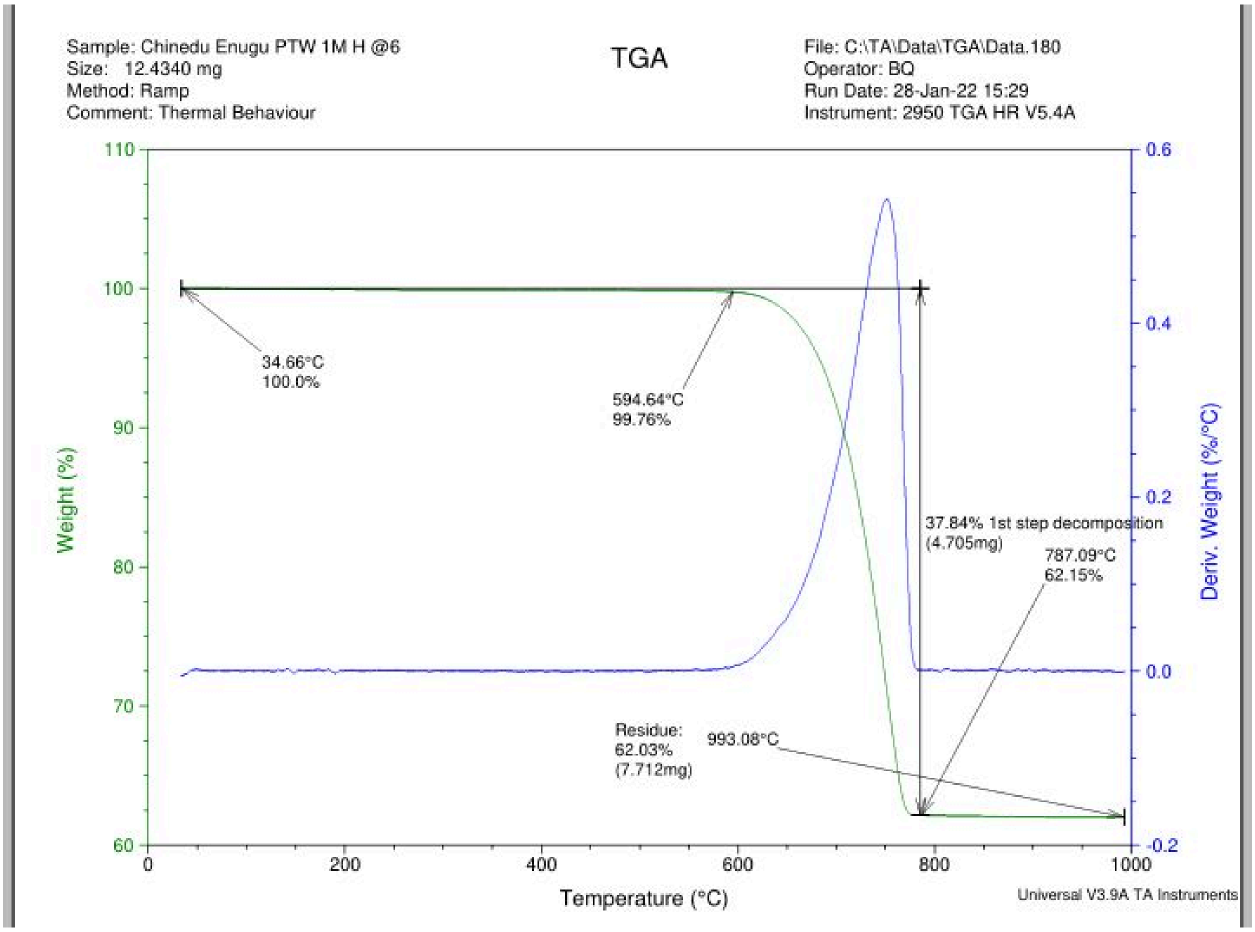

Figure 9. Showed (DTA/TGA) curve of *Pila globosa* shell treated with 1 mole H_2SO_4 Calcined at 600˚C. (PTW1M).

Te in the compound. The broad band at 1448 cm^{-1} indicates the presence of, (CO_3^{2-}). It was the most intense peak. That absorption band can be ascribed to the asymmetric stretching of (CO_3^{2-}) molecules [30]. The other two major absorption bands observed at 857 and 712 cm^{-1}, can be ascribed to the out-of-plane band and the in-plane band modes of vibration patterns of sea snail shells according to Alonso *et al.* [32]. The Infra-Red spectra of *Pila globosa* Shell calcined at 800˚C (CP8) shown in **Figure 11**. The FTIR Spectrum of the *Pila globosa* Shell calcined at 800˚C (CP8) for 1 hrs has shown major shifts and changes in the absorption bands. Absorption was observed at 2511 and 1793 cm^{-1}, the shifts were attributed to the asymmetric stretching vibration, mode of carbonate

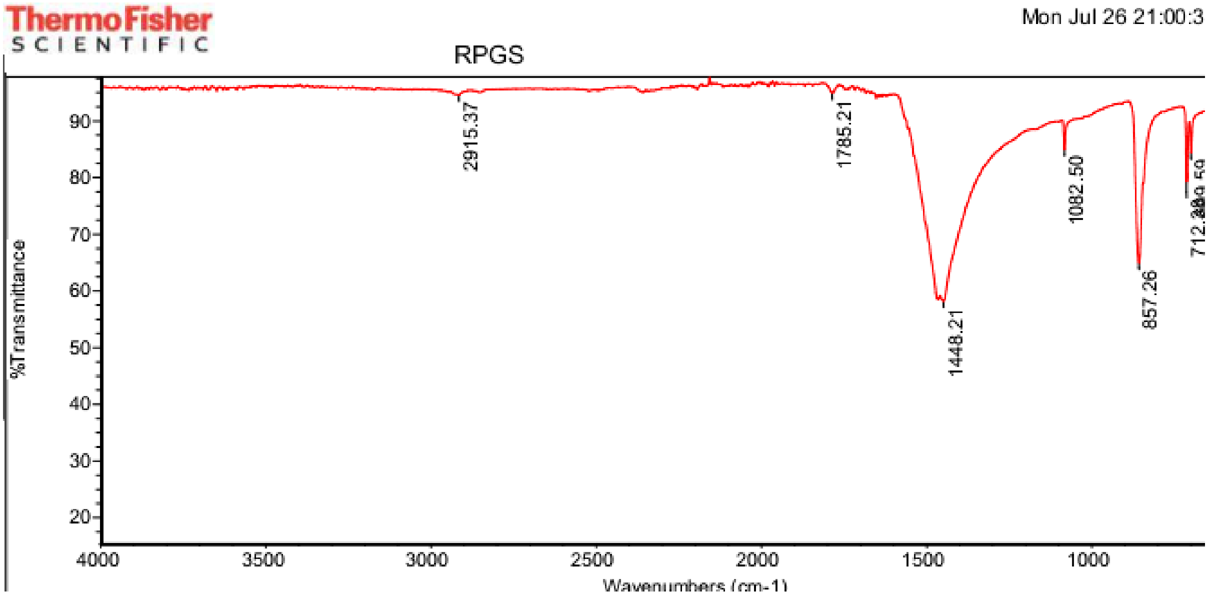

Figure 10. Infra-Red Spectra of Raw Pila Globoa Shell (RPGS).

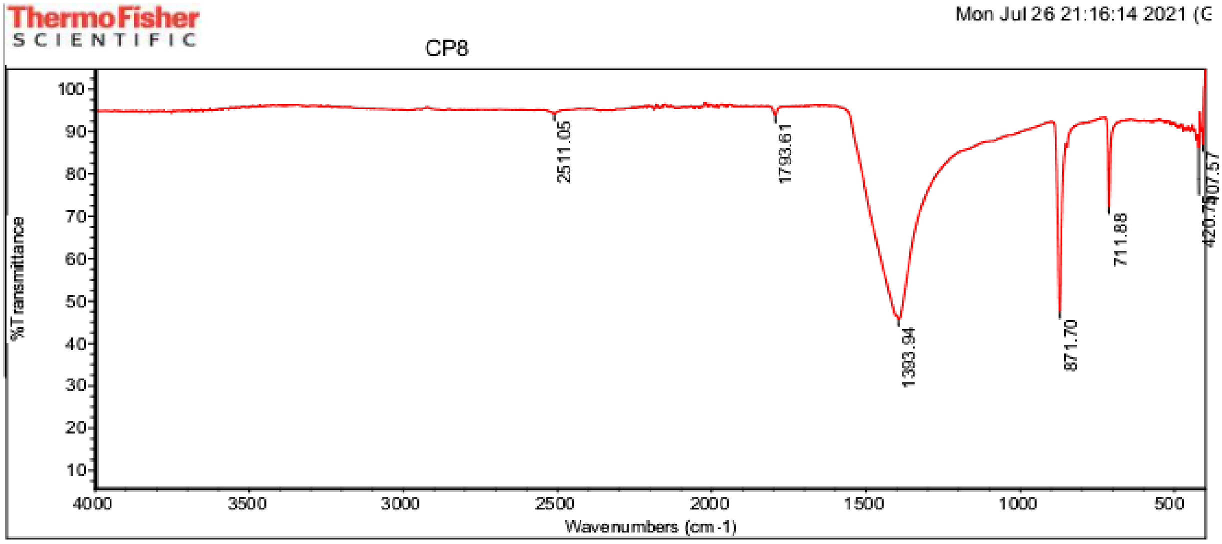

Figure 11. Infra-Red Spectra of Pila Globoa Shellcalcined at 800˚C (CP8).

species (CaO) in the catalyst surface. The raw catalyst had the peaks at 2915 and 1785 cm^{-1}, so the shift to a lower wave number of 2511 was as result of the conversion of the (CO_3^{2-}) to CaO [30]. Very prominent peak occurred at wavenumber 1363 instead of 1448, the absorption is due to the formation of CaO, then the bond at 1082 disappeared completely due to calcination [33]. A very sharp peak occurred at 871 cm^{-1}. This peak can be attributed to the formation of CaO_4Te (Calcium Tellurate). **Figure 12**. Infra-Red Spectra of *Pila globosa* treated with 1 M H_2SO_4 and Calcined at 600˚C (PTW1M) was shown in Figure 4.2.9 absorption bands were observed at 2508 and 1794 cm^{-1}, which are attributed to the asymmetric stretching vibration, mode of calcium oxide species. (CaO) in the catalyst surface [30]. The raw catalyst had the peaks at 2915 and 1785 cm^{-1}, so the shift to a lower wave number of 2508 was as result of the conversion of the (CO_3^{2-}) to CaO. Other prominent peaks occurred at wavenumber 1394, 1112, 872,711, 675, 614 cm^{-1}, etc. The peak at 1112 cm^{-1} was due to the formation of $CaSO_4$. The wavenumber for the absorption of $CaSO_4$ ranges from 1100 - 1200 [32]. The EDX analysis of the sample confirmed the formation of $CaSO_4$. The sharp Peak at 871 cm^{-1}, is Calcium tetraoxotellurate CaO_4Te. More peaks are observed in the sample of Pila *Pila globosa* treated with 1M H_2SO_4 and Calcined at 600˚C (PTW1M). This is because of formation of other groups when the compound was treated with 1 M H_2SO_4. It could be argued that the changes in the absorption band of raw, calcined and acid treated *Pila globosa* sea snail shell is as a result of the influence of CaO_4Te as reported by [34].

3.5. Optimization of Process Parameter for Transesterification Reaction

In this study, four process parameters affecting the transesterification reaction

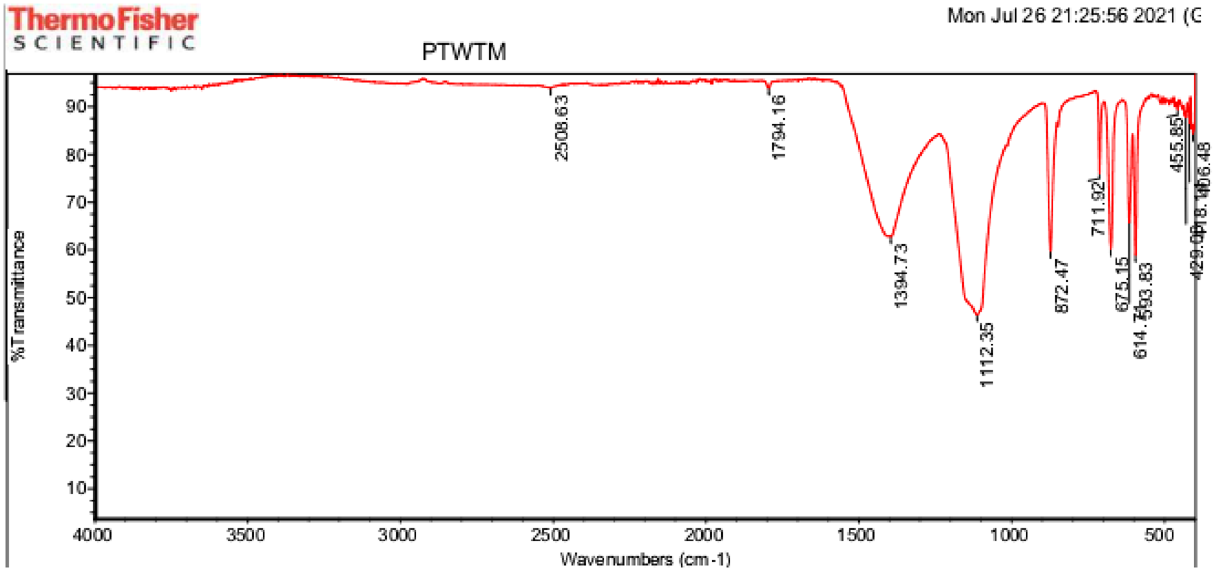

Figure 12. Infra-Red Spectra of Pila Globoa Shell treated with 1 M H_2SO_4 and Calcined at 600˚C (PTW1M).

namely catalyst loading or concentration, temperature, reaction time and agitation speed were determined for optional biodiesel production using the two catalysts of CP8 and PTW1M.

3.5.1. Effect of Catalyst Concentration

The result obtained from **Figure 13**, showed that the catalyst concentration increases from 1 wt% - 3.5 wt%, a progressive increase in percentage conversion in the reaction was achieved and thereafter a decrease in yield above this concentration (2 wt% and 3 wt%) for CP8 and of PTW1M Catalyst respectively was observed. It was obvious that an increased in catalyst concentration beyond 2 wt% and 3 wt% of catalyst resulted in a decrease in biodiesel yield as was shown in the graph. Okeoma and co-workers reported 3.00 wt% while Olutoye and Hammed reported 3.32 wt% as the optimum catalyst loading. The researchers working on heterogeneous catalysts made similar findings [30] [35].

Other Reaction conditions are temperature 60˚C, reaction time 70 min, mole ration (3:1). Then 800 rpm for CP8 and temperature 70˚C, reaction time 60 min, mole ration (3:1). PTW1M gave optimum yield when the rpm was 600.

3.5.2. Effect of Temperature

Temperature plays an important role during chemical reactions. Biodiesel production is inclusive. This is because the rate of reaction is strongly influenced by the reaction temperature. **Figure 14** showed the result of temperature variation from (40˚C - 80˚C) at a catalyst concentration of 2 wt% and 3 wt%. As the temperature increases from (40˚C - 60˚C) the conversion yields of biodiesel also increase for CP8 considerably. While for PTW1M, the optimum temperature was observed at 70˚C. Further increase in temperature beyond 60˚C for CP8 and 70˚C for PTW1M, resulted in decrease in the yield of biodiesels. This finding was also confirmed by many other researchers [24] [30]. Oterio *et* al [24] reported 55˚C, Olutoye *et al.* reported temperature of 182˚C. In this study, optimum temperature for the production of biodiesel was 70˚C.

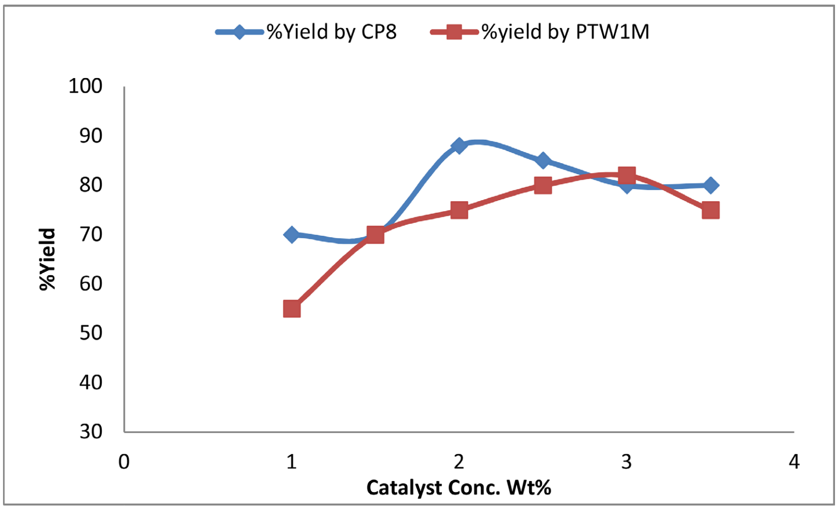

Figure 13. Effect of catalyst loading on the percentage conversion of oil to biodiesel.

Other Reaction conditions are temperature 2 wt%, reaction time 70 min, mole ration (3:1). Then 800 rpm for CP8 and temperature 3 wt%, reaction time 60 min, mole ration (3:1). Then 600 rpm for PTW1M.

3.5.3. Effect of Reaction Time

Figure 15 reflects optimum transesterification time for *Hydnocarpus weightiena* seed oil. The maximum biodiesel yield was obtained at 70 min. for CP8 and 60 mins for PTW1M. The yield was found to be 90% and 87% respectively. At first few minutes, the reaction time was slow due to dispersion of interaction between molecules was still in progress [35]. As the reaction time increases, the yield also increased due to the highly effective collision occurring. Beyond the reaction time of 70 min and 60min for each of the catalysts, there was decrease in the yield of the biodiesel. The yield at those times is optimum time is 90% and 87% respectively. Some researchers have reported similar findings [30].

Other Reaction conditions are temperature 2 wt%, reaction time 60˚C, mole

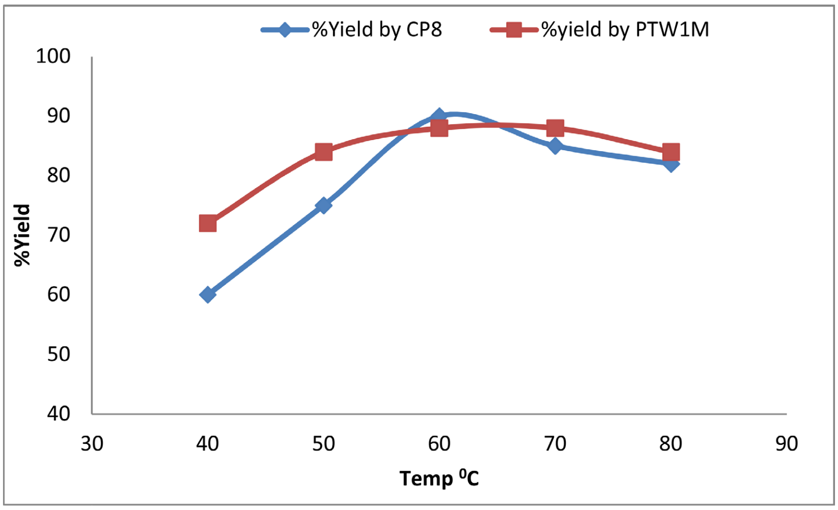

Figure 14. Effect of temperature on the percentage conversion of oil to biodiesel.

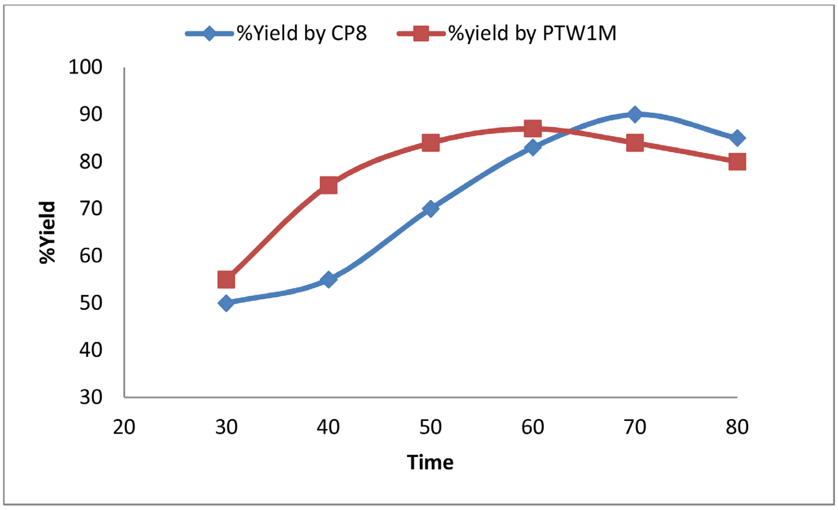

Figure 15. Effect of time on the percentage conversion of oil to biodiesel.

ration (3:1). Then 800 rpm for CP8 and temperature 3wt%, reaction time 70˚C, mole ration (3:1). Then 600 rpm for PTW1M.

3.5.4. Effect of Agitation Speed (rpm)

The effect of agitation speed on biodiesel yield was shown in **Figure 16**. Agitation keeps the reacting particle in motion. Increased agitation increases the chance of a collision as well as effective collision and the yield [34]. *Hydnocarpus Weightiena* methyl ester (HME) had the optimum yield at 800 rpm and 600 rpm for CP8 and PTW1M. Beyond those, the yields are decreased. Asir and co-workers made similar observations [36].

Other Reaction conditions are temperature 2 wt%, reaction time 60˚C, mole ration (3:1) time of 60 mins for CP8 and temperature 3 wt%, reaction time 70˚C, mole ration (3:1) and time of 70 mins for PTW1M.

Fuel properties of the produced from *Hydnocarpus weightiena* seed oil and that of fossil diesel are compared with the biodiesel standard (ASTM 6751) and are presented in **Table 6**. Kinematic viscosity is a measure of the resistance of fluid flow under the influence of gravity [30]. The result from this work shows a kinematic viscosity of 4.03 at 100˚C and 17.99 at 40˚C which is varied with the ASTM However blending the biodiesel with fossil diesel lowers the viscosity and makes it conform to the standard. Most of the result is however standards are in agreement with the ASTM. Viscosity of fuel is related to the fuel lubricity. Low viscosity fuels are unlikely to provide satisfactory lubrication in fuel injection pumps; these often lead to seepage and an increase in wear [37]. High viscosity in fuel is responsible for atomization of fuel, incomplete combustion and increased exhaust emissions, choking off the injections thereby forming larger droplets on injector, ring carbonization and accumulation of the fuel in the engine [23]. The result from this study shows that biodiesel from *Hydnocarpus Weightiena* seed oil can be used for biodiesel production Specific gravity of the fuel is very important in diesel engines because fuel injection system operates on a volume metering basis. The values of specific gravity obtained for *Hydnocarpus*

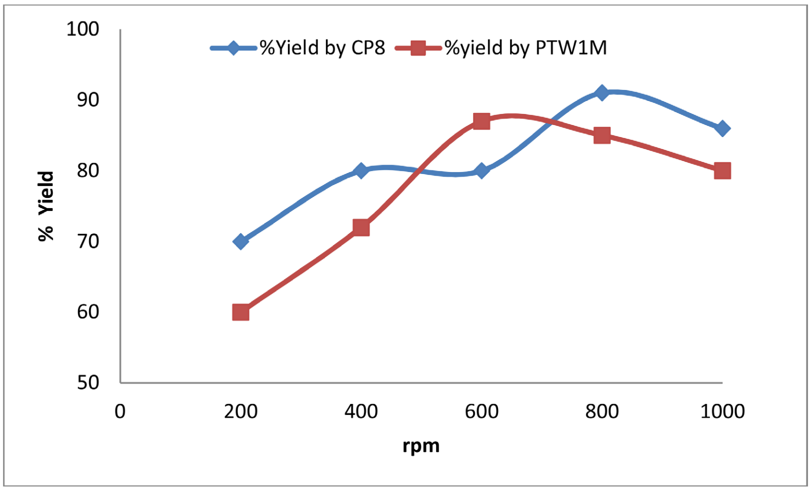

Figure 16. Effect of rpm on the percentage conversion of oil to biodiesel.

Table 6. Comparison of biodiesel properties and fossil diesel with ASTM standard [38].

Property	Biodiesel (HME)	ASTM 6751	Diesel
Ash content	0.00	0.05	0.02
Viscosiy@40˚C mm^2/s	17.99	1.9 - 6.0	1.13
Pour point ˚C	−9	−10	−1
Flash Point ˚C	85	Min 93	55
Water crackle point	–	0.05	–
Specific gravity	0.86		0.87
Calorific value (Kj/Kg)	45,124	Minimum 37.27	44,938
Acid value (mgKOH/g)	2.49	0.05	0.23
Carbon residue	0.03	0.05	1.17
Density ($g * mL^{-1}$)	8.60	8.60 - 9.00	8.70

weightiena seed oil methyl ester was 0.86 with a corresponding density value of 860 kg/m^3. This value lies within the notable standards and also in close proximity to the findings of other studies [30]. Flash point is the minimum temperature at which a fuel must be heated for it to ignite an air-vapor mixture. The U.S. Department of Transportation specified 90˚C as the flash point for non-hazardous fuel [23] [24] [25]. The flash point for this work is 85˚C. This result shows appreciable consistency with both ASTM, EN standards for biodiesel and works of other researchers. The high value obtained in this study clearly signifies that the biodiesel produced could be free from methanol; this is because even small quantity of methanol can reduce the flash point reasonably and also negatively affects diesel engine parts such as fuel pumps, seals and elastomers. The cloud and pour point are criteria used for low temperature performance of a fuel. This work reports values −9˚C pour point. These properties help to show the behavior of the biodiesel under a specified climate setting. This shows the biodiesel produced from *Hydnocarpus weightiena* can be used in cold climate regions [30].

3.6. Kinetic of the Transesterification Reaction Modeling

Kinetic of the Transesterification Reaction Modeling

Kinetic Modeling

Verification of Rate Constant and Order of Reaction.

Transesterification reaction is a reversible reaction that follows Equation (3)

$$\mathrm{RCOOH} + \mathrm{R'OH} \rightarrow \mathrm{RCOOR} + \mathrm{H_2O} \tag{3}$$

The reaction may exhibit pseudo-first order kinetics, in which the rate is controlled only by the concentration of free fatty acids (FFAs), and this is most likely to occur when the concentration of alcohol is high enough to remain nearly constant during the process. The rate can be expressed in terms of the disappearance of FFAs (A) as represented in Equation (4).

$$-d[A]dt = k[A] \tag{4}$$

Integrating Equation (4) Will Yield Equation (5) and the equation can be used to describe the substrate concentration variation in relation to time (4).

$$\ln[A]_t = -kt + \ln[A]_0 \tag{5}$$

where $[A]_0$ and $[A]_t$ represent the initial and final concentration of FFAs (mgKOH) after a time, *t*. Transesterification reactions can exhibit second order kinetic, in which the rate is determined by the concentrations of the two reactants (alcohol and FFAs), as shown in Equation (5), and this can occur when the alcohol to FFAs ratio is low.

$$-d[A]dt = k2[A][\mathrm{ROH}] \tag{6}$$

The values of the rate constant obtained from the experiment were used to determine the activation energy (*Ea*) through a plot Ink versus the reciprocal of absolute temperature according to Arrhenius Equation (5)

$$\ln k = (-Ea/R)/T + C \tag{7}$$

where *Ea* is the activation energy, *R* is the gas constant, *k* is rate constant and *C* is the constant. The plots are shown in **Figure 8** and **Table 6** and **Table 7**. Activation energy is the minimum amount of energy a reacting molecule must possess before a reaction can take place. The activation energies of methyl transesterification of the base oil sample of *Hydnocarpus weightiana* is 49.49 KJmol while the R^2 is 0.9866. The activation energies are determined from the experimental rate constants.

$$\text{Slope} = -Ea/R$$

$$-5952.5 = -Ea/R$$

$$R = 8.314\ \text{J/K·mol}$$

$$Ea = -(-5952.5)\ (8.314\ \text{J})$$

$$Ea = 49{,}489.085\ \text{J/mol}$$

$$\text{Activation Energy} = 49.49\ \text{KJ/mol}.$$

Figure 17 shows a plot of ln*K* versus 1/*T* plot. From the plot, the value of the activation energy was calculated to be 49.49 KJ/mol. Using the formula, Slope = −*Ea*/*R*.

Table 8 shows the activation energy of the reaction. The activation energy obtained is lower than that obtained by ethylation of C. Bateri 56.1 KJmol but slightly higher than that obtained by Methylation of C. Bateri *Ea* = 43.7 KJmol.

Table 7. Determination of activation energy for the second order methyl transesterification of *Hydnocarpus weightiena* methyl ester.

Temp (˚C)	Temp (K)	1/*T*(k^{-1})	*K*	ln*K*
30	303	0.0033	0.0287	−3.551
50	323	0.0031	0.1200	−2.120
70	343	0.0029	0.1142	−1.170

3.7. Catalyst Re-Usability

One of the most important advantages of heterogeneous catalysts over homogenous ones is the re-usability of heterogeneous catalysts.

CP8 and PTW1M were subjected to further transesterification after the initial use to determine their stability after several uses under their established reaction conditions. (Figure 18) At the completion of the reaction, the catalyst was recovered by separating the spent catalyst after each reaction cycle via centrifugation and washing with solvent (n-hexane) to remove any absorbent which is mainly the physic-sorbed oil. The washed catalysts were later dried in an oven at the

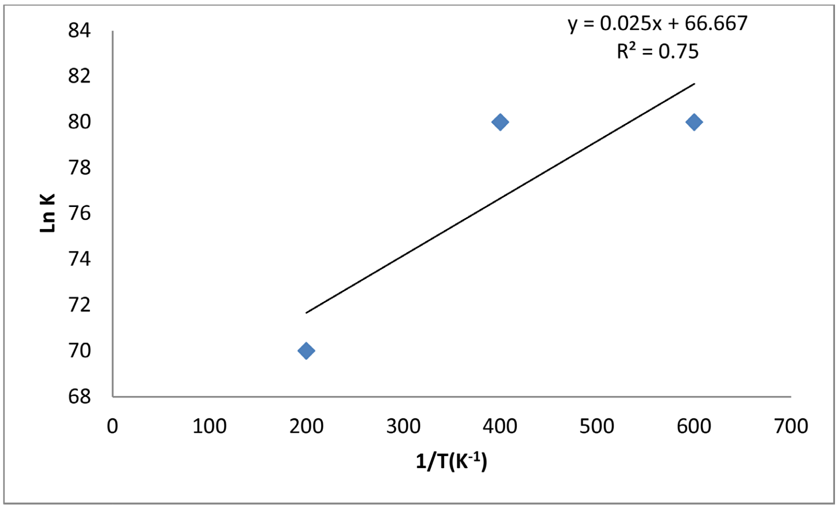

Figure 17. Determination of activation energy from plot of ln*k* versus 1/*T*.

Table 8. Shows the results for activation Energies of the methyl ester of *Hydnocarpus weightiena*.

Esters	*Ea* (KJmol)	*R*²
Hydnocarpus weightiena methyl ester	49.49	0.9866

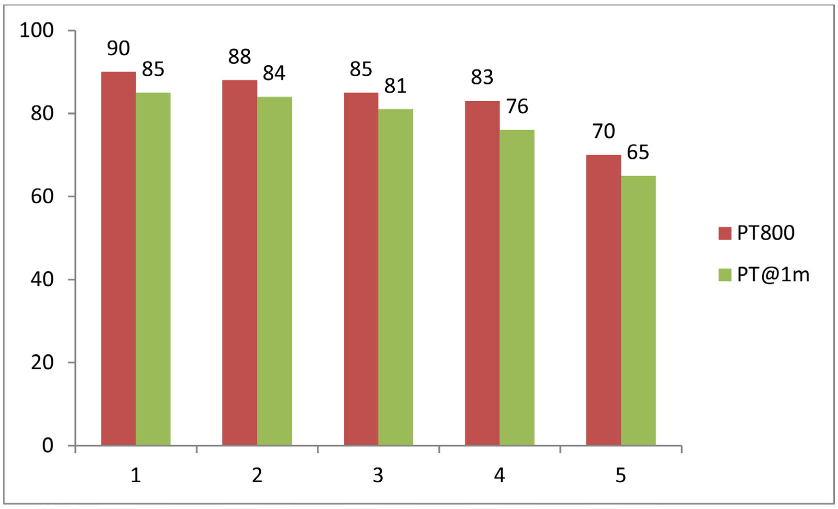

Figure 18. The reusability test of CPT8 and PTW1M.

temperature of 105˚C for 12 hrs before being used again in the transesterification of the seed oils. From the results, the catalysts lost its activity gradually up till the fifth run when it dropped to about 70% FAME yield. This reduction in the activity was probably due to the structural changes leading to its failure to maintain its form. The observed reduction in activity of the catalyst could also be due to the decrease in the catalyst quality due to the filtration and washing that followed each step. This might be attributed also to the deactivation of the catalyst by oil, moisture, CO_2 and other trapped impurities [30]. The leaching of soluble content and active elements of the solid base catalysts is one of the drawbacks of heterogeneous catalysts. Calcium oxide is slightly soluble in alcohol and could also lead to the reduction in quality of the catalyst. For the two catalysts, the stability is of the order PT@1M > PT800.

4. Conclusion

CP8 and PTWM are excellent catalysts for biodiesel production using *Hydnocarpus weightiena* seed oil. *Hydnocarpus weightiena* on its own is suitable for the production of biodiesel which has similar properties to petrol diesel. The oil yield of the seed is about 55% which is very high compared to other oil seeds. The optimum parameters for the biodiesel production were recorded at an agitation speed of 800 and 600 rpm, temperature 60˚C and 70˚C, catalysts concentration 2.00 wt% and 3 wt% and reaction time of 70 and 60 min and the highest yield of 92% and 85 methyl ester was recorded respectively. The result of the physiochemical properties shows that the oil is suitable for the production of biodiesel. The result of the fuel properties shows that the fuel fulfills most of the ASTM standards and can be used as a possible alternative to petroleum fuel. *Pila globosa* sea snail shell contains high percentage of calcined $CaCO_3$ CaO_4Te which can be used as alternative catalysts to the conventional (NaOH and KOH). The heterogeneous catalyst synthesis from the *Pila globosa* snail shell is cost effective compared to the homogeneous catalyst. Finally, at the end of the study, it was observed that the calcined catalyst (CP8) showed a superior catalytic performance as compared to the acid treated catalyst PTW1M.

5. Recommendation

This work on biofuel production from *Hydnocapus weightiana* Seed Oil Using Waste Natural Heterogeneous Catalyst recommends the cultivation of *Hydnocapus weightiana* since the oil content is of commercial quantity. It is equally recommended that *Pila globosa* snail shell calcined and acid treated should be used as a good heterogeneous catalyst for biofuel production. It is recommended that the government should fund research on biofuel production due to its immense benefits and environmental friendliness.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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