Characterization, Application and Optimization of Low Cost Heterogeneous Catalyst in the Production of Biodiesel Using Waste Vegetable Frying Oil

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ABSTRACT

The continuous hike in the price of diesel fuel and the environmental as well as health havoc caused by its utilization is answerable to the generation of a more sustainable alternative fuel. Therefore, in this research biodiesel is produced in the presence of H_2SO_4 wet-impregnated snail, egg and crab shell catalyst using waste vegetable frying oil (WVFO). The uncalcined egg, snail and crab shell catalysts were identified as CE, CS and CC respectively while $CS_{800}{}^{o}{}_{C}/H_2SO_4$, $CC_{900}\ {}^{o}{}_{C}/H_2SO_4$, and $CE_{900}\ {}^{o}{}_{C}/H_2SO_4$ represents calcined/impregnated snail, crab and eggshell catalysts respectively. Each of the calcined/impregnated snail, crab and eggshells were reacted singly with the WVFO for the biodiesel production. The fatty acid composition was determined using GC-MS. For the characterization of the catalysts, both the calcined/impregnated and the uncalcined catalysts were characterized using SEM, BET, FTIR, XRF and XRD. The Taguchi Orthogonal array design was the pattern adopted in the transesterification reaction in this study were the optimal conditions were obtained and the fuel properties of all 27 samples of WVFO biodiesel products determined. The result revealed the presence of both saturated (C – H) and unsaturated fatty acids (C ═ O). Saturated fatty acids such as palmitic and stearic acids were obtained at percentage concentrations of 2.50 % and 7.16 % respectively. The highest biodiesel yield was obtained at optimal conditions of 1:6 oil to methanol ratio, 3 wt% catalyst loading, 60 ^{O}C reaction temperature and 90 min reaction time traced from WVFO-crab shell biodiesel product obtained using the E specification/reaction conditions (WC_B). Results from the characterization of biodiesel products obtained from WVFO showed 79, 6.00 m^2/s and 926 kg/m^3 as maximum values of cetane number, kinematic viscosity and density traced from WS_E, WC_E and WC_E respectively. The fuel properties analyzed for all 27 biodiesel samples produced showed that some values obtained were in conformation with the ASTM standard while others were not.

Keywords: Transesterification, Heterogeneous Catalysts, Wet Impregnation

INTRODUCTION

Crude oil is a product obtained from carbonaceous materials such as natural gas, coal, petroleum etc. and as such fossil fuel will utmostly result in the emission of greenhouse gases, global warming and other sustainability issues [1-3] owing to the continuous rise in globalization and industrialization especially in developing countries [4, 5]. The continuous use of fossil fuel is said to cause serious environmental and health havoc arising from its toxicity, non-biodegradability and flammability [6]. This has triggered the energy enthusiasts, scientist and researchers in looking for a more sustainable and eco-friendly replacement for fossil fuel which is totally free from unburned hydrocarbon and carbon monoxide emission [7, 8]. Biodiesel has been found to be the most befitting for this position as it is constantly generated from agro-based products such as; agricultural and forestry by-products [9]. Biodiesel is a product obtained from an alcoholysis reaction when an oil or fat is reacted with an alcohol in the presence of a catalyst. Homogeneous catalysts are effective but the set-backs associated with them such as; high waste water output, difficulty in catalysts recovery and reusability, high energy consumption among others has qualified the use of heterogeneous catalyst especially the CaO – base catalyst in biodiesel production [5, 12, 20]. However, studies have shown that that the use of CaO – base heterogeneous catalysts consumes large amount of energy and causes leaching away of calcium ions from the CaO which gradually reduces the catalytic activity external surface active species in the reaction [11, 13]. Therefore, charging a heterogeneous base catalyst by wet impregnation can help to modify the catalyst's surface to meet the requirements of specific applications and solve the issues associated with the use of homogeneous as well as heterogeneous catalyst [5, 8]. Impregnating the metal oxides are highly beneficial as it enhances their basic and acidic strength, increase the surface area and stability. This can be achieved to build a CaO catalyst with both acidic and basic reactive sites with zero limitations.

Therefore the aim of this study is characterize, apply and optimize wet-impregnated crab, egg and snail shells in the production of biodiesel using waste vegetable frying oil. Optimization was carried out to determine the best reaction conditions that supports the production of a high biodiesel yield. This was achieved using the Targuchi Orthogonal array design as it allows for the simultaneous evaluation of four reaction conditions which are catalyst loading, temperature, time as well as oil to methanol ratio.

Therefore, charging a heterogeneous base catalyst by wet impregnation can help to modify the catalyst's surface to meet the requirements of specific applications and solve the issues associated with the use of homogeneous as well as heterogeneous catalyst [5, 8]. Impregnating the metal oxides are highly beneficial as it enhances their basic and acidic strength, increase the surface area and stability. This can be achieved to build a CaO catalyst with both acidic and basic reactive sites with zero limitations as there is total involvement of both internal and external [19, 20]. The use of edible vegetable oils such as soybean oil, rape seed oil etc. results in competition between the food and fuel oil market and as such, triggers a hike in the cost of purchase of vegetable oil and biodiesel. With zero competition, easy accessibility and unique adaptive features, waste vegetable frying oil oil has been found worthy, attractive and attainable by researchers and energy enthusiasts to be used in place of edible oils [10].

MATERIALS AND METHODS

2.1 Materials

Some of the materials utilized are; muffle furnace, desiccators, soxhlet extractor, centrifuge, separating funnel, retort stand, conical flasks, beakers, pipette & burette, water bath, magnetic stirrer heating mantle, thermocouple, reflux condenser, 500 mL round bottom 3 neck glass reactor, SEM-EDX, XRD, FTIR, XRF, GC-MS, and BET.

2.2. Reagents

Hydrochloric acid, ethyl alcohol, n- hexane, methanol, tetraoxosulphate (VI) acid, potassium hydroxide, phenolphthalein indicator, chloroform, potassium iodide solution. hanus solution, isopropyl alcohol.

2.3 Methods

2.3.1 Sample Collection

The waste vegetable frying oil (WVFO) used in this study is that whose major constituent is palm olein oil popularly known as Devon kings oil. This oil was collected in a clean pre-washed can after repeated frying from military shopping complex Oshodi, Lagos state while the snail shells were collected from a dumpsite at the popular mile one market, the egg shells were obtained from a campus restaurant in Yabatech and the crab shells from at bariga market, Lagos State.

2.3.2 Sample Pretreatment

2.3.2.1 Catalyst pretreatment

The egg, crab and snail shells were washed thoroughly with hot water and subsequently with distilled water. After washing, they were placed at 105 ^{O}C in an oven for 24 hr, crushed and sieved in a 60 mesh size sieve to separate the crystals from the fine particles. The egg and crab shells were calcined at 900 ^{O}C for 2 hr while the snail shell was calcined at 800 ^{O}C for 4 hr. For the impregnation method, about 100 g of each of the calcined shells were charged with 500 ml H_2SO_4 in drops while stirring using a glass rod, the mixture was stirred subsequently with magnetic stirrer for 6 hr and placed in an oven to dry at 105 ^{O}C for 24 hr. To ensure complete thermal dissociation, the shells were recalcined as the snail shell was placed in a muffle furnance at 800 ^{O}C for 2 hr while the egg and crab shells were recalcined at 900 ^{O}C for another 2 hr.

2.3.2.2 Catalyst identification

After pretreatment the catalyst were identified as;

Table 2.1: *Identification of Catalysts after Pretreatment*

Catalysts	**Uncalcined Catalysts**	**Calcined Catalysts**	**Calcined/Impregnated Catalysts**
Snail Shell	CS	$CS_{800\,^{o}C}$	$CS_{800\,^{o}C}/H_2SO_4$
Crab Shell	CC	$CC_{900\,^{o}C}$	$CC_{900\,^{o}C}/H_2SO_4$
Egg Shell	CE	$CE_{900\,^{o}C}$	$CE_{900\,^{o}C}/H_2SO_4$

2.3.2.3 Oil Pretreatment

The WVFO was collected in its crude form

2.3.3 Sample Characterization

The surface area, pore volume and pore diameter were determined using BET while the microstructure and surface morphology were revealed using the scanning electron microscope (SEM). On the other hand, the elemental and chemical compositions were both determined using XRF and XRD respectively and the organic composition obtained using the FTIR. These were determined for both the uncalcined and the calcined/impregnated catalyst samples. The crude WVFO was characterized using GC-MS to quantitatively determine the free fatty acid present in them.

2.3.4 Esterification and transesterification processes

The high FFA shown from the result of the physiochemical analysis is the reason for its subjection to acid esterification before the main transesterification process. A mixture of 0.14 ml of H_2SO_4 and 55 ml of methanol in a conical flask is heated in a water bath to attain a temperature of 60 ^{O}C. On the other hand, 100 g of the WVFO is also heated to attain same temperature. The content of the conical flask is added to the preheated oil and stirred for 1 hr at a speed of 800 rpm. On cooling it is placed in a separatory funnel and the esterified oil recovered. For the transesterification process, a mixture of catalyst and methanol is prepared and heated to attain a 55 ^{O}C temperature and added to 100 g of the preheated oil in a glass reactor and heated for 1 hr at a 300 rpm stirring speed. The biodiesel produced is separated from the layer of catalyst and glycerol as well as methanol in a separatory funnel, centrifuged and wet washed with warm water. Its percentage yield is determined by;

% Biodiesel Yield = (Weight of esterified oil / Weight of biodiesel) x 100

The biodiesel produced was characterized according to the various methods proposed by the ASTM standards.

RESULT AND DISCUSSION

Table 3.1. Physiochemical Evaluation of Crude WVFO

Properties	Units	ASTM Value	WVFO Values
Moisture content	%	0.05	0.070
Acid value	mgKOH/g	0.4 – 4	4.20
Saponification value	mgKOH/g	175 – 187	189.7
Iodine value	$mgI_2/100g$	82 – 88	5.07
Free fatty acid	–	0.2 – 2	2.62
Density	g/ml	–	0.915
Viscosity at 40 ^{O}C	m^2/sec	0.957 – 0.968	40.25

As seen from table 3.1 above, all values obtained for moisture, saponification value, acid value as well as free fatty acid value were all higher than the above stipulated ASTM values. Therefore, the high FFA obtained from WVFO is answerable to its compulsory subjection to esterification before the main transesterification process.

3.1 Characterization of the Uncalcined and Calcined/Impregnated Snail, Crab and Egg Shell

Below are the results of BET, SEM, XRD, XRF as well as FTIR analysis carried out on all uncalcined and calcined/impregnated snail, crab and egg shell;

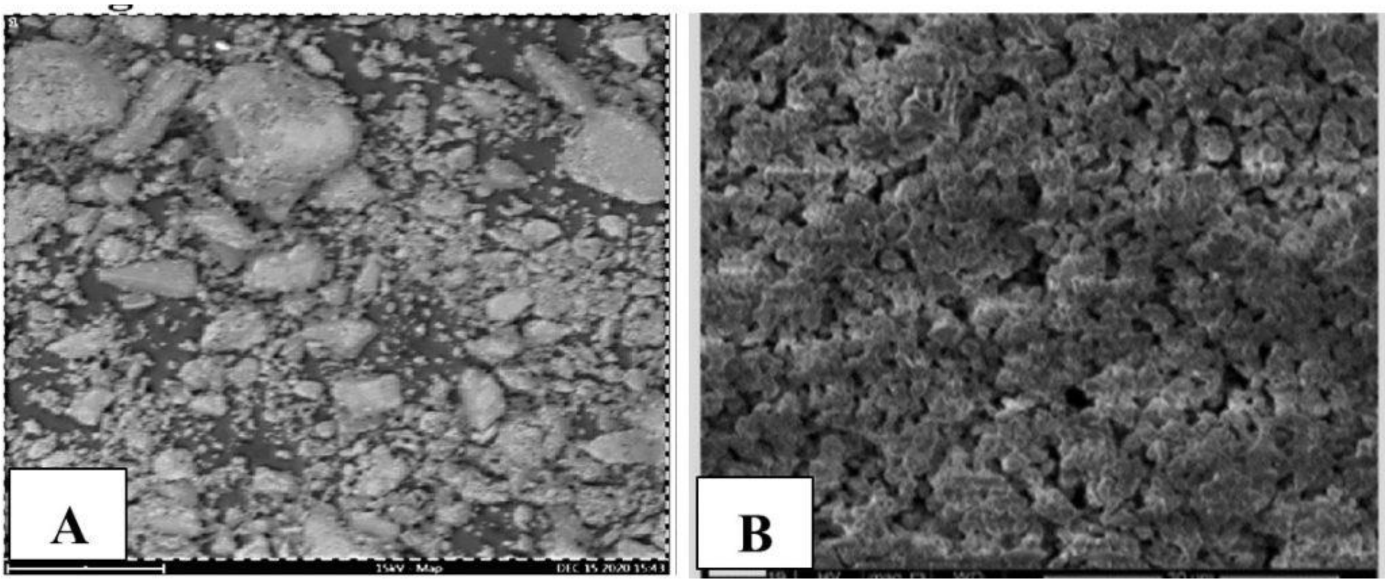
Table 3.2. *BET Analysis of Catalyst Samples*

Catalysts	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (Å)
Uncalcined snail shell	3.80	0.0062	2.015
Calcined snail shell/H_2SO_4 (CS $_{800}{}^{o}C/H_2SO_4$)	2.60	3.461	2.513
Uncalcined egg shell	3.260	2.580	2.105
Calcined egg shell/H_2SO_4 ($CS_{800}{}^{o}C/H_2SO_4$)	3.925	5.50	2.621
Uncalcined crab shell	9.78	0.03	2.46
Calcined crab shell/H_2SO_4 ($CS_{800}{}^{o}C/H_2SO_4$)	170.21	2.08	5.84

The BET result obtained from table 3.2 above shows that all calcined/impregnated catalysts samples produced a high surface area when compared to their uncalcined counterparts. The uncalcined crab shell produced a surface area of 9.78 m^2/g which became higher after calcination and impregnation at 170.21 m^2

/g and therefore is expected to give a higher biodiesel yield. This is followed by calcined/impregnated egg and snail shell at 3.925 and 2.60 m^2/g respectively. This can be attributed to the finer and smoother feel presented by crab and egg shell as compared to the rough feel from snail shell which was physically observed during the size reduction of the catalyst in the preparation stage.

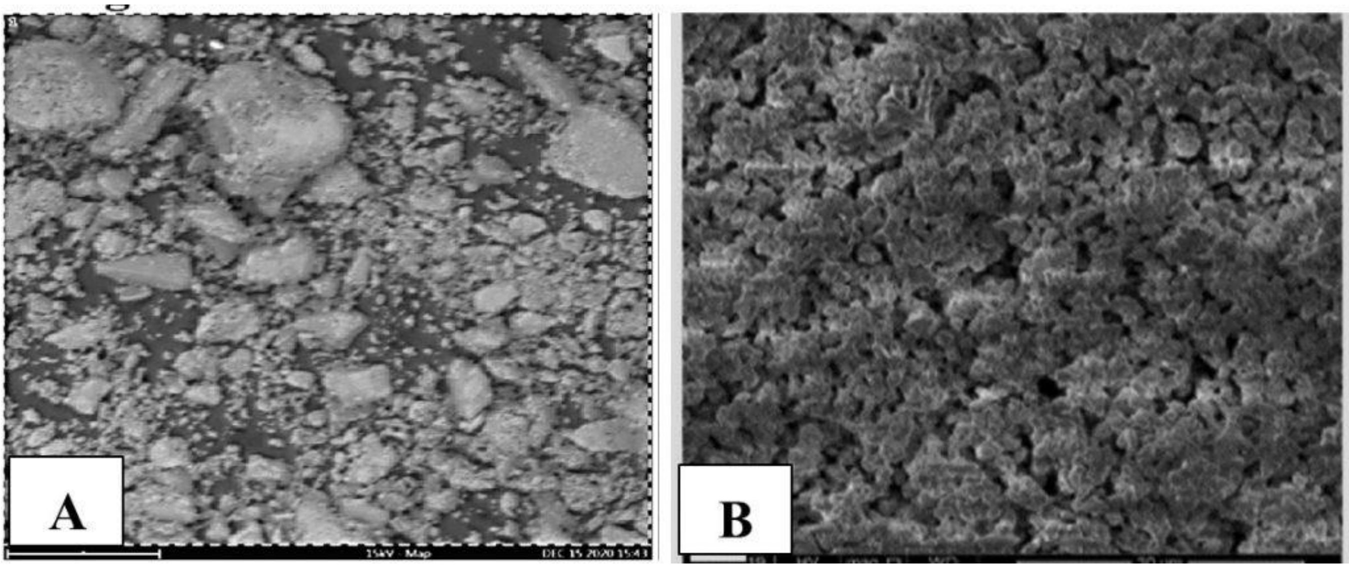
3.1.1. SEM Analysis of Uncalcined and Calcined/impregnated Samples



A = Uncalcined B= Calcined/impregnated

Figure 3.1: SEM Image of Uncalcined and Calcined/ Impregnated Crab Shell

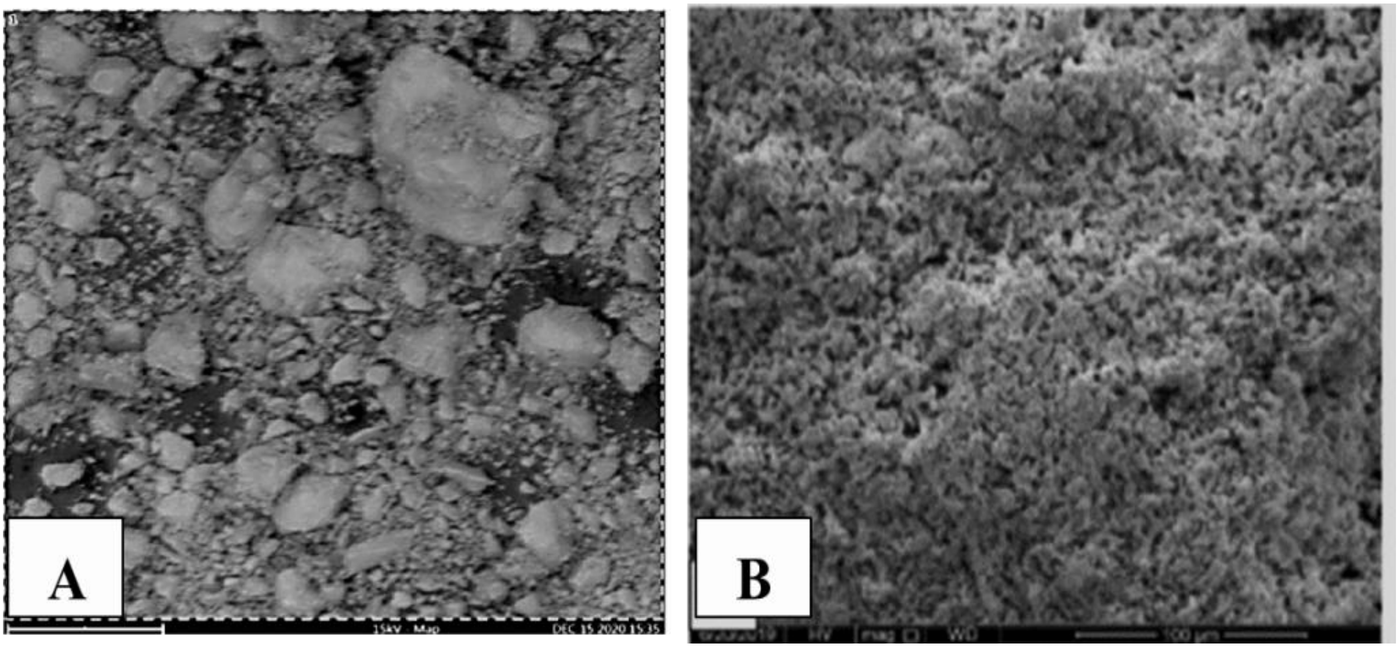
The SEM image of the uncalcined and calcined/impregnated crab shell revealed that for the uncalcined crab shell, its particles were presented with a structural pattern of varying shapes that looks like a sphere. while that of the calcined/impregnated shell was contradictory as its presents a surface filled with tiny holes and pores which can be wired from the distortion which arise from the escape of CO_2 from the surface of the catalyst.



A = Uncalcined B= Calcined/impregnated

Figure 3.2: SEM Image of Uncalcined and Calcined/ Impregnated Snail Shell

The calcined/impregnated snail shell came out in form of a well-structured mold with microspores which can be spotted on its surface and attests for its catalytic ability as seen from figure 3.2 above. Whereas that of the uncalcined snail shell was seen in form of a rod of varying sizes which delineates no form of adsorption potency. Same structure was communicated by [14].



A = Uncalcined B= Calcined/impregnated

Figure 3.3: SEM Image of Uncalcined and Calcined/ Impregnated Egg Shell

From the result obtained from figure 3.3 above, uncalcined crab and egg shells showed striking resemblance in their images as an unstructured arrangement of spherical particles from small to large sizes was spotted. While that of the calcined and impregnated shell showed a thermally decomposed shell with great absorption and catalytic strength.

3.1.2. XRF Analysis of Uncalcined and Calcined/Impregnated Catalysts

Table 3.3: *XRF Results of Uncalcined and Calcined/Impregnated Snail Shell*

Elemental Name	Atomic Conc. Uncalcined Snail Shell	Weight Conc. Uncalcined Snail Shell	Atomic Conc. CC 900OC/H_2SO_4	Weight Conc. CC 900OC /H_2SO_4
Calcium	90.70	89.52	89.38	88.57
Yitrium	0.92	2.02	0.96	2.10
Silver	0.73	1.94	0.75	1.99
Niobium	0.54	1.23	0.66	1.52
Potassium	1.21	1.16	1.30	1.25
Chlorine	0.86	0.75	1.06	0.93
Sulphur	0.88	0.70	57.93	55.32

From the result displayed above, it is very glaring that the main element present in snail shell is calcium as it constitute about 90 % of the total element present. But its concentration decreased to 88.57 % after calcination and impregnation which clearly depicts that calcination at 800 ^{O}C provoked its gradual loss from the $CaCO_3$ so that the main component CaO can emerge. On the other hand, the atomic and weight concentrations of sulphur sprouted up to 57.93 and 55.32 % respectively after calcination and impregnation which is very much expected as it attest for the presence of H_2SO_4 in the catalyst.

Table 3.4: *XRF Results of Uncalcined and Calcined/Impregnated Egg Shell*

Element	Atomic Conc. Uncalcined Egg Shell	Weight Conc. Uncalcined Egg Shell	Atomic Conc. CC $_{900OC}$/H_2SO_4	Weight Conc. CC $_{900OC}$ /H_2SO_4
Calcium	85.38	85.55	88.84	89.35
Yitrium	1.03	2.29	0.88	1.94
Sulphur	1.47	1.18	64.30	61.80
Carbon	41.30	28.76	25.50	23.45
Phosphorus	0.69	0.53	0.60	0.46
Magnesium	0.78	0.47	0.88	0.53
Oxygen	44.37	46.10	50.33	42.51

The XRF result displayed from table 3.4 below also depicts that calcium still remained the most dominant element in all uncalcined and calcined/impregnated catalyst samples. It also showed that atomic and weight concentration of carbon began to decrease after calcination and impregnation which is attributed to the loss of volatile phases which are CO_2 and H_2O from the catalyst at high calcination temperature of 900 ^{O}C. Generally the result showed higher atomic and weight concentration for calcium, oxygen, sulphur and carbon which are the dominant elements present in the catalyst while other elements such as yitrium, phosphorus and magnesium were said to be present but in trace amounts.

Table 3.5: *XRF Results of Uncalcined and Calcined/Impregnated Crab Shell*

Element	Atomic Conc. Uncalcined Crab Shell	Weight Conc. Uncalcined Crab Shell	Atomic Conc. CC $_{900OC}$/H_2SO_4	Weight Conc. CC $_{900OC}$ /H_2SO_4
Calcium	79.54	81.94	85.05	87.82
Phosphorus	4.38	3.49	4.08	3.26
Yitrium	0.70	1.93	0.74	1.68
Niobium	2.20	0.38	0.29	0.69
Carbon	40.33	21.30	26.50	24.54
Sulphur	4.19	1.29	66.70	61.58
Oxygen	48.32	44.28	53.97	50.87

The XRF result displayed in table 3.5 above also depicts that with atomic concentrations of both uncalcined and calcined/impregnated crab shell samples at 79.54 % and 85.05 % respectively, calcium maintained its stance as the most dominant element present. While other elements such as yitrium and niobium were said to be present but in trace quantities.

3.1.3 XRD Analysis of Uncalcined and Calcined/Impregnated Catalysts

The result of the XRD analysis reveals that;

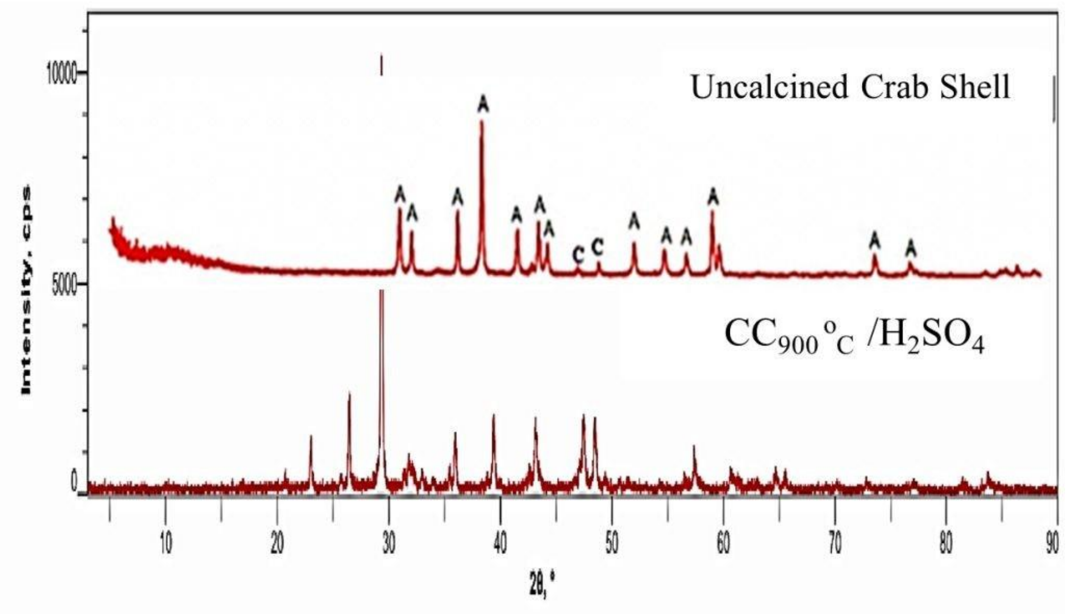


Figure 3.4: *XRD Pattern for Uncalcined and Calcined/Impregnated Crab Shell*

Aragonite and calcite crystalline phases are dominantly present in the spectrum of the uncalcined crab shell as seen from the XRD result in figure 3.3. It clearly shows that the uncalcined crab shell catalyst produced trace amount of calcite but was largely dominated by the aragonite crystal phase at a 2 range of 26.103 ^{O}, 32.398 ^{O} and 34.013 ^{O}. While that of the calcined/impregnated crab shell showed that the spectrum at a 2 range presented general diffraction peaks at 23.00^{O}, 26.41 ^{O}, 29.30 ^{O}, 39.33 ^{O}, 43.09 ^{O}, 47.40 ^{O}, 48.40 ^{O}.

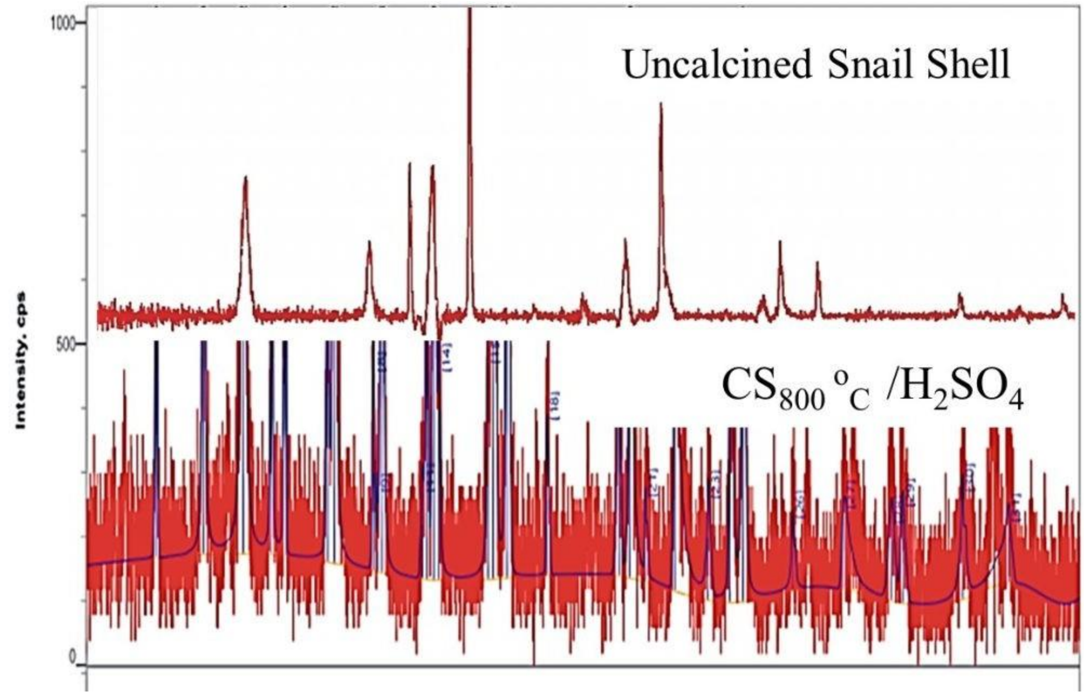


Figure 3.5: *XRD Pattern for Uncalcined and Calcined/Impregnated Snail Shell*

The result revealed that the aragonite phase defined the crystalline nature of the uncalcined snail shell and also classified it as the most dominating phase produced. The above description was spotted at theta ranges of 23.36 ^{o}, 34.22 ^{o}, 37.19 ^{o}, 38.16 ^{o} and 44.22 ^{o}. This result confirms that the composition of eggshell mostly consist of $CaCO_3$. The diffraction peaks presented from the spectrum of the calcined/impregnated snail shell were considered rough as compared to that of its uncalcined counter path. The qualitative result of the analysis was determined using the phase data view which showed the various phases produced by the spectrum.

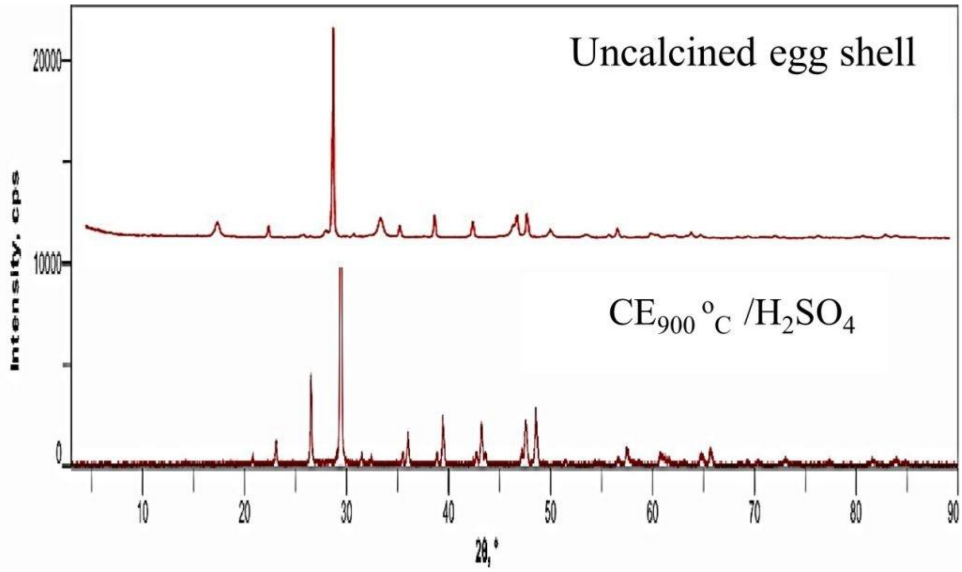
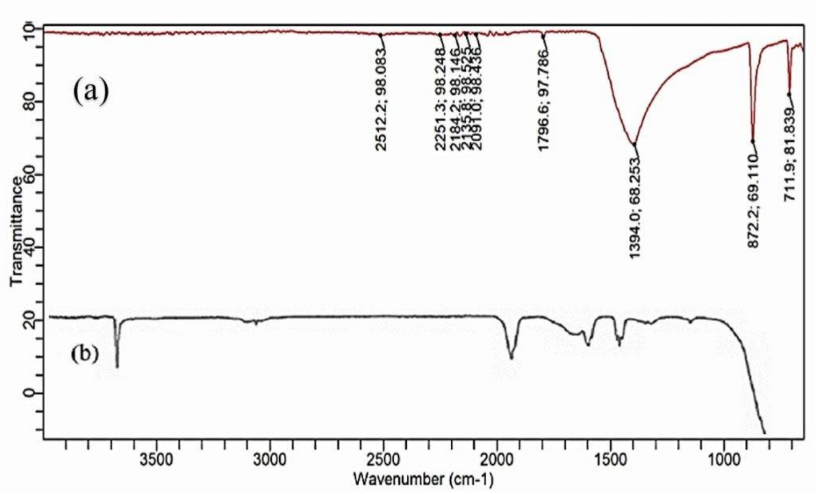


Figure 3.6: *XRD Pattern for Uncalcined and Calcined/Impregnated Egg Shell*

The x-ray diffraction patterns obtained for the calcined and uncalcined eggshell particles shows diffraction peaks which suggested a crystalline phase of the main material calcium carbonate in the form of calcite. The major intense peak was traced at a 2θ angle of 27.2° while 22.2°, 30.5°, 37.1°, 36.6°, 41.9°, 46.9°, and 47.7° were minor peaks discovered. For the calcined/impregnated egg shell, the trigonal crystalline phase of the calcite obtained displayed a major peak of 29.40 which detected the disappearance of calcite $CaCO_3$ and the emergence of CaO.

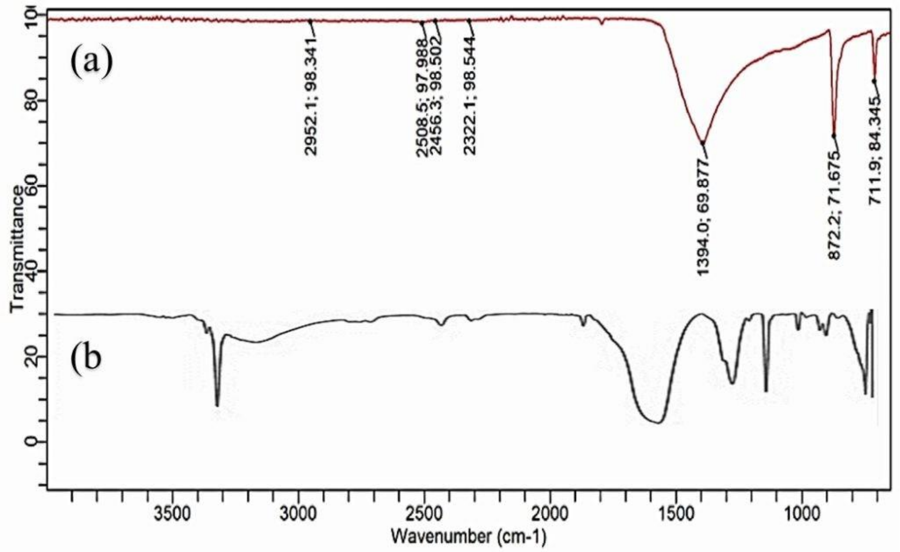
3.1.4 FTIR Analysis of Uncalcined and Calcined/Impregnated Catalysts



(a) Calcined/impregnated snail shell (b) Uncalcined snail shell

Figure 3.7: *FTIR Analysis for Uncalcined and Calcined/Impregnated Snail Shell*

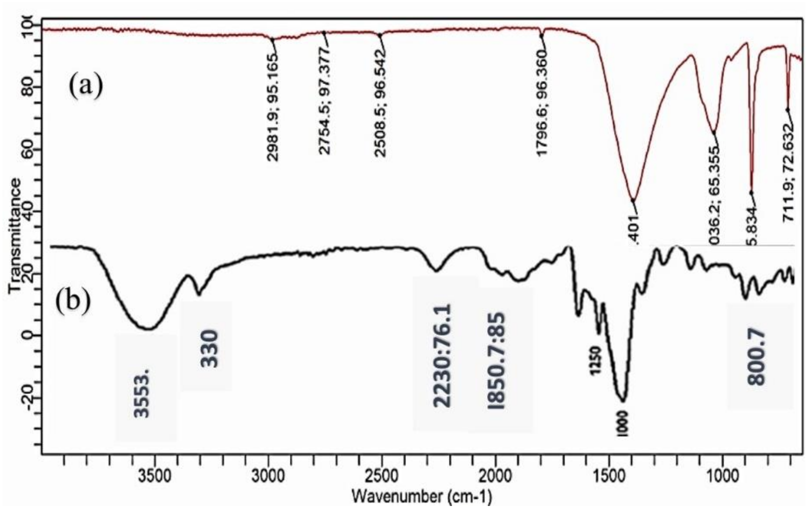
As seen from figure 3.7 above, the spectrum of the uncalcined snail shell, showed the presence of various infrared band one of which is that attained at 3651 cm^{-1} owing to the presence of weak O – H bond which attests to the presence of OH group of water molecules on the surface of the CaCO3 of the snail shell catalyst. While that of the impregnated and calcined snail shell (CS800oC/H2SO4), revealed the presence of very sharp peaks of 711 and 872 cm-1 which depicts the out-of-plane and in-plane bending and deformation of CaCO3.



(a) Calcined/impregnated crab shell (b) Uncalcined crab shell

Figure 3.8: *FTIR Analysis for Uncalcined and Calcined/Impregnated Crab Shell*

The FTIR spectrum of the uncalcined crab shell showed the presence of a wide stretching peak at 1550 cm^{-1} which depicts the presence of asymmetry stretching vibration of the O ═ C ═ O thereby affirming the presence of carbonate ion in the shell. While that of the calcined/impregnated crab shell gave a sharp and intense stretching band at 872cm^{-1} which shows the C ═ O stretching and bending of the CaCO$_3$ especially towards the finger print region. [15].



(a) Calcined/impregnated egg shell (b) Uncalcined egg shell

Figure 3.9: *FTIR Spectra Analysis for Uncalcined and Calcined/Impregnated Egg Shell*

From figure 3.9 above, the FTIR spectra for uncalcined egg shell showed various band adsorption peaks one of which is the sharp stretching peak at 1400 cm^{-1} which connotes the presence of the bending vibration of the C – H alkane bond. On the other hand, the major absorption bands of the egg shell impregnated and calcined at 900 ^{O}C (CE$_{900}^{o}_{C}$/H$_2$SO$_4$) was detected through the values obtained from the in-plane and outplane stretching of the carbonate group which were recorded at 711.9 cm^{-1} and 872.2 cm^{-1} respectively.

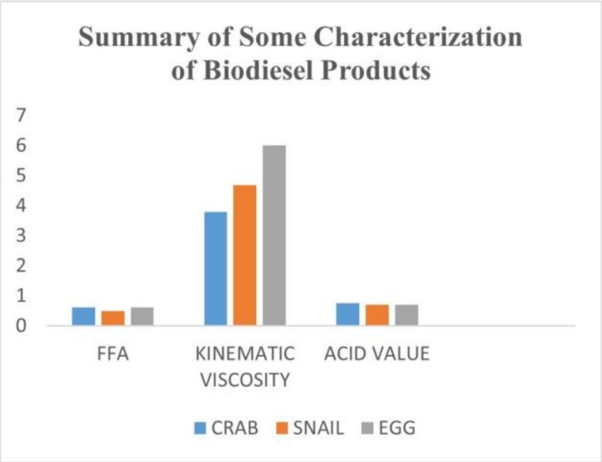
3.1.5 GC-MS Analysis of Waste Vegetable Frying Oil (WVFO)

Table 3.6: *Percentage Concentration of Free Fatty Acid from WVFO*

Fatty Acids	**Molecular Formula**	**Length of Carbon Chain**	**Obtained Values (%)**
Lignoceric acid	$C_{24}H_{48}O_2$	C24: 0	0.05
Myristic acid	$C_{14}H_{28}O_2$	C14: 0	0.10
Palmitoleic acid	$C_{16}H_{30}O_2$	C16: 1	0.72
Arachidic acid	$C_{20}H_{40}O_2$	C20: 0	0.85
Stearic acid	$C_{18}H_{36}O_2$	C18: 0	2.50
Palmitic acid	$C_{16}H_{32}O_2$	C16: 0	7.16
Eicosenoic acid	$C_{20}H_{38}O_2$	C20: 1	1.50
Linoleic acid	$C_{18}H_{32}O_2$	C18: 2	20.35
Linolenic acid	$C_{18}H_{30}O_2$	C18: 3	6.80
Oleic acid	$C_{18}H_{34}O_2$	C18:1	59.97

The result obtained from the GC-MS analysis of waste vegetable frying oil above revealed the presence of both saturated and unsaturated fatty acids such as palmitic and stearic acids were obtained at percentage concentrations of 2.50 and 7.16 % respectively while that of unsaturated fatty acids such as oleic, linoleic, eicosenoic and palmitoleic acids all produced percentage concentrations of 59.97, 20.35, 6.80, 1.50 and 0.72 % respectively. Therefore with proper observation from the table 3.5 above, it is confirmed that oleic acid is the most dominant fatty acid in waste vegetable frying oil as it emerged with a percentage concentration of 59.97 %. This is in agreement with the result obtained by [16] who also affirmed the position of oleic acid as the highest produced fatty acid with concentration of 28.8 %.

3.1.6 Characterization of the Biodiesel Produced from WVFO



WC, WS and WE = waste vegetable frying oil crab, snail and egg shell biodiesel products. Subscripts C = reaction specification of 1:6, 65 ^{O}C, 5 wt%, 120 min, E = 1:9, 60 ^{O}C, 5 wt%, 120 min, F = 1:9, 65 ^{O}C, 3 wt%, 60 min.

Figure 3.10: *Summary of some Characterization of Biodiesel Produced*

Figure 3.10 above shows the summary of some fuel properties analyzed in the biodiesel produced. The result showcased some of the biodiesel products with the highest FFA, kinematic viscosity at 40 ^{O}C as well as acid value amongst other properties analyzed obtained from WVFO. The highest FFA value of 0.62 mgKOH/g was produced from WC_C biodiesel product while the highest kinematic viscosity value of 6.00 mm^2/s was spotted from WC_E biodiesel product. Also a value of 0.75 was recorded as the highest acid value traced from WC_C product. All values were higher than the ASTM stipulated standard value while other values are said to fall within the standard value.

3.2 Optimization of Process Parameter for Transesterification Reaction

The optimization process used in this study is governed by the Taguchi Orthogonal array design as seen from the table 3.7 below;

Table 3.7: *Array Design of the Effect of Various Reaction Conditions on WVFO Egg, Snail and Crab Shell Biodiesel Yields*

Reaction Specif.	**Oil to Methanol Ratio**	**Reaction Temp (^OC)**	**Catalyst Loading (wt%)**	**Reaction Time (min)**	**WVFO Biodiesel**
A	1:6	55	1	60	WS_A
B	1:6	60	3	90	WS_B
C	1:6	65	5	120	WS_C
D	1:9	55	1	120	WS_D
E	1:9	60	5	120	WS_E
F	1:9	65	3	60	WS_F
G	1:12	55	3	90	WS_G
H	1:12	60	5	60	WS_H
I	1:12	65	1	90	WS_I

Where A, B, C….I = various reaction specifications for the reaction conditions applied in batches for each of the biodiesel production. WS_A, WS_B ***…..*** WS_I ***= WVFO-snail shell biodiesel products produced using the various reaction specifications****.*

Table 3.7 above shows the array design governing the transesterification of biodiesel products from WVFO-calcined/impregnated snail shell. However, this table will be replicated for biodiesel products from calcined/impregnated crab and egg shell making a total of 27 samples of biodiesel produced in the study. The effect of reaction temperature, reaction time, catalyst loading and oil to methanol ratio on the various yields of biodiesel were determined to aid in the optimization process.

3.2.1. Effect of Oil to Methanol Ratio on Biodiesel Yield

Table 3.8: *Effect of Oil to Methanol Ratio on Yields from WVFO*

Oil Methanol Ratio	**Reaction Time (min)**	**Catalyst Loading (wt%)**	**Reaction Temp. (^OC)**	**EggShell Biodiesel Product**	**Snail Shell Biodiesel Products**	**Crab Shell Biodiesel Products**
1:6	60	1	55	WE_A 88.30	WS_A 84.61	WC_A 88.30
1:6	**90**	**3**	**60**	WE_B 89.70	WS_B 86.90	**WC_B 93.74**
1:6	120	5	65	WE_C 91.60	WS_C 87.70	WC_C 93.50

1:9	120	1	55	WE_D 91.50	WS_D 91.60	WC_D 88.40
1:9	120	5	60	WE_E 92.35	WS_E 89.50	WC_E 92.10
1:9	60	3	65	WE_F 90.00	WS_F 92.90	WC_F 90.00
1:12	90	3	55	WE_G 76.51	WS_G– 92.61	WC_G 91.50
1:12	60	5	60	WE_H 91.00	WS_H– 89.30	WC_H 89.70
1:12	90	1	65	WE_I 88.00	WS_I– 84.00	WC_I 87.00

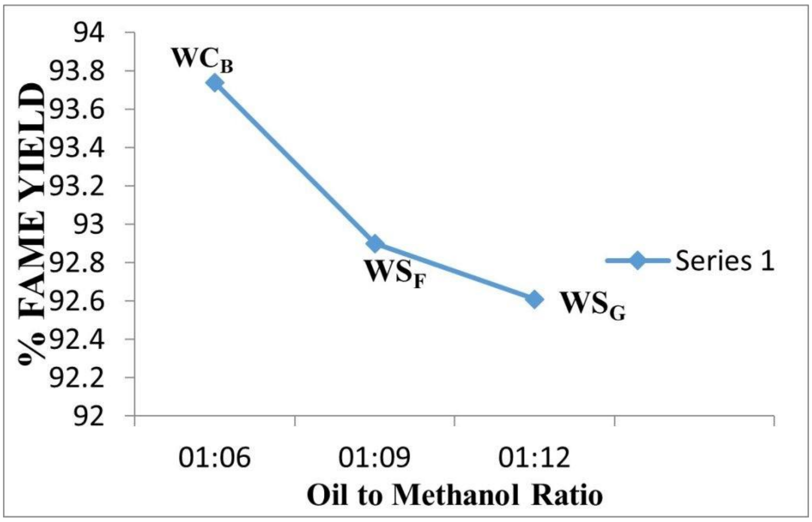


Figure 3.11: *Effect of Oil to Methanol ratio on WVFO – Egg, Snail and Crab shell Biodiesel Yields*

From the result obtained in figure 3.11 above, it can be deduced that the highest biodiesel yield of 93.74 % was obtained at a 1:6 oil to methanol ratio as seen from WVFO oil crab shell biodiesel product with B specification WC_B. The high yield of biodiesel produced can also be attributed to the temperature of 60 ^{O}C used as seen from the B specification displayed in table 3.6 above which was below the boiling point of methanol as well as the fact that each mole of biodiesel produced is accounted for every mole of methanol used in the reaction [17].

3.2.2. Effect of Catalyst Loading on Biodiesel Yield

Table 3.9: *Effect of Catalyst Loading on Yields from WVFO*

Catalyst Loading (wt%)	**Reaction Time (min)**	**Oil to Methanol Ratio**	**Reaction Temp (^{O}C)**	**EggShell Biodiesel Products**	**Snail Shell Biodiesel Products**	**Crab Shell Biodiesel Products**
1	60	1:6	55	WE_A 88.30	WS_A 84.61	WC_A 89.30
1	120	1:9	55	WE_D 91.50	WS_D 91.60	WC_D 88.40
1	90	1:12	65	WE_I 88.00	WS_I 84.00	WC_I 87.00

3	**90**	**1:6**	**60**	WE_B 89.70	WS_B 86.90	**WC_B 93.74**
3	60	1:9	65	WE_F 90.00	WS_F 92.90	WC_F 90.00
3	90	1:12	55	WE_G 76.51	WS_G 92.61	WC_G 91.50
5	60	1:12	60	WE_H 91.00	WS_H 89.30	WC_H 89.70
5	120	1:6	65	WE_C 91.60	WS_C 87.70	WC_C 93.50
5	120	1:9	60	WE_E 92.35	WS_E 89.50	WC_H 89.70

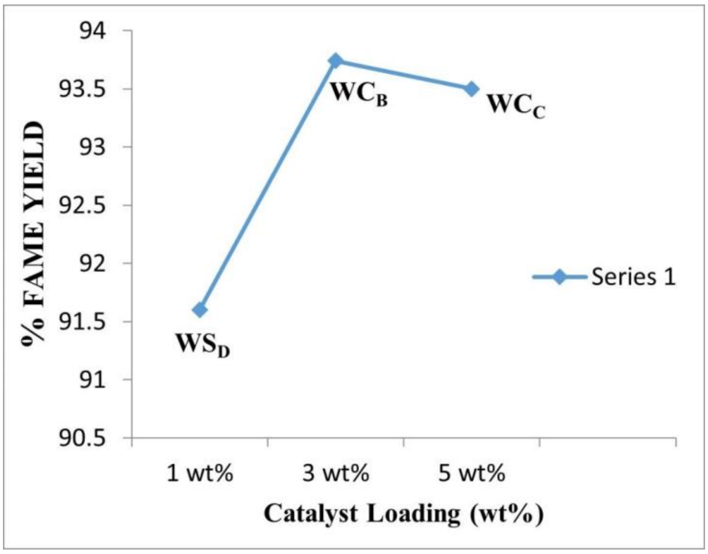


Figure 3.12: *Effect of Catalyst Loading on WVFO – Egg, Snail and Crab shell Biodiesel Yields*

The result displayed on figure 3.12 above depicts that among all biodiesel products obtained, WVFO crab shell product WC_B produced the highest yield of biodiesel of 93.74 % at a catalyst loading of 3 wt%. The highest biodiesel yield at 3 wt% catalyst loading accompanied by a temperature of 60 ^{O}C only depicts that a moderate catalyst loading and temperature increases the enthalpy of the reaction which automatically increases the activation energy of the reaction [18]. Also from table 3.9 displayed above, B specification is accompanied with product concentrations of 1:6 oil to methanol ratio which matches the weight of the catalyst at 3 wt%. This is in agreement with the result from [19]. While a slightly low yield of 93.50 % was obtained from WVFO crab shell biodiesel product WC_C at 5 wt% catalyst loading.

3.2.3. Effect of Reaction Time on Biodiesel Yield

Table 3.10: *Effect of Reaction Time on Yields from WVFO and Castor oil*

Reaction Time. (min)	Reaction Temp. (^{O}C)	Catalyst Loading (wt%)	Oil to Methanol Ratio	EggShell Biodiesel Products	Snail Shell Biodiesel Products	Crab Shell Biodiesel Products
60	55	1	1:6	WE_A – 88.30	WS_A– 84.61	WC_A – 88.30
60	60	5	1:12	WE_H – 91.00	WS_H – 89.30	WC_H – 89.701
60	65	3	1:9	WE_F – 90.00	WS_F– 92.90	WC_F – 90.00

90	55	3	1:12	WE_{G}- 76.51	WS_{G}– 92.61	WC_{G} – 91.50
90	**60**	**3**	**1:6**	WE_{B} – 89.70	WS_{B}– 86.90	**WC_{B} – 93.74**
90	65	1	1:12	WE_{I}- 88.00	WS_{I}– 84.00	WC_{I} – 87.00
120	60	5	1:9	WE_{E}- 92.35	WS_{E}– 89.50	WC_{E}– 92.10
120	55	1	1:9	WE_{D}- 91.50	WS_{D}– 91.60	WC_{D} – 88.40
120	60	5	1:6	WE_{E} – 92.35	WS_{E}– 89.50	WC_{E}– 92.10

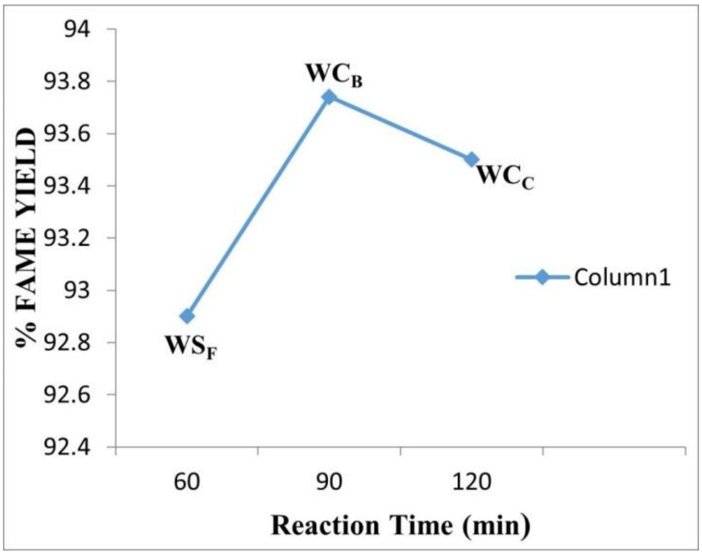


Figure 3.13: *Effect of Reaction Time on WVFO – Egg, Snail and Crab shell Biodiesel Yields*

Among all biodiesel samples produced, the highest yield of 93.74 % was obtained from WC_B biodiesel product with a retention time of 90 min as seen from figure 3.12 above. Extending the retention time above 120 min increases production cost as much amount of energy will be lost in the process of conversion. Meanwhile at 93.50 %, WVFO – crab shell biodiesel product WC_C recorded a yield slightly lower than that of WC_B. Haven being achieved at a temperature of 65 ^{O}C which is close to the boiling point of methanol, it is not out of place to state that some of the methanol was lost by evaporation in the cause of the transesterification process which reduced the yield of the biodiesel produced [20].

3.2.4. Effect of Reaction Temperature on Biodiesel Yield

Table 3.11: *Effect of Reaction Temperature on Yields from WVFO*

Reaction Temp (^{O}C)	**Reaction Time (min)**	**Catalyst Loading (wt%)**	**Oil to Methanol Ratio**	**EggShell Biodiesel Products**	**Snail Shell Biodiesel Products**	**Crab Shell Biodiesel Products**
55	60	1	1:6	WE_{A} 88.30	WS_{A} 84.61	WC_{A} 88.30
55	90	3	1:12	WE_{G} 76.51	WS_{G} 92.61	WC_{G} 91.50
55	120	1	1:9	WE_{D} 91.50	WS_{D} 93.50	WC_{D} 88.40
60	**90**	**3**	**1:6**	WE_{B} 89.70	WS_{B} 86.90	**WC_{B} 93.74**
60	120	5	1:9	WE_{E} 92.35	WS_{E} 89.50	WC_{E} 92.10

60	60	5	1:12	WE_H 91.00	WS_H 89.30	WC_H 89.70
65	90	1	1:12	WE_I 88.00	WS_I 84.00	WC_I 87.00
65	60	3	1:9	WE_F 90.00	WS_F 92.90	WC_F 90.00
65	120	5	1:6	WE_C 91.60	WS_C 87.70	WC_C 93.50

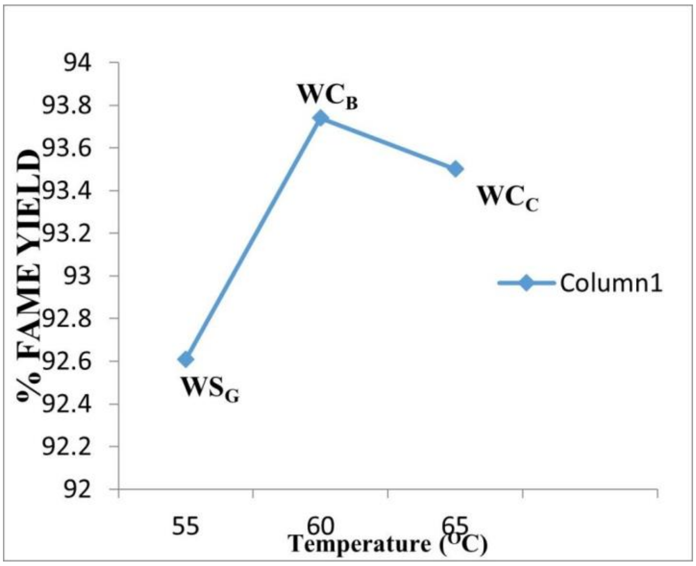


Figure 3.14: *Effect of Reaction Temperature on WVFO – Egg, Snail and Crab shell Biodiesel Yields*

The highest biodiesel yield obtained at 60 ^{O}C reaction temperature depicts that the temperature was high enough to initiate a translational energy within the molecules of the compound which is said to be equal or even higher than the activation energy. Also, it is expected that increase in temperature would increase the product yield and a higher temperatures above 65 ^{O}C (boiling point of methanol) would destruct the reactants collision process by gradually diminishing the volume of methanol as it evaporates into the air [21].

CONCLUSION

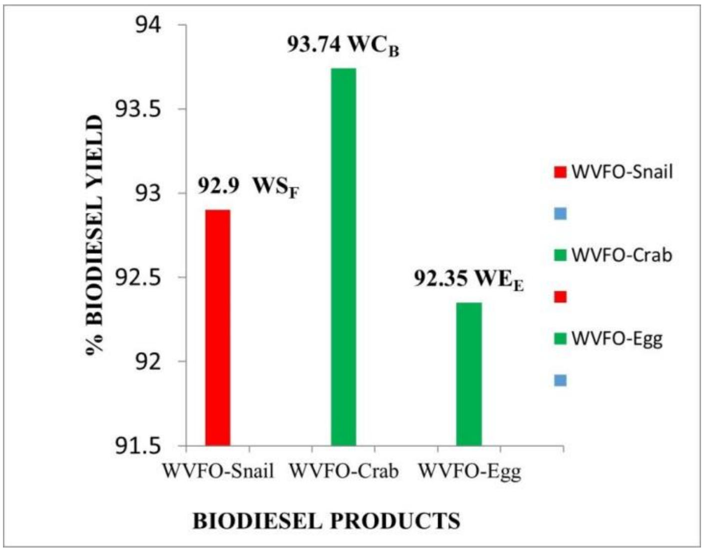


Figure 4.1: *Summary of Biodiesel Yields from WVFO- Snail, Egg and Crab shell Biodiesel Products*

In this study aimed at characterizing, applying and optimizing low cost heterogeneous catalyst from the sulphonation of crab, egg and snail shell in the production of biodiesel using waste vegetable frying oil. The highest biodiesel yield of 93.74 % was produced from WVFO crab shell biodiesel product WC_B at optimal conditions of 3 wt%, 1:6, 60 ^OC and 90 min.

RECOMMENDATION

The continuous use high FFA feedstock in the production of biodiesel has and will always be a major problem commonly confronted by researchers and energy enthusiasts. Therefore, there is need to invest knowledge, time and resources in the development of an improved specie of crops as a perfect replacement for high FFA feedstock so as to annul completely this havoc caused. Secondly to develop a technology for the containing of the CO_2 released after thermal decomposition so as to promote resource recovery as well as greenhouse gas reduction.

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